

DEVELOPMENTS IN SEDIMENTOLOGY

43

G.V. CHILINGARIAN and K.H. WOLF
(Editors)

DIAGENESIS, II

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DIAGENESIS, I

DEVELOPMENTS IN SEDIMENTOLOGY 43

DIAGENESIS, II

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DEDICATION

Dedicated to Drs. G. Müller, R.A. Berner, H. Borchert, G.M. Friedman, H. Füchtbauer, J.L. Bischoff, R.W. Fairbridge, E.T. Degens and A.E. Gurevich for their important contributions in the field of chemical fluids related to diagenesis (among others), and to K.J. Hsü on the occasion of his 60th anniversary.

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INTRODUCTION

A scientific – philosophical view of methodology

KARL H. WOLF and GEORGE V. CHILINGARIAN

This Introduction – and its philosophies – are dedicated to the late Johann (Hans) Steiner (Canada) and John Elliston (Australia) for their respective concepts offered far ahead of most of their contemporary fellow scientists. That is, Steiner's ideas in "The sequence of geological events and the dynamics of the Milky Way Galaxy – the present cosmic year; a preliminary study" (J. Geol. Soc. Aust., 1967, 14(1): 99 – 132) which will eventually be proven to be part of the astronomical, long-distance controls on diagenesis; and Elliston's physicochemical theories expressed in numerous publications, the latest of which treated the crystallization of hydrosilicates (based on thixotropy, for example) equally applicable to diagenetic systems (cf. Earth-Sci. Rev., 1984/85, vols. 20 – 22).

Although the previously published and forthcoming volumes on Diagenesis deal almost exclusively with purely "scientific-cum-technical" methodologies¹ and information, the ever-increasing demands on the theoretical ("academic") and applied/practical researcher and explorationist are forcing us (occasionally, at least) to re-examine the underlying "philosophies" of our sciences². But the just-stated demands are too multifarious to be dealt with here in detail; hence, only a few selectively chosen topics are preferentially treated. These are: (1) categories of research; (2) interdisciplinary approach; (3) interrelationships of geology – geochemistry – geophysics, (4) geochemical – mineralogical systems; (5) some laboratory-based (micro- mesoscale) investigations; (6) exemplar of interconnections between methodologies and some natural variables; (7) logic – validity – ambiguity – soundness – assumptions – informal fallacies as part of the Scientific Method; (8) some "practical philosophical" variables and their interrelations; (9) types of definitions; (10) the Real – Systems – Model World Trilogy; (11) the Objectivity – Reliability – Accuracy Spectrum/Continuum; (12) Wolf's "Belief – Fact – Hypothesis – Con-

¹ "Methodology – procedure by which new knowledge is acquired by a knower. Various mathematical, dialectical, operational, and problematic methods have enjoyed a vogue . . . in both philosophy and science. The enormous success of the empirical method in the sciences since the 17th century has induced scholars in many disciplines, including philosophy, to attempt to duplicate that achievement" (Encyclopaedia Britannica).

² "Philosophy of science – a discipline in which the elements involved in scientific enquiry (observational procedures, patterns of argument, method of representation and calculation, and metaphysical presuppositions) are analyzed and discussed; and the grounds of their validity are evaluated from the points of view of formal logic, practical methodology, and metaphysics" (Encyclopaedia Britannica).

vention – Metaphysics Pyramid’’; (13) modes of analysis – methods of modelling/reconstructing; and (14) some practical/applied geological problems of the Scientific Method.

Geology is a science, a philosophy and an art – and so are diagenetic – catagenetic studies an integral member of sedimentology, petrology, and paleoenvironmental reconstructions. Likewise, metamorphic investigations (often mentioned here as a logical extension of diagenesis – catagenesis) are founded on petrographic + petrologic + geochemical “concrete” science – philosophy – “abstract” art. These three groups of phenomena are complexly intertwined and often inseparable, so that we deal with the art of science or the art of the scientific method; the art and science of philosophy, or the philosophy of science, for instance. That these phenomena are not based purely on “a play of words” and have an ever-increasing practical application in our computer age, will be demonstrated below.

In spite of the use of chemical and physical (and mathematical) methods and concepts in the studies of diagenesis, certain “philosophical – psychological” principles will remain our basic tools as part of the Scientific method¹ – the way we think, gain knowledge and wisdom, and how we utilize experience, intuition, etc., ought to be also of concern to us, even if we prefer to “home in” on more directly “useful” topics². It seems, however (as already discussed in many publications, such as those related to designing computer languages and programs, in the interpretation of their results, as well as in developing the 5th-generation computers and emphasis on expert systems; Feigenbaum and McCorduck, 1984), we are compelled to return to more basic philosophical/methodological questions and enigmas to find a solution because we ended up in an “intellectual/technological/humanistic dead-end” in certain aspects. To put it into a nut-shell: our thinking pattern has to be refined and sharpened if progress is to be made. Can we say the same about certain geological – sedimentological – diagenetic problems? An answer will be partly provided in the following sections.

Categories of research. Basically, there are two categories of research, namely “pure” and “applied”, with the latter divisible into four sub-groups: problem- and goal-oriented, developmental, and operational (Fig. 1). Diagenetic – catagenetic – metamorphic, etc., studies certainly fall into all five categories.

These five research types are not isolated from each other, but are complexly interrelated (i.e., which means, as in all other linkage-cum-concatenation models: transitions/gradations, overlaps, continua/spectra), as highlighted in Fig. 2.

¹ Similar to the approach of Ch. 1 (in Vol. 1) on ore-genesis-related diagenesis, the descriptions/discussions that follow will be in abbreviated, point-by-point style.

² There are always a few scientists who recognize “philosophical” demands in both theoretical and applied domains – see for example Toffler, 1974, 1983; Encel et al., 1975; Watzlawick, 1976; Woodcock/Davis, 1978; Evans, 1979; and Postle, 1980; among many more.

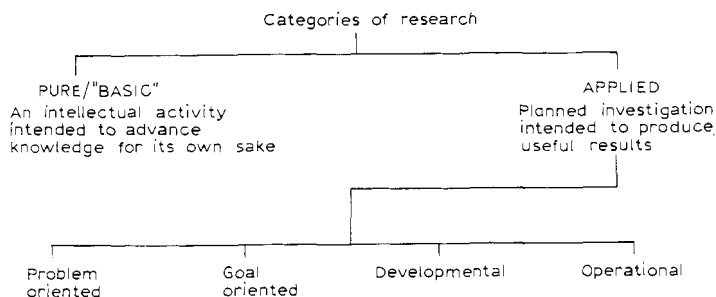


Fig. 1. Classification of research (from Beveridge, 1980, p. 79).

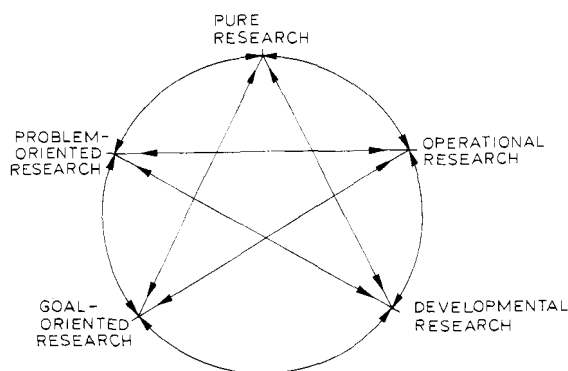


Fig. 2. The classification of research in Fig. 1 has been transformed into a linkage/concatenation-type model to stress the interrelationships (i.e., transitions/gradations, overlaps, and continua/spectra of the five types of research. (After Wolf, 1986, unpublished.)

"Research may be defined as original investigation in any field whether in science, literature, or art. Its limits coincide with the limits of the knowable. In the field of research the function of the Institution should be organization, the substitution of organized for unorganized effort wherever such combination of effort promises the best results; and the prevention, as far as possible, of needless duplication of work. Hitherto, with few exceptions, research has been a matter of individual enterprise, each worker taking up the special problem which chance or taste led him to and treating it in his own way. No investigator, working single handed, can at present approach the largest problems in the broadest way thoroughly and systematically."

Board of Trustees of the Carnegie Institution of Washington when established during 1901 – 1902. From Rabbitt (1980, p. 330).

An interdisciplinary approach is needed, as many researchers "philosophically" realize, but frequently cannot put into "actual" realization (excuse the pun), for several all-to-common human limitations. Nevertheless, let us structure/classify the

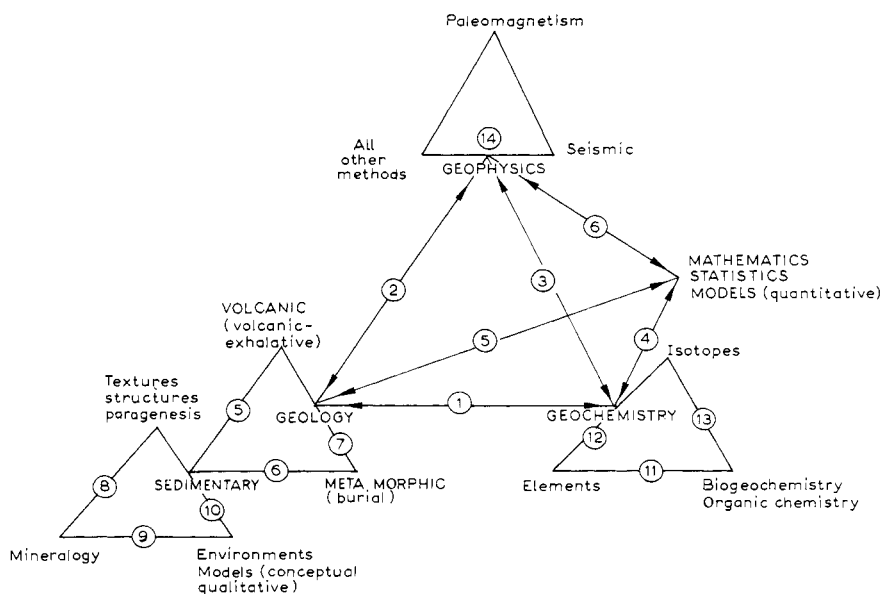


Fig. 3. Interdisciplinary earth-science approaches in diagenetic studies; depicted by methodological continua/spectra (Wolf, 1984, unpublished).

(1) Geology – geochemistry continuum. Isotopes, elements, and organic matter are routinely studied in unravelling diagenesis of sediments, whether of clastic, pyroclastic, physicochemical, or biochemical origin; as well as of secondary burial metamorphic or of volcanic – exhalative-hydrothermal formation.

(2) Geology – mathematics continuum.

(3) Geochemistry – mathematics continuum. Application of quantitative methods (with or without use of computers) in the investigation of diagenesis. (Quantitative geophysical techniques, e.g., paleomagnetism, in the diagenetic studies may become more widespread in the future.)

(4) Geology – geophysics continuum; although geophysical methods have been applied in basinal analysis, correlation of formations and members, stratigraphic and, thus, regional environmental reconstructions, several geophysical methods can directly also be used in local or microscopic diagenetic studies but their application is rare and underdeveloped. One exception is the study of iron-rich and sulfide-bearing sedimentary rocks using paleomagnetism.

(5) Sedimentary – volcanic continuum. There are several aspects to be considered: (a) Diagenesis in pyroclastic and volcanoclastic deposits is different from that in other lithologies as a consequence of the highly specialized precursor material. (b) Volcanic – exhalative processes can greatly control or change more “normal” sedimentary diagenesis.

(6) Sedimentary – metamorphic continuum: all varieties of sedimentary diagenetic processes and products grade into catagenesis and burial metamorphism in respect to both time and space.

(7) Volcanic – metamorphic continuum: the diagenesis of volcanic rocks are transitional into metamorphism per se (cf. no. 6 above).

(8, 9, 10). Various continua among diagenetic studies of sedimentary (clastics, pyroclastics, physicochemical, biochemical) rocks: no specific methodology is conclusive; they are all supportive (but sometimes offer contradictory results) and supplementary.

(11, 12, 13) Various continua – as above.

(14) As mentioned above, geophysics has been applied in sedimentology more on a regional and district basin-size scale – with some recent rare exceptions when paleomagnetic studies of specific minerals were undertaken. These techniques can also be applied to diagenesis: e.g., diagenetic changes controlling magnetic properties.

interdisciplinary earth-science approach as it may apply to diagenetic en toto investigations in general.

In Fig. 3, pyramid A depicts the four principal earth-science disciplines geology – geochemistry – geophysics – mathematics. The various types of interconnections are marked by arrows (nos. 1 – 6). On at least the first three apices, secondary/auxiliary triangles have been placed to permit a refinement of our philosophy: e.g., Geology comprises sedimentary – volcanic – metamorphic subdisciplines, and then Sedimentary geology consists of many others, exemplified by mineralogy – environments – textures, etc. Some details on continua/spectra are given in the caption of Fig. 3, which makes the approach self-explanatory. Let us say, however, that inasmuch as we cannot utilize all potential combinations (e.g., of methodologies) in any specific research project, careful selection is of utmost importance in order to achieve the most plausible and useful results. This is obvious to all researchers, but how many publications list the inevitable, unavoidable limitations, assumptions,

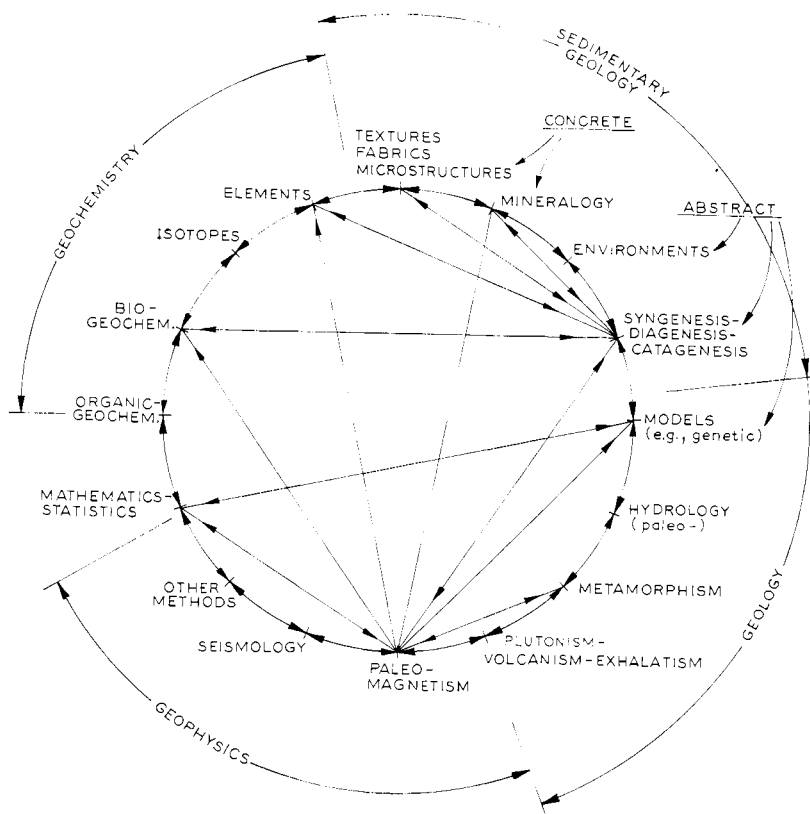


Fig. 4. Potential interrelationships of geology + geochemistry + geophysics in the investigation of diagenesis – catagenesis, etc. (see text).

etc., imposed by this forced selectivity? An “intellectual snafu” may be the consequence!

The *potential complex interrelationships of geology – geochemistry – geophysics* are better stressed by proffering some specifics. In Fig. 4, a few selected (again preferentially) variables/parameters/factors of each major discipline have been added – most, if not all, are intricately related in practical concrete *and* in abstract/theoretical forms. However, only one was chosen to demonstrate this concatenation diagram. The controls of paleomagnetism on several variables (e.g., biogeochemistry, elemental composition, mineralogy, textures – fabrics) are depicted as well as the possible metamorphic modification – obliteration, and finally the potential need for genetic models and/or mathematical – statistical treatment of the data.

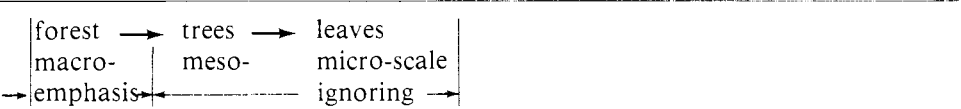
Despite Folk’s (1973, p. 137) wise (crack?!) advice “Damn the variables. Full speed ahead!”, the time has now arrived when we do have to consider *all* inter-related variables as part of one system; be it a micro-, meso- or macro-complex one is investigating. (For a valuable treatment, see Fuller’s “Synergetics”).

The more we dig into particulars, and the more refined our methods and concepts become, the more surprising the discoveries will be; see Williamson’s (1987) deliberations on dowsing, revealing that many organisms contain tiny magnetite particles, e.g., certain “bacteria are actually microscopic living compass needles”! How does diagenesis affect magnetism, demagnetization and remagnetization?

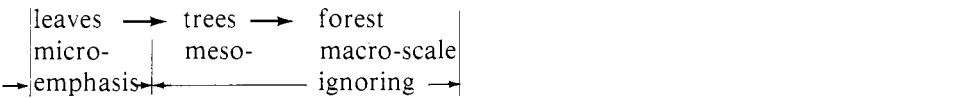
To push the above enigmatic situation into an even greater unknown setting: how do the five natural forces (gravity, electromagnetism, strong and weak interactions, and the as yet ill-understood “fifth force”) control or influence chemical, physicochemical, physical and biological diagenesis? (See Anonymous, 1986, 1987a; DeRujula, 1986.) Can we still deal with isolated, selectively chosen (based on what criteria?) phenomena?

Geochemical – mineralogical systems of diagenesis are too often investigated in “fragmented” approaches, i.e., only one or two methods are used, as just stated above. To compound this “isolation of data”, the information obtained is not integrated with already available data, or the problems encountered (related to methodology, information obtained, hypotheses used, etc.) are not placed into context which would have permitted a “comparative phenomenological perspective or overview”. As elsewhere in this Introduction, one has to reiterate that by using structured linkage-type diagrams, as in Fig. 5, one would be compelled to put all aspects into perspective. (Only Observations versus Interpretations and Fluid Inclusions have been related to all other variables in this figure.) Such diagrams have been utilized for specific purposes also, i.e., in petrography and petrology and then can be called “petrogenetograms”, and in diagenetic studies as “diagenetograms” (numerous types), which often are of the flow-chart-like variety. (The matrix-style tables or models have already been illustrated in the Introduction of Vol. I. Note: According to the Oxford Dictionary, a “matrix” as defined in mathematics is “a rectangular arrangement of quantities or symbols”). Linkage-concatenation flow diagrams have been employed by Bolger and Weitz (1952), and Robertson and

Vandever (1952) to depict mineralogical paragenetic and reaction relations, e.g., to outline replacement time – space sequences.



Motto: “The *generalist* cannot see the trees and leaves for the forest”.



Motto: “The *particularist* cannot see the forest and trees for the leaves”.

Some *laboratory-based (micro- and meso-scale) investigations* are highlighted in Fig. 6. These could be considered as an auxiliary diagram of the previous one, but one should take into account another philosophic enigma in geology: if Fig. 6 is founded on laboratory types of investigations, we must “correlate” these variables (and the results) with those pertaining to regional (macro-scale) studies. (See Wolf, 1985, for comments on “scale-jumping”.) [The observation – interpretation, mineralogy, and statistics – mathematics variables have been selectively stressed (see Wolf, 1985)].

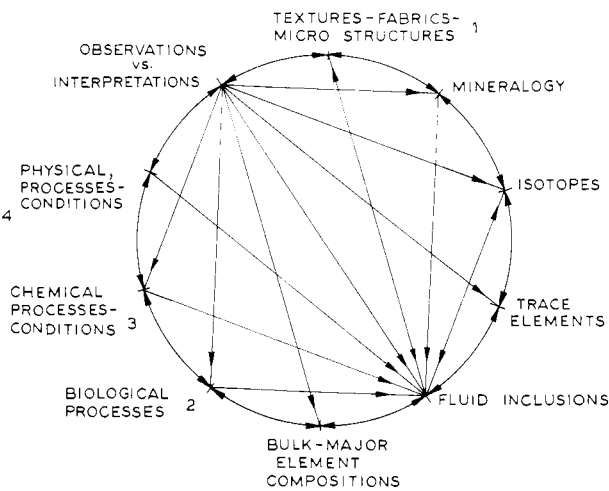


Fig. 5. Concatenation model of a geochemical – mineralogical system. (Wolf, 1986, unpublished.) 1 = Mineral zoning, grain size, grain shape, etc.; 2 = bacterialogical, etc.; 3 = leaching, replacement, etc.; 4 = recrystallization, devitrification.

Question: Related to any specific study, which types of statistical techniques were employed in all those *separate* cases (totalling nine) linked by the lines + arrows radiating from the statistics point? Are the techniques and respective results “compatible”, e.g., in degree of reliability, precision, number of analyses made, etc.? What are the assumptions in each case?

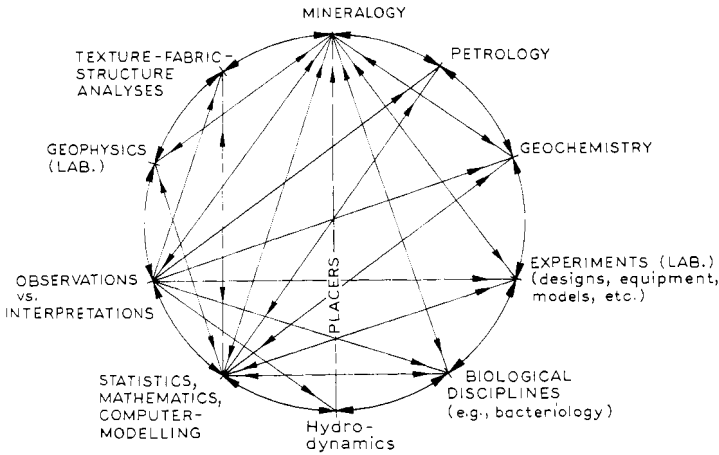


Fig. 6. Some “variables” to be considered in laboratory-based (micro- meso-scaled) studies.

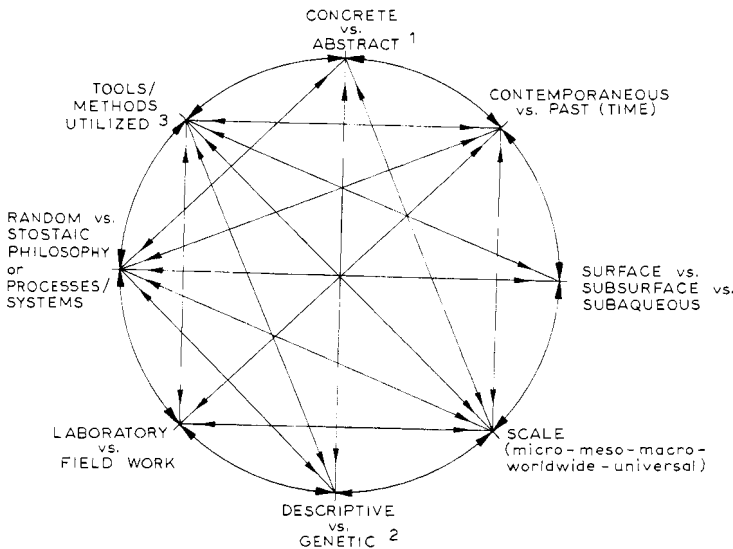


Fig. 7. Exemplar of interconnectedness between methodologies and some natural variables – note emphasis on both concrete and abstract phenomena (see text). 1 = Information/data versus hypotheses/concepts; 2 = observations versus interpretations/extrapolations; 3 = objectivity – subjectivity, degree of accuracy/reliability, etc., changes with methodology used. Thus, each earth-science discipline has its own specific (characteristic?) reliability, etc.

Exemplar of interconnections between methodologies and some natural variables, exemplified in Fig. 7, stresses a few additional variables that must be given attention in any study which claims “perspectivity” and some “degree of completeness”. Note the emphasis on both concrete and abstract phenomena, the former including tools/methods used in laboratory and/or field work (connected by line + arrows because of their reciprocal relationship), and the latter by philosophy + process system analysis, descriptive versus genetic interpretations, etc. All aspects depicted here apply directly to any practical or theoretical studies of diagenesis.

In Ch. 1 (of Vol. 1) on ore-related diagenesis, the writers have made reference to “fragmentation” of the sciences – what is desperately needed are techniques/methodologies and philosophies that result in *decompartmentalization*, *defragmentation*, and conceptual *demodulation*.

“Geological bonism: our methodologies and hypotheses are good, but not always the best possible for numerous human reasons.”

K.H. Wolf, April 27, 1987, Canberra, A.C.T.

(Note: Bonism – Doctrine that the world is good, but not the best possible. Oxford Dictionary.)

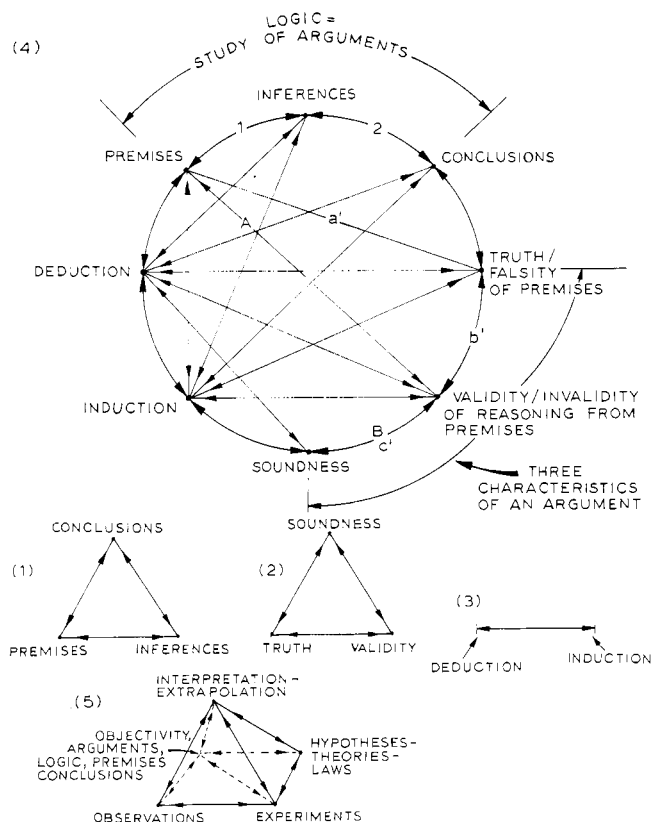


Fig. 8. Logic–validity–ambiguity, etc., as part of the Scientific Method, and their potential inter-relationships (see text.)

Logic – validity – ambiguity, etc., as part of the Scientific Method should “logically” (excuse the pun) be the next topic. Many frustrations in our communications (in differences in opinions; in preferential interpretations or selection of hypotheses; indeed in obvious mis-reconstructions of concrete and abstract data; etc.) are the result of not fully understanding some philosophical principles supporting the Scientific Method, and thus the whole field of the earth-sciences. Well, it is known that discussions of our “thinking processes” smack of “common sense” (but what is that, precisely?). However, Engel’s (1982) book on “*With Good Reason – An Introduction To Informal Fallacies*”, and similar ones on a more professional level that deal with Logic, show that “mistakes in reasoning” are not exactly unknown in the sciences and all other human endeavours. To support Engel’s discussions, Fig. 8 is offered – note the differences between Truth – Validity – Soundness parameters (cf. his table 1.1 of four types of argument).

In super-precise work (and who does not wish to aim for it?), especially if one includes “reliability” and “data-acceptability” (even if only in relation to reconnaissance regional studies), and in particular if super-exacting computer studies are carried out, one ought to know the differences between (see Fig. 8) premises – inferences – conclusions (triangle 1), truth – validity – soundness (triangle 2), and deductions – inductions (triangle 3).

In the linkage – concatenation circle (no. 4 in Fig. 8) these eight abstract variables are interrelated, whereas in the pyramid (no. 5) the variable “hypotheses – theories – laws” has been related or correlated with four other terms. Figure 9 then considers three supplementary “philosophical factors” as an extension of presumption – truthfulness, i.e., overlooking of the present facts – evading facts – distorting facts. We cannot claim as yet that these abstract variables can be ignored in geological investigations – including in diagenetic ones because of inevitable human influences.

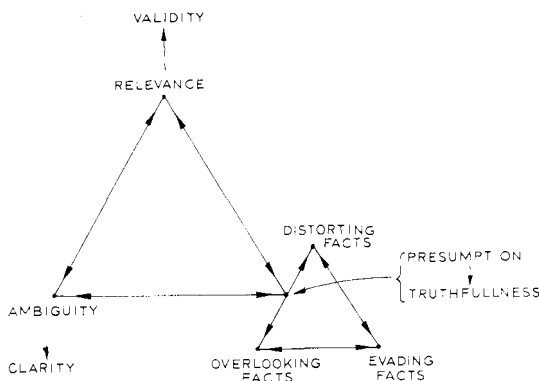


Fig. 9. Supplementary factors (in support and as an extension of Fig. 8) of ambiguity – relevance – presumptions, etc. (see text).

Figure 10 depicts the actual and potential interrelationships of “phenomena” as utilized directly and indirectly when the mind of the investigator applies the scientific method. Can a computer imitate all these phenomena and operations?!!¹

It may be a good place here to also point out the progress made in formulizing “expert systems”, which have been partially or fully successful, depending on circumstances. However, note also the limitations (indeed “misdeeds”) of “scientific experts” in forensic settings (cf. The Canberra Times, May 25, 1987; and especially Freckelton, 1987).

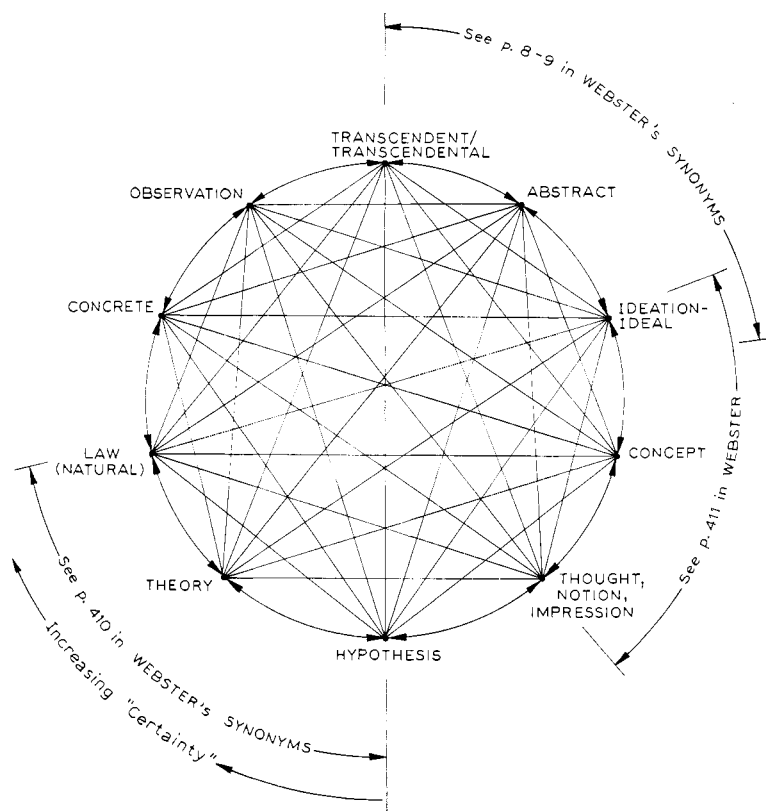


Fig. 10. Actual and potential interconnections between three sets or groups of “phenomena” employed in the “scientific method”: (a) abstract – ideation – transcendental (versus concrete?); (b) idea – conception – thought, notion, impression; and (c) hypothesis – theory – law (note the increase in “certainty”). See Merriam – Webster, 1984, for synonyms – analogues – discriminated words. No arrows, either uni- or bidirectional (reciprocal), have been provided for simplicity’s sake.

¹ Remember that a computer has no conception of “Ignoratio Elenchi”, i.e., no notion (as yet?) of the “ignorance of the conditions of a valid proof (Aristotle)” (Oxford Dictionary) and behaves as though it does not need such proof.

The above ought to find a place in our search for precision, accuracy, reliability, and applicability. And there are at least seven more pertinent topics to be covered below.

“Sound geologic conclusions cannot be reached by following a few narrow lines of investigation, but all such lines of research must be followed that each may shed light upon the other. Unless this principle is fully recognized, a geologic survey might lead to conclusions of no value to the people at large, or conclusions might be reached so erroneous as to be misleading.”

John Wesley to the Allison Commission in the United States in 1885.

Note that “The principle is sound, but Powell, like many others of his time, did not fully comprehend the magnitude of the task that he proposed of encompassing all knowledge of a given science before applying any part of it”.

From the Preface in Rabbitt (1980).

Some “practical philosophical” variables and their interrelations is our next “contextual philosophical matter” related to our concrete and abstract techniques. Wolf (1981) has offered some thoughts on “degrees of perceptability, resolution, reliability, accuracy” and related topics, such as pro- versus contra/anti-indicators or criteria, or non-supportive versus supportive indicators. These “degrees” (of reliability, etc.) are often a direct consequence of our terminologies and classifications, as much as of the limiting hypotheses we use – and a result of our “confining fragmentation – compartmentalizing or modulizing thinking processes”. (Oh, yes, there are so-called “intellectual – conceptual modules”, as the authors like to call them!)

So, how can we coax our intellect to be more efficient? One way is to take into account the following eight variables (again either concrete, abstract, or a combination of both): assumptions, limitations, alternatives, transitions/gradations, overlaps, continua/spectra, and not to forget *unknowns*. Any study “worth its salt” (allow us this colloquialism), must consider these seven parameters. (As the master said to the apprentice/trainee: “If you don’t, you are hiding something!”) That they are influential as separate identities, or in combination of two or more, as well as being complexly interrelated (in various ways), is stressed in the linkage diagram in Fig. 11.

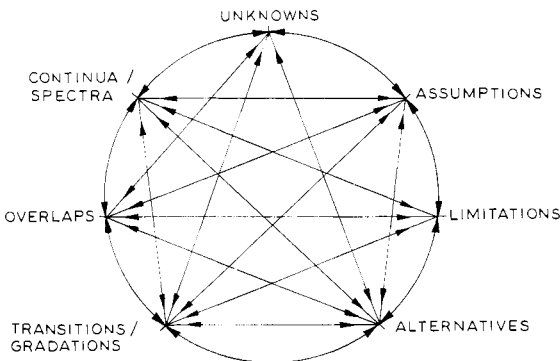


Fig. 11. Some “practical philosophical” variables and their interrelationships (see text).

The eighth parameter is “context” (or “perspectivity”). This has led the senior writer (Wolf, 1974, unpublished) to some interesting conclusions related to the application of scientific concepts, namely to a number of “contextual relationships” in the earth-sciences (and in other fields). Let us start with “contextual separation” as based on “scale-jumping” and “context per se – jumping”. Wolf (1981, see also above) has referred to the theoretical and practical “mismatching of data” that has been obtained from micro- meso- and macro-studies: a few thin-section data can hardly support logically a continent-wide study (to use an extreme case to drive home the argument by an exaggeration). The same applies to “context per se – jumping” when, for example, a claim is made that the teachings of the bible can explain organic evolution or marine transgressions – regressions! Or consider the famous monkey trial; or when diagenetic data purely based on pH/Eh, low-temperature/pressure, short-time laboratory experiments are applied to metamorphic, higher T/P, extremely long-time phenomena by extrapolation. Thus, one has to be extremely careful in “contextual transferences”.

Based on the above, there is little doubt that there are different degrees of “contextual hiatuses” or “separations” also. The application of sedimentological – diagenetic to surface – volcanic phenomena illustrates a plausible direct contextual transfer. But to compare surface diagenesis with deeper-subsurface burial metamorphism demands a “contextual jump” to bridge a “contextual separation” that may make a reasonable, sound and plausible correlation of data between the two systems invalid. Enough has been said to demonstrate the fundamental need for putting matters into context or perspective. But do consider also the following other types of contexts: contextual continua/spectra, contextual linkages/interrelations, contextual overlaps, and contextual transitions/gradations.

*Types of definitions*¹. As every scientist knows, definitions are part of our communication system: no clear delineation of words/terms, concepts, etc. – no clarity and therefore confusion. Defining is a “honing mechanism” to improve thinking. But there is more to the “phenomena of definitions” (as the writers call it) than one usually gives credit to this aspect – we go as far as saying that we earth-scientists have nearly totally ignored the “definition problem” (except for some absolutely necessary philosophizing about it when we are forced to do so) – an important technique or tool that needs to be periodically sharpened. Note that what many loosely called “definitions” are actually “explanations” (and then often incomplete) (cf. Bates/Jackson, 1980; and Laznicka, in Wolf, 1985, vol. 11, p. 137, footnote).²

¹ “Definition – This topic is treated under the following titles: classification theory; logic, formal; logic, history of; and semantics . . . the idea of definition plays an important role” (Encyclopaedia Britannica).

² To some readers these “terminological expansions” based on defining and redefining may appear to amount to “logomachical games” or “word play” or verbage – which, of course, is wrong, and to be convinced about the usefulness of introducing new names one merely has to read Laznicka’s (1985) and Wolf’s (1981, 1985) deliberations, among many others. No “verbomania” á la Ogden/Richards (1985, p. 45) is involved.

Many researchers avoid what they consider to be fruitless philosophical enigma of definitions, but the ever-increasing meticulousness in the use of computers, modelling, and systems analysis requires comparable honing of our terms and classification schemes. Unfortunately, the methodology of defining scientific terms has not kept up with our research requirements in some instances.

Fogelin (1982, pp. 91 – 93) opined that: “Definitions are . . . important, but to use them correctly, we must realize that they come in various forms and serve various purposes. There are at least five kinds of definitions . . .”, which are: (1) lexical, or dictionary, definitions; (2) stipulative; (3) precisising; (4) disambiguating; and (5) theoretical definitions. Fogelin also mentioned “contextual definitions”.

Ogden/Richards (1985, 2nd ed., pp. 109 – 138) offered a preliminary “practical” classification of the relationships between definitions and the referent: (1) symbolization; (2) similarity; (3) spatial relations; (4) temporal relations; (5) causation: physical; (6) causation: psychological; (7) causation: psychophysical; (8) being the object of a mental state; (9) common complex relations; and (10) legal relations.

Other philosophical researchers in science have also referred to “operational” and “contextual” definitions, and the definitions of (re)mobilization as used by Marshall/Gilligan (1987) are certainly of this variety – i.e., their definitions within the context of metamorphic (re)mobilization permit unequivocal discussions because their terms have been well defined-cum-explained.

One further aspect common to all definitions is that they consist of two parts: one is “overt” (open, unconcealed, manifest, extrinsic, visible, directly revealed, obvious) because the wording of the definition deals directly and unequivocally with certain specifics; and the other is “latent” (covered, hidden, concealed, invisible, intrinsic, indirectly connected/related to the “overt” parts). The latent parts of a definition can be changed into overt/revealed ones by redefining, broadening, extending any definition. All (without exceptions?; depending on the premises, assumptions, etc.) scientific and other types of descriptions, discussions and models have overt and latent parts. One of the purposes of modelling many variables and their interrelationships is to highlight overtly the hidden/latent assumptions and complex intercontrols which, all too frequently, escape one’s attention.

Another very common problem is the existence of synonyms or analogues (see Webster’s New Dictionary of Synonyms, 1984) – see Wolf (1981) for some related discussions. An extension of this is the widespread confusion and reciprocal substitution in the scientific/technical literature of general for specific terms, or vice versa, specific for general more broadly applicable ones. Even whole genetic hypotheses can be represented by a specific term or expression which automatically/intrinsically/implicitly incorporates a process or concept and thus is so “hidden or camouflaged” that this process/concept is lost in the contextual matrix of the major phenomenon, i.e. it took up an undeserved latent/covert position and, consequently, may be unconsidered or taken for granted! Take, for instance, the process of a diagenetic system: how often do we consider “(re)mobilization” as part of a “source – transportation – (re)precipitation” continuum? The same applies to the phenomena of diagenetic – catagenetic – metamorphic transformation, alteration,

zoning, lateral secretion, leaching, etc., all of which require (re)mobilization of fluids, ions, etc. (the senior author has counted without effort 32 processes all dependent on remobilization).

Inasmuch as definitions are an implicit and explicit part of classifications, let us list the “domains of classifications” (see Encyclopaedia Britannica on “Classification Theory”); another phenomenon computer specialists and system analysts must incorporate in their refinements:

- (a) Classification of perceptual and non-perceptual objects,
 - of morphological and genetic criteria,
 - by differences of kind and of degrees, and
 - by differences of quantity and of quality.
- (b) Classification in the natural sciences,
 - in the social sciences,
 - in the applied sciences and medicine, and
 - of information.

As to the role of classification in the Scientific Method, one can list

- (c) Its relation – to and dependence on theory,
 - to nomenclatures, and
 - to philosophical issues regarding classification.

“The adoption of a nomenclature is to an important extent an attempt to establish the categories of classification; but every stage in the progress of knowledge is marked by a stage in the progress of classification, and any attempt to fix permanently the categories for a nascent science must be futile. Insofar, then, as proposed uniform methods of nomenclature and representation are designed to establish the fundamental categories, no good can be accomplished.”

John Wesley Powell in 1881; from Rabbitt (1980, pp. 62–63).

“So long as historical geology continues to be a living science, no definite system of nomenclature can hope to be permanent, nor even, perhaps, to give temporary satisfaction to a majority of geologists. Nevertheless . . . teachers and geological surveys must have definite systems, and so the task of making and remaking them is a sort of necessary evil.”

Grove Karl Gilbert to the International Congress of Geologists in 1887; from Rabbitt (1980, p. 287).

“It is wise to guard oneself against the attractiveness of what appears to be novel, and hence presumably an advance on previously conceived ideas, and not to confound speculative assumptions with demonstrations.”

S. F. Emmons referring to J. E. Spurr’s genetic classification of ore deposits; from Rabbitt (1980, p. 333).

The Real – Systems – Model Worlds Trilogy. In the past, we have relied on “more simple” (always a relative phrase to put into perspective with our progress through time) methods and concepts – often by merely utilizing our highly developed “common sense” and “ordinary thinking processes”, to put it simplistically. Today we have computers¹ and other techniques and tools to reach far beyond the human

¹ As to some sober warnings, see Roszak’s (1986) book on “The Cult of Information: The Folklore of Computers and the True Art of Thinking”, and Aleksander’s book-review thereof.

confines inherited biologically – see, for example, Negatia (1985) for systems analysis, expert systems, and “fuzzy systems” (and the many references therein). Plustwick/Schreiber (1985) have briefly described “the trilogy for real time information” and “three different types of worlds”, as depicted in Fig. 12.

When studying diagenetic–catagenetic–metamorphic–etc. processes in the “real world” (i.e., the geology of a region or thin-sections), we wish to “copy” it to establish “systems world” by utilizing computers in collecting the data, for instance. Then we formulate the “model world” or “conceptual model” as founded on our scientific knowledge. Using these models we interpret, measure and observe another geological area or phenomenon – we use “model logic” (Fogelin, 1982, p. 175). And so the scientific method continues. In our “data presentation–systematization–model presentation” in studying secondary geological mechanisms and environments, we must clearly know where we are within the “trilogy of worlds”. We still deal with a “fuzzy world” – a concept that is being increasingly employed in the earth-sciences also.

The Objectivity–Reliability–Accuracy¹Continuum/Spectrum has been offered by one of the present authors (Wolf, 1981, 1985) as Table 1 (see accompanying explanatory comments). Note that the studies of diagenesis–catagenesis–metamorphism covers the whole continuum from the top to approximately the center of the continuum, i.e., from the most reliable/exact/precise (i.e., mathematics,

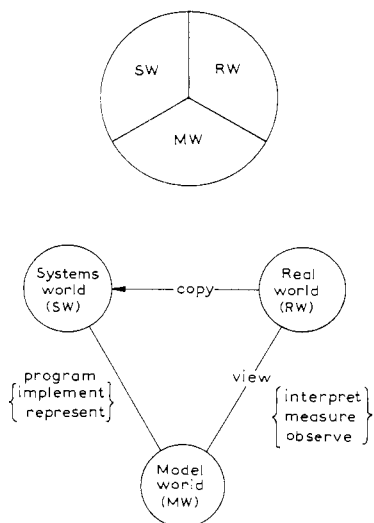


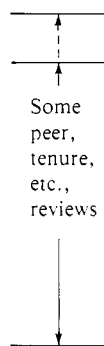
Fig. 12. The Real–Systems–Model Worlds Trilogy (see text for explanation and reference).

¹ A comprehensive philosophical and mathematical summary of this topic (specifically written for earth-scientists) is long overdue – including discussions on “random or statistical errors”, “systematic errors”, “illegitimate errors (blunders)”, repeatability, estimators–estimations–guestimations, precision versus accuracy, “significant numbers”, etc.

TABLE 1

Continuum/spectrum of objectivity¹ of various disciplines^{2,3} (Wolf, 1985, table I, p. xv). Diagenetic studies comprises many of the disciplines⁵

Continuum ³	Disciplines ^{2,3}
Greatest objectivity-reliability ¹	Mathematics (pure, theoretical)
	[Physics Astronomy] 4
	[Chemistry Medicine Biology] 4
	Geology⁴ e.g., crystallography (more exact) e.g., plate tectonics – paleo- geography (less/least exact)
	[Climatology (weather forecasting) Economics Politics Sociology Psychology Etc.] 4
	[Religion Astrology Metaphysics Telepathy – precognition – clairvoyance – etc.] 4
Lower-least (?) objectivity – reliability	



¹ "Greatest objectivity" is more or less equivalent to "least subjective", "most exact", "greatest accuracy", "highest degree of precision", and "greatest reliability" in regard to both methodology, concepts, and results obtained. (But beware of exceptions.) This scheme is very generalized and "averaged-out". For precise thinkers there are, of course, certain differences and similarities between objectivity, accuracy, exactness, precision, and reliability, depending on the context these terms/concepts are employed.

² "Disciplines" comprises the natural sciences, "humanities" and "arts".

³ The whole spectrum is in reality an approximation only, each of the major disciplines could be divided into a spectrum (or several sub-spectra?) reflecting the "degree of objectivity", etc. See range of Geology.

(Footnotes continued on next page.)

physics) to the intermediate disciplines [(through chemistry and biology to various sub-disciplines of geology to (paleo-)climatology (ignoring for the present the more metaphysical topics)]. Consequently, diagenesis encompasses several investigatory fields ranging in accuracy and reliability from the highest to a much lower level!

Concentrating on geology per se as a major discipline comprising many sub-disciplines, Table 2 has divided that latter into two major groups: (A) consists of the more precise; and (B) of the less precise fields. Further generalized meaningful subdivisions are impossible because of the innumerable potential combinations of the 9 A-type with the 12 B-type sub-disciplines. Only when specifics are outlined, can one arrange these sub-disciplinary combinations from the most to the less precise or less objective ones.

To be sure, in any unequivocally well-planned research or exploration project, one ought to list (see Table 3) the sub-disciplines selected and give the corresponding aims/purposes/results required; the concepts, etc., used and assumptions made; the range of scales selected (micro-, meso- and/or macro-scales); methodology chosen; and their respective precisions – accuracies – degree of reliabilities.

Wolf's "Belief – Fact – Hypothesis – Convention – Metaphysics Pyramid" was first offered in 1985 and is reproduced in expanded (i.e., corrected) and modified form here. Of the five phenomena, the four B – F – H – C (some would maintain also the fifth, M) are directly applicable to the philosophies involved in diagenetic studies (Fig. 13).

We definitely encounter in all research projects of secondary geological – geochemical phenomena a whole range of beliefs, facts, hypotheses and “conventional wisdoms” (based on presently accepted and agreed-upon concepts). (See caption of the figure.)

The numerous interrelationships between these five variables (implicitly comprising both concrete and abstract types) are depicted by numbers i – ix. It may well be useful (both from the theoretical and practical viewpoint) to plot ones concepts, data, interpretations, methodologies, etc., on this diagram. Which well-cherished “hypothesis” falls somewhere along the H – F, H – B, H – C, or even along the H – M continuum line? (See Hallam's, 1983, “Great Geological Controversies” for some turning points in the evolution of geological thought, how changes came

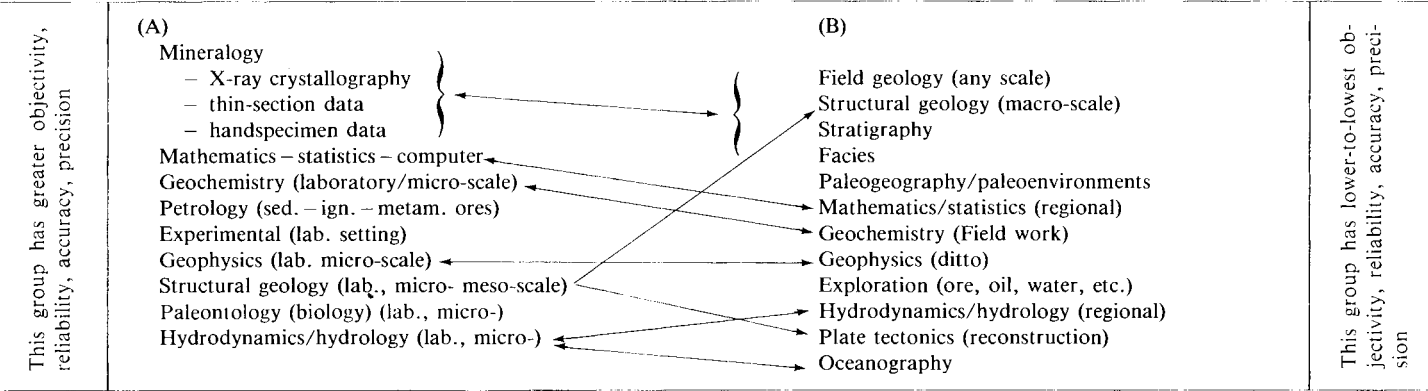
⁴ The brackets lump together those disciplines of approximately equal degree of objectivity.

⁵ Many of these major disciplines (and, thus, many of their sub-disciplines) are complexly interrelated – which could well be modelled by linkage/concatenation-type diagrams to increase the accuracy of this philosophical outline. Some interrelationships, of course, have resulted in weird phenomena, e.g., clairvoyance – geological exploration, religion – explanation of organic evolution, whereas others are accepted interdisciplinary combinations that have proved to be highly successful (e.g., mathematics + chemistry + geology) or are becoming increasingly recognized as having a great potential (e.g., chemistry + biology + medicine + climatology + sociology – pollution + climate-induced-allergy controls; for comment, see Wolf, 1986, on some vitally significant interdisciplinary studies needed in the future, many directly related to “contemporaneous diagenetic systems”).

All the above major disciplines, as well as respective sub-disciplines thereof, can be placed into a pyramid or tetrahedron with “fact”, “convention”, “belief”, “faith”, and “metaphysics” at its apices (Fig. 13).

TABLE 2

Two groups of earth-science disciplines: their degree of precision, reliability, scale-application, and objectivity (Wolf, 1978, unpublished)¹



¹These abstract phenomena depend on so many specific methodological combinations and styles of application that only these two groups (A and B) are possible in a general treatment (see text). Between each member of A and B, there are many continua/spectra, overlaps, and gradations/transitions. (Compare with Table 3.)

TABLE 3

Six concrete and/or abstract “variables” that are part of most earth-science projects and which ought to be clearly planned/designed, structured and described (an exemplar)

Sub-discipline	Aims – purposes – results required	Concepts – hypotheses – theories – laws used; assumptions ²	Range(s) of scales of application	Methods – tools used ²	Degree of reliability – accuracy – precision needed ²
Mineralogy – petrology + Geochemistry + Statistics + “Feinstratigraphy”	Diagenetic facies controlling oil – ore (Pb – Zn – Ba – F) association and genetic inter-dependence in carbonate – evaporate – shale complex	Basin sediments’ dewatering, compaction – lateral-secretion concept, with or without diagenetic controls and/or exhalative fluid supplying material	Micro- meso- macro-continuum/ spectrum bridging logically all scales ¹		

¹The “scale-continuum” is stressed here, because the aims, concepts-theories, methods – tools and degree of reliability/precision, etc. all form separate, but complexly interconnected, continua/spectra depending on the subdisciplines (and combinations thereof) utilized. E.g., there are mineralogy – petrology spectra, petrology – geochemistry spectra, etc.; ore – oil association spectra; and these are applied to the micro- to-macro-continuum! Indeed, careful planning is needed!

²To be carefully selected/determined.

about, and discussions of the ways in which scientific concepts develop, are tested, and become modified.)

Modes of analysis—methodology of modelling/reconstructing. Earth-scientists (like mathematicians, physicists, chemists, and others) must occasionally remind themselves of how, what, why, and where they measure in order to fully comprehend the meaning, usefulness/application, accuracy/precision, and limitations of their methods. Without doubt, this is also the case in diagenetic investigations. The related topics are vast and only some comments can be made with references to a few selected publications.

Stevens (1985) discussed in general terms several pertinent subject matters: mathematics versus measurement, the nature of scale (identity, order, intervals, ratios), the operational principle, and conflicting laws. As a “classification of scales of measurement” he established four groups with respective rules or basic empirical operations, mathematical group-structures, and permissible statistics (invariantive). Thus, anyone making measurements of the nominal (see some references to that

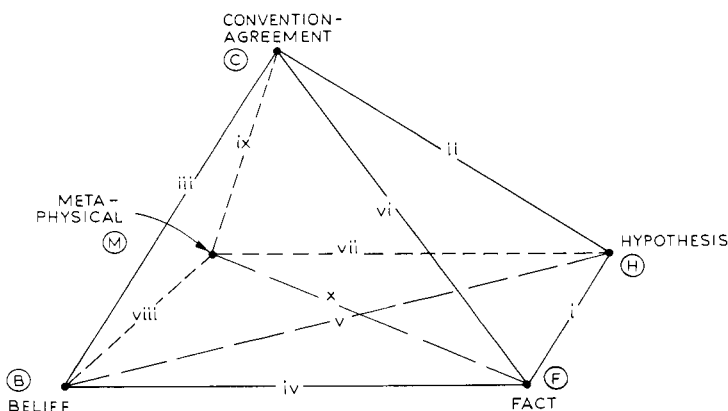


Fig. 13. The “Wolf B – C – F – H Pyramid” based on ten continua or spectra (modified/corrected from Wolf, 1985, fig. 1, p. xvi). (Note that philosophers engaged in more exact deliberations may consider this approach too simplistic – but the pyramid and ten spectra are “practice-based”.) At least one basic assumption is made, namely that there is human freedom in the system; meaning that no forced negative-brain washing and/or “negative-concept-coercion” is interfering. Diagenetic studies (concepts, methods, results, thereof) are, no doubt, a combination of at least B – C – H – F).

B-pole – Belief = opinion/faith-based, such as in religion and in dreams; out of range of scientific methods.

C-pole – Convention or agreement-based, such as in the usage of nomenclatures, classifications, scale (temperature, pressure, length, etc.); language, linguistics; monetary systems; judiciary laws; customs, social rules.

H-pole – Hypotheses (development/experiment-based), concepts, principles, methods (all have a degree of subjectivity, and are interpretive, extrapolative, speculative).

F-pole – “Facts”-based on natural laws, more-or-less proved theories, logic and repeatable observations and “objective” data.

M-pole – “Metaphysics”-based fields of investigations, phenomena and concepts or “beliefs”, such as dowsing, telepathy – precognition – clairvoyance and even some type of “predictions” or “prognostications” in the sciences.

below), ordinal, interval or ratio types during petrographic – diagenetic investigations must carefully choose the corresponding “permissible statistical methods” (see Stevens’ table 1).

In “Methodological Problems of the Systems Investigations in Geology”, Kosygin (1970) outlined four groups of “geological specializations” (each with its own “types of problems”), namely static, dynamic, retrospective – historical and retrospective – genetic types of “natural systems”; see Table 3. Examining this table, it is rather obvious that in studying diagenetic systems, for instance, all four systems are to be taken into consideration: our methodologies, philosophies, reconstruction – reliability, etc., change accordingly.

Van de Plassche (1986; see his Introduction) discussed “the production and academic or applied consumption of sealevel-change records”; outlined the methodologies of three main groups of earth science disciplines and correlated these with the type of data obtained and their applicability in evaluating, interpreting and predicting, as well as in formulating models. For their “*research economy*” (i.e., in planning, executing and integrating various research approaches) he had prepared a conceptual model comprising both inductive and deductive methods which, respectively, are linked to hypotheses and models, for instance (see his fig. 3, p. 4) – thus, such a diagrammatic plan would ascertain that any potential research project meets all methodological and theoretical requirements.

As an extension of the just-stated, one would do well to heed Wezel’s (1986) philosophical comments in his Preface. Let us paraphrase or quote a few important gems: “The workshop . . . has been organized with the aim of increasing our understanding . . . on the basis of empiric factual data, rather than particular theoretic models. Reality, in fact, almost always rejects affirmations and speculations built up around a table. Quite often a trivial piece of field data appears to have much more weight than many fascinating hypotheses put forward by the human mind The development of geosciences itself provides numerous examples of statements and concepts which were first said to be impossible but later proved perfectly valid. This tolerant attitude towards unorthodox ideas is not merely that of enlightenment and impartiality but reflects also cautious wisdom in that the heresies of today may perhaps become the truths of tomorrow and the truths of today are not eternally valid dogmas . . . no-one knows the whole geological reality, but each one of us, at most, presents some fragments and splinters which appear to us as tiny illuminated spaces fleetingly glimpsed through the great fog of our ignorance. Thus, it is necessary to stimulate the creativity, originality, intuition and eclecticism of young researchers rather than block them and orientate their minds towards fixed, pre-established doctrines . . . ”To do this, great wisdom is required – and the present Introduction with its emphasis on methodologies, concatenation models, etc., is merely a small plea towards fulfilling our needs.

Wenk (1965/66) stated that in geology we have four methods of modelling or reconstructing (= Methoden der Abbildung):

(a) Through the application of the Law of Uniformitarianism – contemporary processes, products, and environments are studied and compared with those of the geological past (and/or vice versa – the past is compared/contrasted to the Recent). This principle depends on our observation ability, accessibility and geological time.

(b) The empirical approach: analogues and models are used – commonly the conditions are better understood and the relationships are simpler, so that the analogue model's accuracy or reliability ranges from low to relatively high – but the results are still “speculative” and usually qualitative.

The pros and cons of models, and their reliability, limitations, etc., are increasingly being evaluated. For instance, Selley (1985, ch. 12) discussed “mythical and mathematical sedimentary models”, referring to the deductive method based on the subjective understanding of Recent environments and deposits and the empirical approach founded on a mathematical analysis of objective criteria. The first technique is typical of geologists, while the second is more appropriate for a computer – but both the geologist and computer need some kind of conceptual framework; consequently, systems, classifications and models are needed, although each has its “objective characteristics” and “subjective applications”. (The reader is referred to the treatment of “Subjecting and Objecting – An Essay in Objectivity” by Deutscher, 1983, although he deals with concepts beyond those of the scientific method.)

Cox/Singer (1986) dealt with the classification of models, such as descriptive, genetic, probability, quantitative process and other model types. Their “maturity of models” also offers a useful concept applicable to all models in any geological discipline inasmuch as the “mental pictures” we have of geological processes develop or evolve with increasing understanding – especially see their fig. 4 regarding “comparison of relative levels of understanding of some important model types”. A similar evaluation of our diagenetic models ought to be undertaken.

Reading (1987) provided a personal viewpoint of “fashions and models in sedimentology”, discussing some of the “many disastrous consequences in interpretation and understanding” as a result of mindlessly accepting and applying certain models. Reading's philosophizing must be examined by all!, followed by reading of papers such as those by Matthews/Frohlich (1987) on “forward modelling” of carbonate diagenesis (see their comments on inductively “observe and seek to explain” versus deductively “predict and seek to observe”).

(c) The experimental method: Wenk mentioned as an example the pressure – temperature experiments in the laboratory that have resulted in highly useful data, but pointed to the very important geological time-factor that cannot be reproduced. Of course, several dozen other variables can be listed as well as their complex interconnections – at least in a qualitative fashion. Of the hundreds of variables known (the senior writer has prepared a list of them which cannot be reproduced here, however), only a few preferentially selected ones are tested in any one laboratory setting. See the interesting deliberations on “The Neglect of Experiment” by Franklin (1987).

(d) The theoretical method based on physical and chemical laws – however, the geological processes and environments are extremely complex and overlapping, transitional/gradational conditions are often unknown (including continua/spectra phenomena), so that even the “most capable” computers cannot, as yet, solve extremely intricate situations. Also, our models are too simplistic as yet – the mathematical challenges are enormous.

In the Introduction to Vol. I, reference has already been made to “fractals” – how can this rather new concept be applied to physical and chemical laws in, for

example, regional geological studies (see Peitgen/Richter, 1986, for “Images of Complex Dynamical Systems”).

In their book on geochemistry, Allègre/Michard discussed the “modes of analyzing” natural processes (or “modes of thinking”?). There are at least four: (1) In addition to our attempt to design the linkage-cum-concatenation¹ circles or models² (see the Introduction to Vol. I) that overtly highlight interrelationships in time and space. For instance, Allègre/Michard (1974, p. 79) listed the following three: (2) thermodynamic way through the study of irreversibles based on principles of partial equilibrium – exemplified by weathering and metamorphism which involves irreversible thermodynamics; (3) the kinetic method of studying the combined diffusion and reaction chemistry – exemplified by the investigation of the redistribution of certain elements in oceans by using “box models” (including residence-time concepts of solubles and element distribution) (see models of world’s oceans in Allègre/Michard, 1974, pp. 87–90 – they also discussed chemical diffusion–reaction coupling and advection–diffusion); and (4) methods that in some ways approach the preceding one, i.e., elegant methods of calculating balances (also used in the “method of boxes”) as demonstrated by investigations of diagenetic evolution, utilizing the kinetic method.

“He who is at the foot of a mountain sometimes cannot see the summit.”

G.T. di Francia (1976/1981, p. 1), in reference to the fact that many specialists are “too close to their Subject” and may have reached a dead end, concluded that we must digest an enormous quantity of knowledge which we have acquired to gain an overall perspective.

“The epistemology of a given science is inseparable from that science; conceptually, even if not always chronologically, the birth of epistemology is simultaneous with the birth of science. Every advance in science is an advance in its epistemology.” *G.T. di Francia* (1976/1981, p. 3). (Epistemology – The theory of science of the method or grounds of knowledge. Oxford Dictionary.)

A somewhat more specialized discussion dealing with a more specific problem was given by Burger/Skala (1978) in his “study of spatially dependent variables: models, methods and problems”. The abstract stated: “A regionalized variable is any numerical function with a spatial distribution which varies from one place to another with apparent continuity, but the change of which cannot be represented by any workable function. This definition characterizes many variables in geo-sciences as chemical, geophysical and structural data, ore contents, etc.” This definition also applies to diagenetic–catagenetic–metamorphic–etc. facies. The above-cited authors dealt with, for example, distribution, existence of global and local trends, autocorrelation, interpolation, reliability, and others.

¹ Note that most of our investigative methodologies of the past and today have been of the “differentiative” or “analytical” type – in opposition to the “integrative” or “synthesizing” style. These linkage/concatenation models will alleviate (or at least help) in the absence of integration – synthesizing techniques in geology.

² Instead of “circles”, some researchers prefer to use the idea of circuit or circuitation. Thus, the linkage models, when of a circular type, would indeed depict the “natural circuitry” of interconnected variables and environments.

To return to a more fundamental “philosophical” enigma: Kitts (1976) in his “certainty and uncertainty in geology” discussed the role of hypotheses in the explanation, prediction and retrodiction of events. He concluded that “Deductive explanations and predictions are rare in geology, and upon this fact rests the widely held view that geologic knowledge is fundamentally probabilistic in character. But uncertainty in geology can seldom be traced to probabilistically formulated generalizations. Geologic inferences commonly invoke generalizations that are best considered to be normic. Although normic generalizations cannot support predictions, they can often provide adequate support for retrodictions, the most characteristic kind of geologic inferences”. [Compare this with comments by Kosygin (1970) on retrospective – historical and retrospective – genetic systems; Wenk’s (1965/66) on Uniformitarianism, etc.; and Steven’s (1958) on nominal, etc., scales.] Kitts also treated certainty of knowledge as based on natural laws, generalizations (universality) versus particularization, assumptions used, random and deterministic phenomena, methodologies developed, recordability, among others – all these “philosophies” apply to certain aspects during the study of diagenesis.

Watson (1969) in his “explanation and prediction in geology” believes (Abstract) that “recent speculations . . . on the nature of geological science are . . . erroneous. The interest of historical scientists in unique things and events does not mean that they cannot or should not derive laws for explanation and predictions; the usefulness of statistical generalizations does not mean that there is an element of uncertainty of chance in nature; nor does the principle of indeterminacy indicate that there is essential randomness at the base of natural processes”. Thus, Watson described in his paper “the correct nature of geology as a science”!

Watson approached his refutation against others (who have misrepresented the nature, limitations, etc., of geology) by asking and answering some general questions about geology (the writers have added the reference to diagenesis):

- (1) Are there irreducible geologic (diagenetic) facts?
- (2) Are there geological (diagenetic) laws?
- (3) What kinds of laws are possible in geology (diagenesis): (a) cross-sectional laws, (b) functional laws, and (c) historical laws?
- (4) What kind of science is geology (sedimentological, diagenetic, etc., studies)?
- (5) Are there statistical law-like generalizations (in diagenesis – catagenesis – metamorphism, etc.)?
- (6) Is there essential indeterminacy, chance, or randomness in the world (in regard to sedimentological – diagenetic, and other geological systems)?¹
- (7) What are the limits of geology (of sedimentology, diagenetic, etc. systems’ reconstruction)?

¹ Pavlov discussed two models resulting in an analytical paradox: “methodologically, this paradox expresses in the most acute terms the irreconcilability of the ideas of a discrete and continuous world, and that of its variability and stability . . . physics has solved this problem of natural duality by means of quantum physics”. Using a number of concepts, e.g., based on energy content of the Phanerozoic sedimentary rocks, Pavlov concluded that the Heisenberg uncertainty principle functions in geology too. . .

(8) What are the predictive and explanatory potentials of functional laws (in sedimentological, diagenetic, etc. studies)?

“Let us cling to our faith that nature is basically orderly, but let us ask to what limits we are willing to carry our faith. Is nature orderly only to a degree, or is it so rigidly ordered that every movement of every atom is predetermined for all time by the laws of physics and chemistry? This is not really a scientific question, for we have no way of judging how far in space and time the laws of physics and chemistry can be extended. All we know about them, all we can ever know, is that they hold within limits fixed by the ability of our senses and our instruments, to give us information about the world. We may extrapolate them to every movement of every atom if we wish, in order to make the world seem deterministic; but this is an act of faith, unsupported by scientific reasoning or evidence.”

K.B. Krauskopf, from *Bull. Bur. Rech. Géol. Min.*, (2), Sect. II (4), 1972, p. 49.

O'Rourke (1976) elaborated on “circular reasoning”¹ in geology (e.g., using rocks to date fossils and fossils to date rocks) as part of our hard-headed pragmatism. (Here is another case, situation or phenomenon where earth scientists should clearly lay-down the presumptions/assumptions used!) He mentioned: “The radiometric scale also had to be calibrated against the geologic column. The term ‘absolute age’ is *contradictory*, inasmuch as *no process can measure itself*. Indeed, the use of any time scale involves a *degree of circularity*, because successive intervals cannot be compared and are just *assumed* to be equal *from reference to another scale*. Fortunately, geologic time does not enter into the actual work of stratigraphy, as it does into experimental science, so a *consistent argument* is still possible. Stratigraphy should present its case first as a *cognitive process*, from experience; then as a *historical process*, from *inference*. The first part says that countless *sense perceptions* of rock features (lithic, organic and radiometric) have been *compared* as above or below one another by means of maps and sections, and *synthesized* into a geologic column. The second part is the use of this global *standard* as a *chronology*”. Note that the italicized words represent “philosophical – psychological” phenomena discussed by other authors who have been paraphrased/quoted here – and O'Rourke (1976) has employed these phenomenological concepts in a highly practical fashion.

Inasmuch as O'Rourke discussed the philosophies involved in stratigraphic reconstructions, geologic time measurements, rates of processes, “time as an interpretation of space” (p. 48), “physical continuity” versus stratigraphic “immaterial time units”, reality and continuity of units, global classifications, differences between Western and communist stratigraphers in recognizing sedimentary units (as based on pragmatism versus dialectic materialism, etc.); definitions of litho-, bio- and chronostratigraphic boundary – stratotype concepts and its accompanying classical dilemmas; “Law of Transformation of Quantitative into Qualitative Changes”, “Feinstratigraphie”, spatial order, correlation, negative evidence – amount of information, physical time scales – “absolute ages”, regular cyclic processes, average rates of sedimentation, among others, any researcher of diagenesis – catagenesis ought to take his ideas into account.

Woodford (1956) dealt with “geological truth” and opined that, among others,

¹ He stated (p. 54) that this can be either ignored, or denied, or admitted!

“the degree to which a scientific hypothesis may approach ‘geologic truth’ is a complex problem. The hypothesis in question is either (1) mathematically rigorous, (2) the sole surviving one after exhausting other possibilities, (3) intuitive but fitting an extensive series of known factors, or (4) more-or-less doubtful. In diagenetic studies, the above four cases have all been recognized.

A final word: in addition to the above-outlined scientific – philosophical enigmas, we must not lose sight of the frequently superimposed “human – psychological” communication styles. The form of data-presentation adds another variable – we have to suit the style of writing to the requirements. There are four forms of writing, namely, exposition (presenting facts and figures); descriptions (helping the reader to visualize an idea or situation; narration (telling in a chronological story), and persuasion (trying to convince the reader to accept the writer’s perspective). All four styles are used by researchers, explorationists, teachers/professors, managers, etc. – and we must select the correct style of writing to suit the data and purposes/aims of the discourse, among others.

Some practical/applied geological problems of the Scientific Method. The present brief deliberation is founded on publications by Ohle/Bates (1981), Madigan (1984), Ridge (1984), Woodall (1985), Morrissey (1986) and Henley/Stokes (1986) – with a brief reference to some other researchers’ work (e.g., Van Bemmelen, 1961; Koestler, 1964; Köbl, 1967; and Lacy, 1982). Many of the above researchers have dealt with ore genesis and metal exploration (= “economic geology”), but most of the philosophical, phenomenological and methodological problems are directly transferable to any other earth-science discipline inasmuch as we all share certain fundamental enigmas – and that includes the problems of secondary processes, environments and their end-products. Of course, since Ch. 1 of Vol. I reviews ore-genesis-related diagenesis, the ore petrologist will find the following discussion to be an extension of that chapter.

What is particularly intriguing is that most of the above-listed publications advocate a shift away (even if slight only, it is of importance) from the “earth-science norm of thinking”. Madigan (1984) asked for “paradigm shifts” à la Kuhn (1970, a book that has increasingly been quoted by geologists), and Ridge (1984) and Morrissey (1986), at least indirectly/implicitly, made similar requests. However, as we will see, even the “geological free-thinkers” like Ridge, Morrissey, Woodall, Lazenicka, Wolf, Elliston, Stanton, etc. (see References) – although they may deviate somewhat from the general run-of-the-mill earth-scientist – do not agree fully with each other because each applies his unique thoughts to specific situations.

“Observations beget data that beget new concepts/hypotheses, but these in turn beget new observational needs, . . . and so on, ad infinitum.”

Karl H. Wolf, Canberra, A.C.T., Dec. 1986.

Ridge’s (1984) treatment of “genetic concepts versus observational data” governing ore exploration ought to be closely examined by all geologists – geochemists – geophysicists as it is generally applicable as well as specifically to sedimentology – environmental reconstructions and consequently to diagenetic – catagenetic – meta-

morphic systems. But he warns: “What I have said . . . goes directly against all that ore geologists have been taught . . . will be indignantly received by many” – but facts are more useful than any theories!

Ridge opined, by using as exemplars or analogies of seven ore-deposit types, that “these are sufficient to demonstrate the validity of the suggestion that the application of observational characteristics is far more useful in mineral exploration than that of theories of ore genesis”. (Note the highlighting of the “validity – observational characteristics – theories”, which are discussed elsewhere in this Introduction; here is a practical application thereof!) Ridge described/discussed the following ore types (among the seven): carbonate-hosted Pb – Zn, sedimentary/volcanic rock-hosted massive base-metal sulfides, conglomerate-associated Au or Au – U concentrations, and shale- or sandstone-hosted Cu; all these may be either directly or indirectly the result of or can be modified by several types of secondary processes, including diagenesis and of course catagenesis and metamorphism. A few details from Ridge’s publication are presented here.

He strongly argues that for an exploration and exploitation geologist and mining engineer to perform their “function, economic geologists must be sufficiently familiar with the characteristics by which ore deposits are recognized and exploited. It may be desirable, but it definitely is not valid, that they know how and why the deposits were formed as they now are. Arguing by not completely valid analogies, a farmer may grow excellent crops of grains without knowing how the seed germinates; . . ., so a geologist can find an ore deposit even if he cannot explain how it was formed”. Hosking (1974) and Kuznetsov (1973), among several others, have expressed similar ideas (see p. 8 in Ridge, 1984).

But to put matters into correct and fair perspective, Ridge maintained: “This is not to say . . . that the intellectual adventure of trying to explain how and why an ore deposit is where it is not worthwhile – any geologist engaging in it is certainly the better for the experience, for such thought processes as he must use increase his familiarity with ore deposits in general and with the particular type he is considering in particular. If he accumulated all the observable facts (including geochemical, geophysical, and remote-sensing data) pertinent to his genetic problem, his conclusions, if he has reasoned soundly from these facts, probably will be valid. If his observations are incomplete, his concepts still may be true if his geologic intuition is strong enough to supply the missing pieces of his puzzle. But, despite the intellectual satisfaction of his inductive exercise, an ore geologist need not have carried it out to be a good finder of ore deposits”.

“It is hardly appropriate to present to statesmen an argument in favor of the importance of directing scientific research to purposes of industrial utility. There is a sentiment current among ignorant men that profound science is incompatible with practical business, and this arises from the fact that it is difficult to demonstrate the immediate and direct utilitarian purpose of scientific investigation. It is often that such results are not proximate, but only ultimate. When the ignorant challenge the learned for the ‘practical’, or ‘economic’, or ‘utilitarian’ value of their knowledge, the answer is not always rendered in terms within the comprehension of the questioner, and he scoffs at all answers that he cannot understand. Now, there are narrow and dilettant scientists who retort that science is too exalted to be in any manner interested in utilitarian results, and sometimes these wiseacres boast of their devotion to ‘pure science’. But great scientific men, like great statesmen and great men in all departments of society, clearly

recognize the fact that knowledge is a boon in itself and in its utilitarian consequences alike – that wisdom is exalting and knowledge is power.”

John Wesley Powell, abt. 1884 (from Rabbitt, 1980, p. 122).

Several of Ridge’s arguments can be neatly summarized by multi-member pseudo-equations as follows: observation → assumption → agreement with similar earlier observations → agreement with existing concepts → application → further observation. The “concepts”, important to note, do not necessarily include genetic hypotheses, which he feels can be by-passed in many instances! Observations are more important than hypothesizing/theorizing; and in this approach Ridge supports Laznicka’s (1985) descriptive – observational – empirical methodology as outlined in the latter’s book on “empirical metallogeny”.

So, what does Ridge propose as an alternative? – it’s “Total Exploration”, or what the senior writer has been preaching for some time, namely an antifragmentary, integrated approach. That means the application of not merely geochemistry or merely geophysics, but geology and geochemistry, or geology and geophysics, or best of all geology and geochemistry and geophysics. And for “geology”, read “total geology” based on the best-possible descriptions with the data well-classified and well-structured and well-compared/contrasted to highlight similarities/differences, transitions/gradations, overlaps, and continua/spectra as to stratigraphy, structures, petrography/petrology-lithologic associations, ... To this “total data package” belongs the sedimentary – volcanic – metamorphic interrelationships, internal and external depositional and deformational micro-meso-macro-structures; mineralogy of ore gangue and wall-rocks, their paragenetic relations, alteration data (types, zoning, distribution patterns); temperature-of-formation data like fluid inclusions, isotopes; time and timing information; but also concepts of genesis, among others. Total integration is the key!

Like Ridge (1984), Ohle/Bates (1981) stated (p. 767) that a geological model does not have to be fully correct, or one can ignore certain parts thereof (e.g., source of the fluids), to be useful. Consequently, they emphasize the application of “empirical relationships” and “guides to ore”.

“When observed phenomena are not readily explained by forces whose limitations are known to us, we naturally invoke other forces whose limitations are less well understood.”

E.S. Shepard, pers. commun., 1938, to Augustus Locke; from *Econ. Geol.*, 77 (1982): 197 – 198.

Morrissey (1986) elaborated on “new trends in geological concepts” and distinguished “clearly and consistently between geological concepts and geological models”. “If there is a difference, it is that geological *concepts* are ideas and notions, rooted in observation and research, that help to explain geological processes and relationships, whereas geological *MODELS* are attempts to predict the make-up of present-day geological situations, such as ore environments. One attempts to explain *causes*, the other to predict *effects*. Concepts and models may be right, wrong or a mixture of the two. Their main value in mineral exploration is to focus effort and to inspire confidence, ...” These concrete and abstract variables have been interrelated in the linkage model in Fig. 14.

Under the four headings of “limitations” and “successful uses of geological concepts”, and “points of departure”, “fundamental concepts” and “quality controls”, Morrissey outlines the following ideas pertinent/relevant to our present philosophical context related to diagenesis and other secondary processes.

Under “limitations”, he stated: “. . . all exploration . . . is essentially a matter of developing and testing geological concepts and models. Only dowsers and consulting mine-finders of the Yuri Geller school claim to be able to find ore without them. All human endeavours need an intellectual framework, . . . concepts have been part of our intellectual baggage . . . Even so, it is clearly not true that ore can be found only by those whose heads are full of concepts about how orebodies are formed and where they are most likely to occur”. (He gave several examples.) Note that the above partly agrees and partly disagrees with Ridge’s (1984) ideas.

In “successful uses of concepts”, Morrissey announces: “On the opposite side of the coin, some of the major discoveries of recent years, indeed, hinged on smart geological thinking . . .

Serendipity plays an important part in exploration, and the main thing is to have a target concept that inspires confidence long enough for it to be tested adequately”. He also emphasized the use of “factual information” and “persistence” in searching.

In “points of departure”, Morrissey declared that “a more reasonable task than

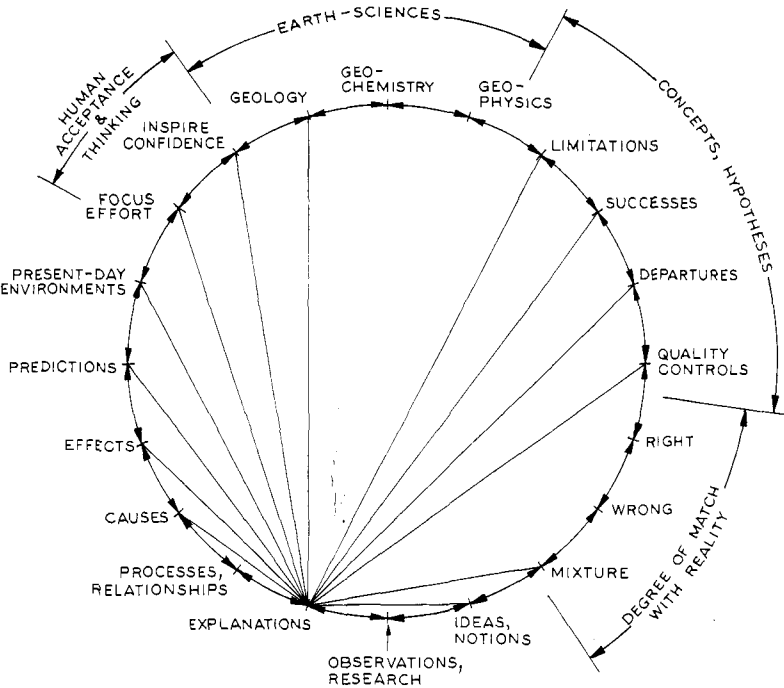


Fig. 14. Linkage/concatenation model (based on Morrissey’s, 1986, discussions) of concrete and abstract phenomena which are to be considered in applying the Scientific Method in research and exploration.

to predict the changes in geological thinking that will be necessary to find ore . . . is to attempt to outline points of departure for possible advances in geological thinking about orebodies, and to indicate a few directions in which advances seem desirable”.

In general, geological thinking about many ore types seem to go at present in opposite directions: (a) some see a “high degree of organization and predictability in ore distribution . . . that one can calculate statistically the ore endowment of any region for which semi-accurate geological maps are available”. Some also go as far as proposing that there are direct and causal links between plate tectonics and metallogeny/minerogeny/minerotectonics; but see the senior author’s opinions (Wolf, 1985). (b) On the contrary, others are intellectually and morally daring, honest and heretical enough to admit unashamedly “a high degree of ignorance about fundamentals of ore genesis and localization, see ore potential in what were formerly regarded as no-hope geological situations . . .”. These intellectual agnostics (read “fence-sitters”) “rest their case on the way in which nature constantly confounds academic predictions, on the highly equivocal results of research into ore genesis . . . the newer concepts (about hydrothermal systems) vastly extend the range of geological environment . . . ores hosted throughout the entire spectrum” of igneous, sedimentary and metamorphic lithologies and settings, as well as spatially and through time.

According to Morrissey, “perils attend both modes of thought”, because ore (and any other material, including diagenetic end-products, for example) is neither randomly distributed nor do we as yet know what constitutes the whole spectrum of prospective environments, let alone all about the genetic mechanisms.

As to “fundamental concepts” (these alone must be difficult to delineate plausibly), Morrissey highlighted (selectively?) the geological environment and age. This is, like the above debate, equally applicable to both ore genesis in general, including to those where diagenesis – catagenesis – etc. had either an indirect (e.g., hostrock conditioning) or a direct (remobilization – transportation – reprecipitation) influence – and, of course, to diagenesis in general, because environment *en toto* and geologic age (absolute, relative, evolution-based) do control many secondary processes.

Geological “products” (ore deposits, industrial minerals, oil, reservoir rocks, etc.) are the result of geological environments. Actualistic/contemporary processes + environments can be observed – new perceptions based on these actualistic evidences allow us to refine some of the crude conceptual models used at present, e.g., Au of Carlin-type. Seemingly different ore types can now be linked and demonstrated to be part of a continuum/spectrum. The importance of environments has led to the recognition “that most of the geological maps that are now in existence are of little use as a guide to paleoenvironments – look at the British Geological maps of the Southern Uplands, for instance”. (It must be made clear, however, that the term “environment” is a general all-encompassing phenomenon/concept, with literally hundreds of variables, and it is not an easy task to sort out the most basic ones.)

“The main reservation that one must have about making environmental indicators, such as rock associations, the touchstone of prospectivity is the time factor

in ore genesis” – the Earth (its composition/structure of crust, mantle – crust relations, atmosphere/hydrosphere) has evolved continually. (But see Laznicka, 1985, for highly relevant discussions.)

Wolf (1981, 1985) and Morrissey (1986) suggested indirectly some “hindsight or retrospective analytical studies”. For example, ore deposits found by geophysical means ought to be examined from the “hindsight/retrospective perspectivity” as to how geological concepts and models could and/or should have located them.

As an interim statement, it must be clarified that the “normal” scientific method (based on the circular investigative stages of problem – collect data – organize data – hypotheses, concepts, theories, doctrines – deductions – verification (experimentation) – either Law or return to new problems; see Wolf, 1973, and Van Bemmelen, 1961), is not contradicted by the “methodological shifts” requested above – merely its application is modified by some “methodological shortcuts” useful during applied/practical problem-solving. The writers, therefore, believe that perhaps one can speak of two (sub-)types of the Scientific Method: (1) a “Pragmatic-Observation-Fact-based” (for practical/applied, daily-routine problems), and (2) a “Hypotheses-seeking and/or Model-verifying-type (for theoretical, academic, longer-time-requiring research problem) Scientific Method. (See Chamberlin, 1897, 1890, 1965, for “The method of multiple working hypotheses”).

If the “methodological short-cuts” in the “Pragmatically Applied Scientific Method” are used à la Ridge, Morrissey, etc., proposals, then one has to carefully define the why, when, where and how these shortcuts are to be implemented. For example, to which natural and/or abstract phenomena, environments, processes and/or end-products can the “short-cuts” be applied most successfully and with the “least of damage” (if that is the correct phrase)? And every time short-cuts are employed, one must clearly explain or delineate them by putting them into full context with other methodologies, for instance.

Not only the earth-sciences, but also medicine, economics, biology, theology, etc., have in common the phenomenon that they search for hypotheses – theories – natural laws, but often do not (cannot?) require them in solving pragmatism-based problems by utilizing instead trial-and-error and observed, verified “facts” that are frequently “unexplainable”. The rapid increase in computer application may well require another modification of the Scientific Method in that a third sub-type has to be formulated. Can this be a “Mathematic- and/or computer-based Scientific Sub-Method”, for instance, separate somehow (but supporting, supplementing), the older standard, grand “General Philosophy-Founded Scientific Method” à la Chamberlin (see Wolf, 1973)? Let us now re-enforce the above-cited opinions by Ridge, Morrissey and others by using the following publication.

Henley/Stokes (1986) discussed developmental trends in computer technology: “Underlying all real computer applications . . . in the future will be the development and maintenance of large databases that contain varied and complex exploration data sets. Because of the variety of the projects that it will have to handle, the database will be managed in a very general and flexible way. The only candidate for this is the ‘relational databases management system’, . . .”. One application is in

ore deposit modelling (and, of course, of petroleum accumulation system modelling encompassing also diagenetic – catagenetic – burial metamorphic complexes). This requires a combination – which is unique in geology – of large data volumes, complex three-dimensional (spatial and time-based) geometry and statistically intractable data. The only parallel is with petroleum reservoir modelling and, indeed, it is probable that the two related fields will develop together, with much cross-fertilization of ideas”. And remember that “reservoir rocks” can be replaced by “sedimentary ore hostrock”!

Even if we do not disagree with the power of the computer (and to do so would be like “putting our mind into the proverbial sand”), some caution is always due: computers are not “our saviours of all dilemmas” as they cannot solve any and all problems. Just read the sober analysis and warnings by Aleksander (1987), among many others, who possess enough intellectual guts to tell us about computer limitations.

Henley/Stokes (1986) also predict an integration of separate techniques¹ application to different areas combined to solve problems in specific geological disciplines, e.g., integrating spatial modelling, finite-element and finite-difference modelling, trend analysis, pattern recognition, etc., in the simulation of ore genesis, e.g., by modelling solute diffusion processes (no doubt, also useful in general diagenetic studies including those of sandstone- and carbonate-hosted types). Pattern recognition has already been used in delineating orebody boundaries; some of diagenetic – catagenetic origin.

The investigation of a diagenetic (and any other) system requires good integrative planning – not a “haphazard shotgun” approach. The following must be well planned: (1) “Research and/or exploration infra-structure”¹, i.e., the purpose/aim, methodology, man-power needs (including experience, temperament, etc.), equipment, time²; and (2) the “scientific domain” to be covered: e.g., type(s) of diagenetic system/complex to be examined, assumptions made, range of concepts/hypotheses to be considered, accessibility of geology, scales of maps available, presence/absence of metamorphism and plutonism, among many others.

Horn (1986) stated that some “exploration models, although possibly very exciting scientifically, had proven valueless in exploration”. The “deep convecting cell” model, “basin dewatering” concept, and the “deep metasomatic sources” as

¹ In university teaching and research (as well as in other institutions?) there is a nearly total lack of interdisciplinary integration on all levels in nearly all aspects one may like to mention. No wonder that this negative, retrogressive philosophy is carried over into the job setting.

¹ Infra-structure (Oxford Dictionary): A collective term for the subordinate parts of an undertaking; substructure.

² The authors believe that the term “infra-structure” (= “intra-structure” in some contexts?) when applied to earth-science projects may include, among others, databases, nomenclatures, classifications, etc. Any concrete and/or abstract system has a “philosophical” and “material” infra-structure. Can we speak of the “Scientific Method’s Infra-Structure”, “exploration and research infra-structure”, and so forth?

well as the Pb–Zn exhalative” idea has not resulted in an orebody discovery. Nevertheless, other models worked well, e.g., the “Colorado Plateau/Western States” uranium model, the “marine phosphate”, “hydrothermal gold”, and “porphyry copper” models are valid and assisted in the selection of ground and in the definition of drill targets (but see again Ridge, 1984, regarding porphyry systems!). The controls of sedimentary exhalative Pb–Zn deposits, sedimentary copper, Mississippi Valley-type Zn–Pb–Ba–etc., or even the volcanogenic Cu–Zn ores are, as yet not properly understood, together with their diagenetic–catagenetic–metamorphic systems (such as remobilization, for example). Horn suggests that one “should look to ‘systems’ rather than crude models and should construct more elaborate continua or ore types”. He offered an example, concluding that “. . . it was an interesting exercise to take two quite different orebodies and link them in that way”. He agreed with Henley/Stokes (1986), who made no flamboyant claims, that large graphics, data handling and multivariant three-dimensional data sets in geology–geochemistry–geophysics are needed. “Fuzzy logic and the derived fuzzy mathematics appeared to be the most appropriate theoretical basis for handling the kind of data that were produced in exploration”, varying from focussed hard data to unfocussed properties These concepts certainly will find application in “fuzzy” diagenetic system studies.

Note the unique (?) demand by Henley/Stokes (1986) (and Morrissey, 1986) for “continua” (even elaborate ones), which the senior writer, among others, has requested for several years now (Wolf, 1981, 1985), and which he referred to as transitional/gradational, overlapping and continual/spectral systems or complexes, and which are tight together, so to speak, by employing the linkage-cum-concatenation models and technique.

Madigan (1984, Pt. 2), discussing exploration, likewise commented on the need of “Scientific innovative thinking”: “. . . we are nearing the end of the outcrop or other surface indication of the good things below. A new era of scientific exploration has begun, and its success will depend more on the mind of man than his feet. We must achieve radical changes in intellectual vision and perception. But can we do that without “thinking about thinking”?! – a topic not exactly in vogue with many earth-scientists. According to Madigan (p. 9): “Not all innovative thinking has to be dramatic, or even obvious, to be effective. The recognition that geologists need to be curious, observant, and meticulous in their field work may not sound like a revelation, but there are many examples to show that this might even qualify as a ‘paradigm shift’ for some people”. (The authors have been told occasionally that “we are not interested in such philosophizing”!) Madigan gave three case studies, based on the discovery of bauxite, manganese and diamond deposits, concluding that we must seek new environmental, geological, geochemical, etc., patterns.

Woodall (1985) opined: “Vision is concerned with making observation: quantitative observations such as measurements, and observations of form and pattern.

Vision is perception: an awareness of the significance of observations and insight or intuition. We live and work with limited vision”.

Based on the above, we can write a pseudo-formula:

vision = perception = awareness of significance, importance, relevance, relatedness/interconnectedness, accuracy, reliability, assumption, limitations, etc.; and

vision = insight, intuition, serendipity, imagination, innovative thinking, etc.

Note that Woodall and Wolf agree about numerous aspects related to the fundamental importance of psychological – sociological – philosophical matters as part of research, teaching, exploration and predictive efforts, among others. (See Wolf, 1985.) Take note also of Woodall’s belief that “Two important lessons were learnt, . . . despite the best endeavours of the best geologists at any one time, we learn slowly; and mineral exploration guided by quality scientific documentation and interpretation can be financially rewarding”; “petrology was reintroduced . . . and disclosed in detail the stratigraphic section, the ten zones . . . which made the improved vision possible”; “so often we look but do not see, our vision being limited by limited education, limited training and limited experience”. This can be compared with the senior writer’s experience he has repeatedly had with “developing an eye” in the field and in the laboratory studies when a specific geologic problem was examined over a period of time either in recognizing ever-increasing details and/or by reexamining several times the material available. Features missed earlier, because they were not recognized, were indeed “invisible”, can be seen after proper and continual familiarization. Psychologically, one becomes intellectually more receptive with increasing experience.

Woodall proffered several success stories based on the “switch” of exploration philosophy (often a reversal, inversion, or mere re-orientation thereof). Like others more recently, he likewise emphasizes the need for complex integrations (scale, time, multi-phasal, etc.), and the consideration of (at present still) potential “unknown” variables, processes and environments.

To drive home his philosophy, Woodall quoted, like so many other geologists before him, the poem “The Blind Men and the Elephant” (see Table 4 and Fig. 15). However, he modified the “moral” of the poem to:

“So oft in scientific wars
We argue much it seems,
And fail to take the times to see
What the other person means,
About a mineral elephant
Not one of us has really seen”.

Lacy (1982) supplemented neatly the above philosophical fable by pointing out the extreme “difficulty to establish with any degree of certainty a cause/effect relationship . . . It may be a bit like the psychologist with a flea trained to jump whenever he blew a whistle; in the course of experimentation he pulled off the flea’s

legs, one-by-one, and when the sixth leg was removed he found the flea no longer jumped at the sound of the whistle. He concluded that ‘when you pull off a flea’s legs you destroy its hearing’ ”. (For a useful explanation of “Humour Can Improve Technical Presentations”, see Gleason, 1982!)

Lacy (1982) in his “Payback of Education” commented on, among others, on “impetus for discovery often comes from seemingly esoteric research and observations”, “the art of ore discovery and the nature of deposits sought, are constantly changing”, etc. He mentioned the early (1952?) instruction geologists received to

TABLE 4

THE BLIND MEN AND THE ELEPHANT¹

It was six men of Indostan
To learning much inclined,
Who went to see the elephant
(Though all of them were blind),
That each by observation
Might satisfy his mind.

The first approached the elephant,
And happening to fall
Against his broad and sturdy side,
At once began to bawl:
“God bless me! – but the elephant
Is very like a wall!”

The second feeling of the tusk,
Cried: “Ho! what have we here
So very round and smooth and sharp!
To me ‘tis mighty clear
This wonder of an elephant
Is very like a spear!”

The third approached the animal,
And happening to take
The squirming trunk within his hands,
Thus boldly up and spake:
“I see”, quoth he, “the elephant
Is very like a snake!”

The fourth reached out his eager hand,
And felt about the knee,
“What most this wondrous beast is like
Is mighty plain”, quoth he;
“‘Tis clear enough the elephant
Is very like a tree!”

The fifth, who chanced to touch the ear
Said: “E’en the blinded man
Can tell what this resembles most;
Deny the fact who can,
This marvel of an elephant
Is very like a fan.”

The sixth no sooner had begun
About the beast to grope,
Than seizing on the swinging tail
That fell within his scope,
“I see”, quoth he, “the elephant
Is very like a rope!”

And so these man of Indostan
Disputed loud and long,
Each in his own opinion
Exceeding stiff and strong,
Though each was partly in the right,
And all were in the wrong.

MORAL:

So, oft in theologic wars
The disputants, I ween,
Rail on in utter ignorance
Of what each other mean
And prate about an elephant
Not one of them has seen.

¹A famous Hindu fable by J. G. Saxe.

establish “recognition characteristics” of the various types of mineral deposits. (Of course, there are also diagenetic – catagenetic – metamorphic recognition guides for metalliferous ores, for industrial minerals, and for petroleum deposits.) The “saturation prospecting” or “blanket search” technique began to decline by the early 1970’s and a new approach evolved, i.e., the development of genetic models and the prediction of the probable environment and position of orebodies. The explorationists’ “prime forte is the ability to organize a mass of seemingly unrelated data into a logical sequence of facts which may lead to an ore discovery”.

Kölbl (1967) pointed out already 20 years ago that “between the rapid development of sedimentology on one hand, and the application of the results to concepts of the petroleum industry on the other hand, a striking discrepancy exists”. The reason for this lies in the fact that “the concept of the petroleum industry, and especially those of exploration, are necessarily influenced by hypotheses which, in



Fig. 15. A group of blind men investigating an elephant (from Hokusai Manga, vol. III). (See Whitkop, front cover of *Am. Sci.*, 55(2), 1967.)

Each scientific field, whether chemistry, physics, geology, or biology, consists of many specialties, and most specialists normally and anxiously try to keep independent as much as convenient. The famous picture by Hokusai illustrates what then happens: 12 blind men investigate individually an animal they have never seen. The ones on the back proclaim it a mountain; the men under the belly report feeling a barrel. The people around the legs say they feel trees. The man at the trunk pictures a snake. The sum of their observations does not necessarily add up to an elephant (see also Table 4).

the course of their application, often become more and more dogmatic. As a result, the value of the concepts used is decreased. It is now an important task of applied sedimentology to confront continually the results of new research with the hypotheses which are commonly in use and eventually to enforce a re-examination of these ideas." Naturally, this applies to diagenesis – catagenesis – metamorphism at that time (1967) and today.

So, let us come to a general conclusion: Koestler (1964) in regard to "creativity and science" demonstrated that all creative activities have a basic pattern: the realization of hidden relationships. He also discusses the concrete and abstract phenomena of "intuitive insight" that leads to new revelations resulting from conscious ("open") and unconscious ("hidden") phases a researcher (and serious, innovative and creative explorationist) experiences: periods of random trial-and-error, incubation, saturation of problems, among others. He believes that during the "period of incubation the creative mind is liberated from the tyranny of over-precise concepts, of the axioms and prejudices engrained in the very texture of specialized ways of thought . . ." This applies to both the objective or outer world and the subjective or inner world (see Van Bemmelen, 1961).

"In regard to the secrets nature is still withholding from us, in contrast to what we already know, we are all 'sciolists' in lesser or greater degrees – science en toto is an attempt to reduce or combat 'sciolism'".

Karl H. Wolf, Dec. 8, 1986, Canberra, A.C.T.

"I have omitted all those things which I have not myself seen, or have not read or heard of from persons upon whom I can rely. That which I have neither seen, nor carefully considered after reading or hearing of, I have not written about."

Agricola (De Re Metallica).

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*Chapter 1***DIAGENETIC PROCESSES IN NORTHWESTERN GULF OF MEXICO
SEDIMENTS**

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INTRODUCTION

The northwestern Gulf of Mexico Basin has functioned as a natural laboratory for the exploration of many facets of geology. In recent years, the thick Mesozoic and Cenozoic sediments of the Gulf Coast have been a focus for the study of diagenetic processes that typify large sedimentary basins. There are several reasons for this. First and foremost is the fact that more than 50 years of hydrocarbon exploration have unveiled a three-dimensional stratigraphic framework and a wealth of additional data. Second, the Gulf Basin is a complex system in which processes of deposition, burial, structural deformation, and mass and energy flux continue to operate much as they have for at least the past 60 million years. Perhaps more than any other well-studied major basin, the present Gulf has truly proven to be a dynamic key to the past. Because of its size and longevity, the basin provides examples of all major lithologic associations, ranging from evaporites, through carbonates, to terrigenous sequences characterized by diverse compositions. Similarly, a broad range of burial histories, thermal gradients, and hydrologic regimes can be examined throughout the basin. Finally, the economic incentive provided by active and increasingly deep hydrocarbon exploration and production has focussed the attention and effort of many organizations and individuals on the problems and opportunities presented by the Gulf Coast Basin.

The purpose of this chapter is fourfold. First, the writers review the geologic framework in which diagenesis has occurred. Second, they attempt to integrate the dynamic aspects of the basin fill — the thermal, physical, chemical, and hydrologic regimes. Third, they synthesize and summarize the observed patterns and products of diagenesis. Of particular interest in this respect is the diagenesis of evaporites, Mesozoic (mainly carbonate) rocks, Tertiary (mostly clastic) sediments and rocks, organic matter, and shales of the Gulf Coast Basin. Finally, the writers conclude with a discussion of some speculative ideas that have emerged from recent research and an outline of major, unsolved problems.

GENESIS OF THE GULF OF MEXICO BASIN*Synopsis*

The northern and northwestern shelf of the Gulf of Mexico Basin (Fig. 1-1) is the

divergent margin of a briefly active trailing margin-type spreading center that formed contemporaneously with opening of the Atlantic Ocean. The following brief account of the origin and early history of the Gulf Basin is based on the work of Buffler et al. (1981) and Buffler (1984).

Early rifting began in the Triassic and extended through Middle Jurassic time. Crustal extension and contemporaneous extrusive and intrusive volcanic activity created the transitional continental crust that underlies the present basin margin. At this stage, the modern basement structural framework of the Gulf was established, and thick salt had been locally deposited within deeper, marine-invaded rift basins (Salvador, 1987).

Rifting and subsidence accompanied by formation of new oceanic crust in the central Gulf occurred briefly in Late Jurassic time. The spreading axis is interpreted to have been oriented NW – SE. By Early Cretaceous, rifting had ended and rapid thermal cooling led to subsidence of the basin. Salt began to flow on a large scale both upward (as diapirs) and toward the basin center. Extensive reef buildup and sedimentary aggradation over the thick, less actively subsiding continental crust

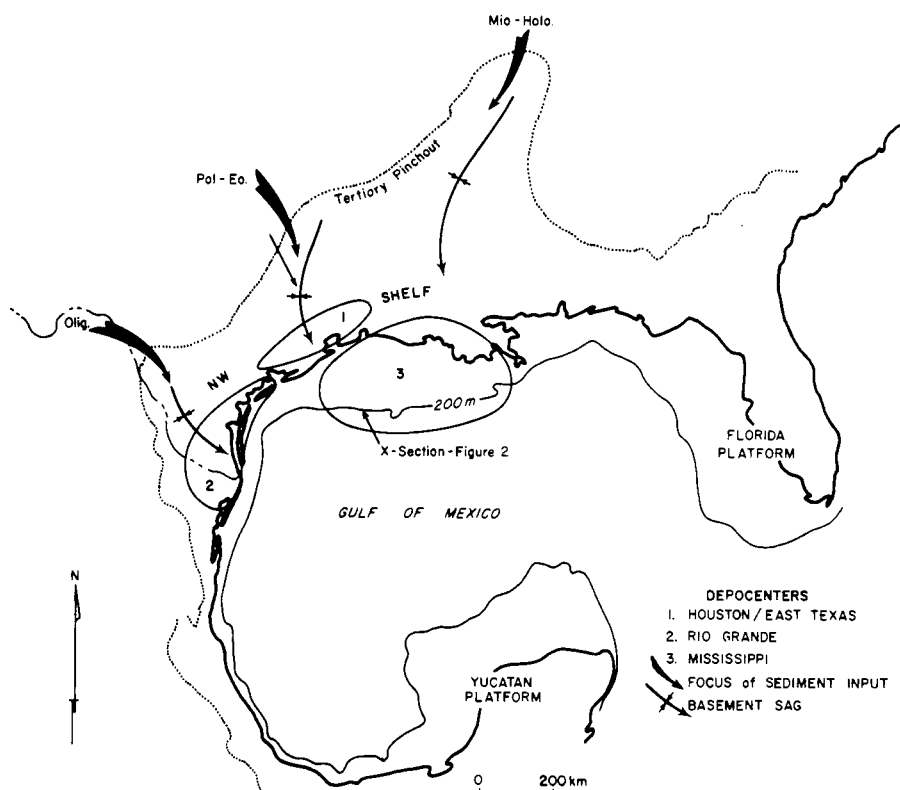


Fig. 1-1. Index map of the Gulf Coast Basin showing the three depocenters and the axes of sediment influx for the northwestern shelf.

created well-defined depositional relief separating the sediment-starved basin center from the fringing shelves. This initial chapter in the history of the Gulf ended in the Middle Cretaceous with the development of a prominent basin-wide unconformity. Widespread flooding of the bounding shelves and marginal craton in the Late Cretaceous preceded the uplift of the ancestral Rocky Mountains and the massive deposition of terrigenous sediment that has characterized Cenozoic time.

By the beginning of the Cenozoic, thermal subsidence had decreased to estimated rates of a few tens of m Ma^{-1} (Jackson and Galloway, 1984). In the Paleocene–Eocene, the first of a series of major sediment influxes entered the basin in response to intracontinental collision and uplift associated with Pacific margin–plate interactions (Dickinson, 1981). Subsequent episodes of large-scale continental shelf progradation and isostatic crustal subsidence occurred in the Oligocene, Miocene, and Plio-Pleistocene.

Stratigraphy and composition of the basin fill

The Mesozoic succession is as much as 5 km thick (Fig. 1-2). It consists of a poorly known substrate of isolated (Triassic?) grabens filled with red-beds and volcanics. Jurassic strata underlie most of the basin and include red-beds, evaporites, and the structurally important Louann Salt. The salt is overlain by the Smackover and equivalent carbonates, in places containing evaporite units. Lower Cretaceous units include the prominent shelf carbonates, terrigenous clastics, and associated shelf-edge reef deposits of the Sligo and Edwards formations.

The Cenozoic sedimentary fill dominates the northern and northwestern Gulf and is characterized by a succession of offlapping depositional sequences, which prograded the continental margin nearly 400 km beyond the Cretaceous shelf edge (Fig. 1-2). Episodes of sand-rich depositional offlap were punctuated by periods of

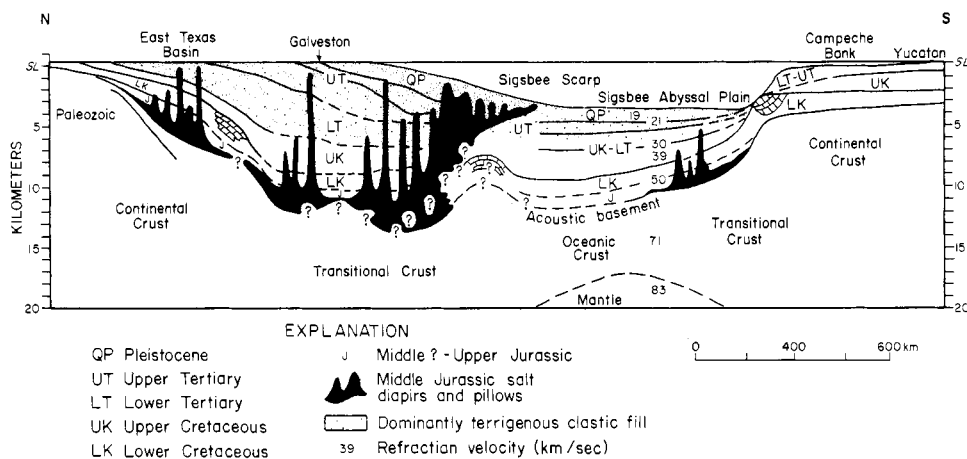


Fig. 1-2. Generalized north–south cross-section of the Gulf of Mexico Basin. The Cenozoic wedge offlaps the older Mesozoic continental shelf edge, accumulating approximately 5 km of terrigenous sediment on top of the basal Mesozoic deposits. (Modified from Buffler et al., 1981.)

widespread transgression (Fig. 1-3). Principal episodes of offlap occurred in the late Paleocene to early Eocene (Wilcox), Oligocene (Vicksburg and Frio), early Miocene, middle to late Miocene, and Plio-Pleistocene. Three broad, basement-controlled sags – the Rio Grande, Houston, and Mississippi embayments (Fig. 1-1) – have localized input of fluvial sediment along the basin margin. Each sag continues to be occupied by major drainage systems. During Cenozoic time continental drainage and sediment-yield patterns have shifted in response to intraplate tectonics and each embayment has periodically served as a depocenter (Winker, 1982). During late Paleocene and Eocene times, progradation of the continental margin occurred through the broad, diffuse Houston embayment. The southern Rocky Mountains, uplifted in the Laramide orogeny, supplied sediments. The composition of these sediments reflects a mix of igneous, sedimentary, and metamorphic terranes.

The depocenter shifted to the Rio Grande axis at the beginning of the Oligocene. At this time widespread volcanism and uplift of the Southern Cordillera of Trans-Pecos Texas and northern Mexico resulted in a flood of volcanic debris into the Gulf, rich in sand-sized volcanic rock fragments (VRFs) and tuffaceous mud. In Miocene time, Basin-and-Range faulting segmented and beheaded the western drainage system. At the same time epeirogenic uplift of the middle and southern Rocky Mountains and integration of an immense proto-Mississippi intracontinental drainage system caused a shift in the drainage axis and depocenter to the Mississippi embayment, where it remains. The composition of the sand and mud reflects a mixed provenance of sedimentary, metasedimentary, plutonic, and volcanic terranes.

As shown in Fig. 1-3, major Cenozoic episodes of deposition reveal similar arrangements of facies. Fluvial and coastal-plain deposits extend to burial depths of about 2 km. Downdip, terrestrial deposits grade into paralic deposits of delta-plain, delta-front, and shore-zone origin. Units of regional transgression are characterized by massive lagoonal mudstones, which separate sandy coastal-plain facies from sandy shore-zone facies. Paralic deposits extend to depths of 6 km within depocenters and are variably intermixed with marine mudrocks of shelf, prodelta, and upper-slope origin. Farther basinward, sandy paralic deposits are replaced by dominantly muddy, marine-shelf and slope deposits. The writers speculate that portions of this thick, muddy facies complex may be underlain by sandy, basal-slope, submarine fans comparable to the modern Mississippi fan. Such deposits would be buried to depths of 6 – 10 km within most of the Cenozoic sedimentary prism. Local sand-rich intraslope basin fills have been encountered by deep exploratory drilling, and a few large Tertiary submarine canyons (now filled) comparable to those at the apex of the Quaternary Mississippi fan are known (Winker, 1984).

Cenozoic units can be subdivided into three broad lithofacies assemblages, or magnafacies (Fig. 1-4). The sand magnafacies contains more than 30% sand and sandstone. The mixed sand – shale magnafacies consists of 5 – 30% sand and sandstone. Overall, this facies forms the bulk of the major and minor depocenter sequences. The mudstone magnafacies represents the finest-grained facies, containing less than 5% sand and sandstone. This facies is volumetrically dominant in the Cenozoic. It underlies the entire sandy magnafacies, and separates the individual depositional sequences as mud-rich tongues.

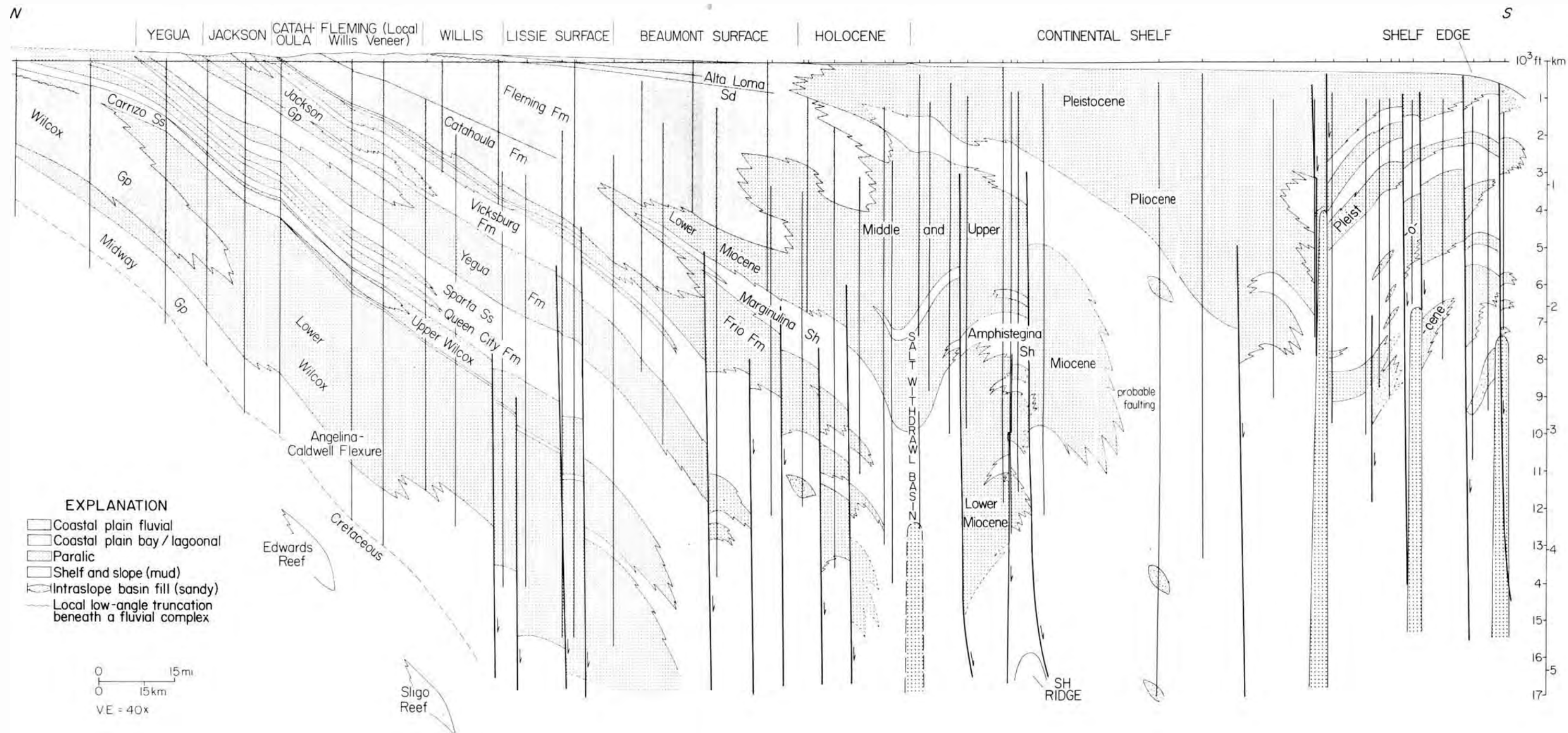


Fig. 1-3. Stratigraphic cross-section showing the stratigraphy and genetic facies of the Cenozoic fill of the Houston embayment and adjacent continental shelf. For location see Fig. 1-1.

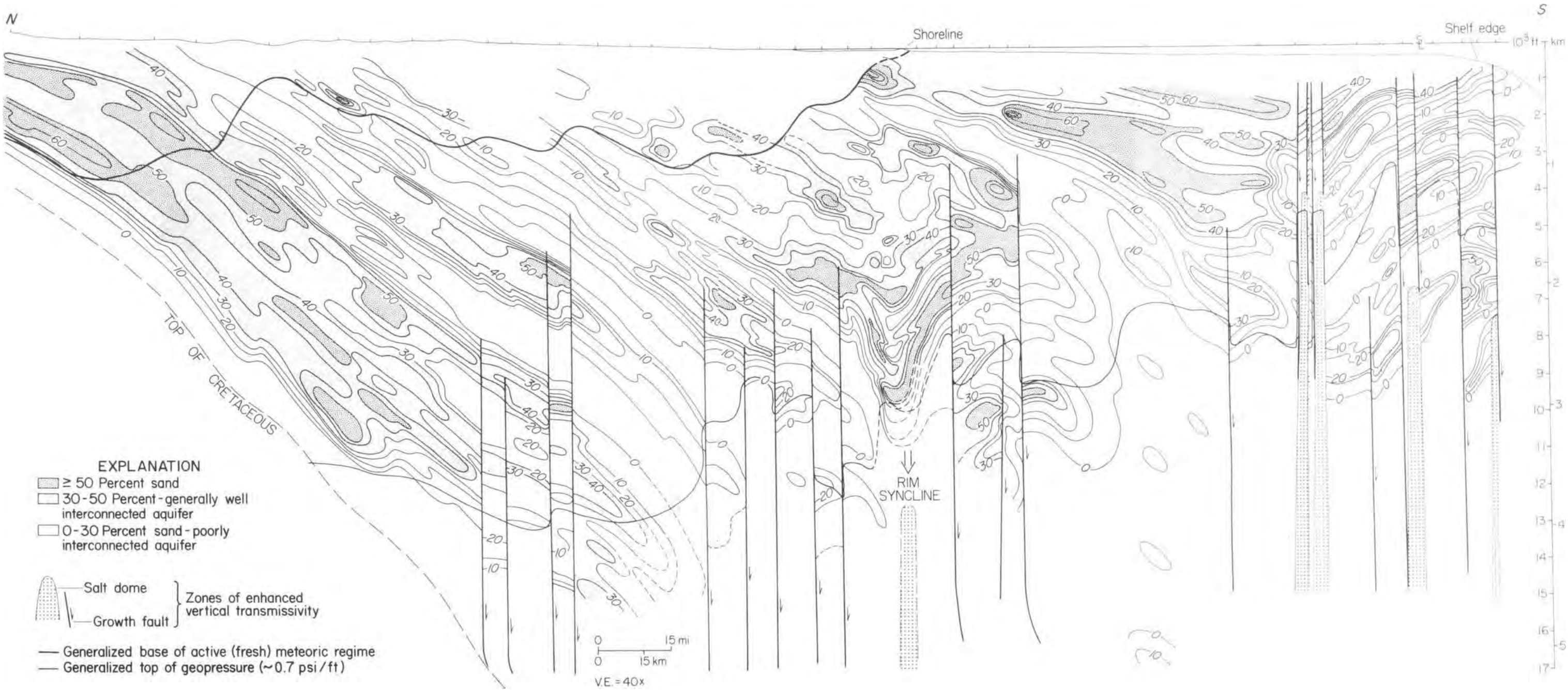


Fig. 1-4. Lithology and hydrologic regimes of the Cenozoic fill of the Houston embayment and adjacent continental shelf. Contours show sandstone percentage calculated at arbitrary 500-ft (150-m) increments in control wells. Compare with Fig. 1-3.

Mineralogy

Cenozoic mudrocks consisted initially of abundant illite and mixed-layer illite/smectite (Burst, 1969; Perry and Howe, 1970; Freed, 1981; Jackson, 1986). At burial depths between 2.5 and 4 km at a concomitant temperature of about 120°C, most of the smectite has converted to illite, releasing bound water and taking up potassium.

Sandstone compositions are variable. However, the typical Gulf Coast sand at the time of deposition is a quartz-rich (> 50%) feldspathic litharenite or lithic arkose (Loucks et al., 1984; and this paper). The ratio of feldspar to rock fragment approaches one, with plagioclase as the dominant feldspar. In general, this suite of minerals is typical of the heterogeneous, ill-defined assemblage derived from a mix of recycled orogens associated with a stable craton (Dickinson, 1985). It is somewhat more diverse than suites found in simple divergent-margin fluvial systems (Potter, 1978).

Cenozoic sediment accumulation rates were rapid, and an average value is 120 m Ma⁻¹. Averages, however, mask the great variability that existed both in time and space. The greatest rates of sedimentation occurred at prograding continental margins. Rates exceeding 1000 m Ma⁻¹ prevailed for as long as a million years. The thickness of the Pleistocene section (representing 2.8 Ma) shown on Fig. 1-3 illustrates the rapid burial rates of sands and muds that accumulated within continental margin depocenters.

Structural framework

The structural fabric of the modern Gulf Basin is dominated by gravity tectonics. The Mesozoic shelf and overlying Cenozoic deposits are cut by normal faults that were induced by basinward creep of the entire sedimentary wedge during plastic deformation of the salt substrate (see Martin, 1978, for a comprehensive review). Salt diapirism, induced by loading of the Louann Salt, caused great local variability in subsidence and uplift rates (Martin, 1978; Seni and Jackson, 1983a, b). Associated fault and diapir boundaries provide discontinuities that transect the full 10 km of the post-Louann sedimentary pile (Fig. 1-2).

Local progradation of a clastic continental margin in Cretaceous time (Tuscaloosa/Woodbine) and large-scale, clastic-margin offlap during the Cenozoic established the second, pervasive structural style that has characterized later basin history. The upper slope and shelf edge of a prograding continental margin define a tensional regime (Winker and Edwards, 1983). Where the margin instability is enhanced because of rapid depositional loading, this tensional regime is manifested by pervasive development of syndepositional, listric, normal faults (Fig. 1-3). The Gulf basin has become a type locality for such growth faults. A complementary compressional regime results in large-scale thrusting, folding, and/or plastic creep of unconsolidated slope sediment at the toe of the continental slope. Large toe structures, such as shale massifs or salt wedges and thrusts, later influence the development of superimposed tensional structures. The entire sediment prism is transected by complex, generally strike-parallel faults that segment the sequence into multiple depositional and structural sub-basins.

Hydrostratigraphy

The hydrostratigraphic framework for the northern margin of the basin is typical of rapidly prograded, clastic, extensional margins. Permeable pathways include both the laterally continuous sand-rich facies and transecting structures (faults and diapirs).

The principal aquifers are all in the sand magnafacies. The greatest depth of penetration of fresh meteoric waters is observed within the sand-rich cycles (Fig. 1-4). Permeable sand bodies become increasingly isolated with increasing depth by mudrock within the mixed sand/shale magnafacies. Because of loading by rapid burial and low permeabilities, lower parts of the mixed magnafacies cannot dewater and compact at a rate equivalent to the shallower facies. Abnormal fluid pressures develop in the deeper facies as the pore waters begin to bear part of the weight of the overburden (Bredehoeft and Hanshaw, 1968). Consolidation under conditions

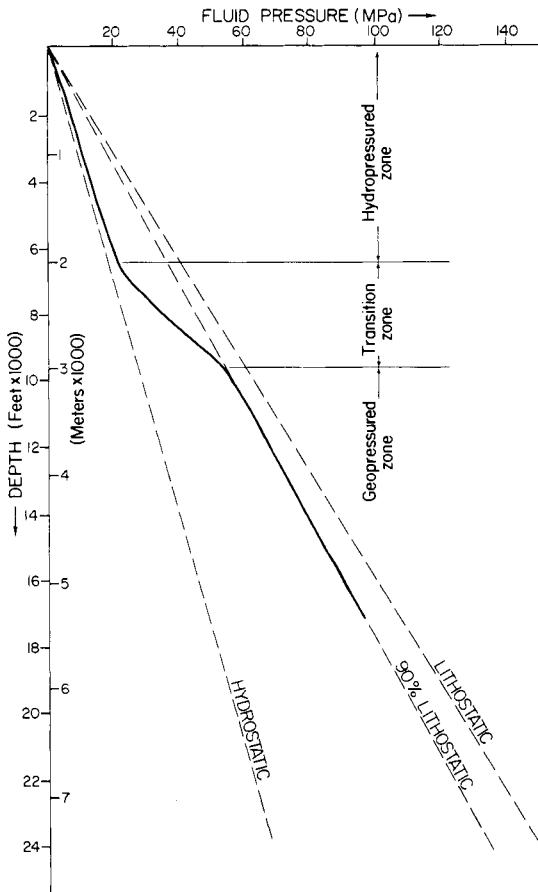


Fig. 1-5. Typical fluid pressure gradient as a function of depth.

of compaction disequilibrium results in a deviation from a normal mudstone compaction gradient and may result in abnormally high porosities (and, conversely, low rock densities) at depth. In the deeper, hotter section, the conversion of smectite to illite (e.g., Burst, 1969), the generation of hydrocarbons, and thermal expansion may augment development of overpressure. Fluids in much of the mudstone magnafacies exhibit substantial overpressures, with pressure gradients approaching the lithostatic gradient of approximately 22.5 kPa m^{-1} (1 psi ft^{-1}), as shown in Fig. 1-5.

The impact of growth faults and diapirs on the hydrology of the basin is profound. Both may enhance permeability, yet elsewhere they can form permeability barriers that cut across stratigraphic conduits. Mechanisms and timing of fluid transport along structural discontinuities remain speculative, but considerable circumstantial data (Galloway, 1984; Bodner et al., 1985) supports the importance and magnitude of vertical flow. The data include:

(1) Sulfidic alteration of shallow Neogene aquifers which can be related to discharge of sulfide-rich waters found only in the Mesozoic roots of the basin.

(2) The majority of liquid hydrocarbons occur in reservoirs that lie a kilometer or more above the shallowest, thermally mature, source beds. Moreover, physical properties of oils and condensates suggest that vertical migration was accompanied by chromatographic segregation.

(3) Temperature, pressure, and compositional distribution patterns exhibited by formation waters indicate vertical flux and mixing in and around structures (Morton and Land, 1987).

(4) Lead – zinc ores found in salt-dome cap rock appear to have been precipitated from discharging deep-basin brines (Ulrich et al., 1984).

From the morphology of the surface defining the top of geopressure shown on Fig. 1-4 it is obvious that faults can also act as lateral pressure seals. The apparent contradiction that faults act both as permeable pathways and barriers to flow may be partially reconciled by the inference that discharge is sporadic (Cathles, 1981; Bodner et al., 1985). This idea is supported by observations listed above and by conceptual analysis of in situ fracturing mechanisms within overpressured mudstones (Magara, 1978). Further, it should be re-emphasized that structures, particularly growth faults, develop in a regional tensional stress regime. The listric geometry of growth faults results in horizontal displacement of the down-dropped block that is as much as several times the vertical displacement. In fact, cumulated horizontal displacements exceeding 10 km are known.

Diagenetic regimes

The diversity of depositional, structural, and hydrologic regimes, as well as the complexity of their evolution and interaction, forces us to clearly differentiate diagenetic regimes responsible for the alteration and lithification of basin sediments. Following is a summary of the fundamental diagenetic regimes as defined by Fairbridge (1967).

(1) *Syndiagenesis* includes the suite of chemical and physical reactions that occur within the first few meters or tens of meters of burial below the depositional surface.

Syndiagenesis is the approximate equivalent to eogenesis as defined by carbonate petrologists. Syndiagenetic processes generally lead toward the equilibration of sediment pore-fluid chemistry with the chemistry of reactive solid components, such as opal and organic matter. Syndiagenesis of rapidly sedimented clastics and carbonates rarely results in significant modification of framework grains, or in their cementation. Because of the close association with the surface, syndiagenetic response is commonly closely related to the depositional environment.

(2) *Burial diagenesis* occurs in an environment of increasing temperature, fluid pressure, and confining pressure. Physical compaction results in expulsion of trapped, geochemically evolved pore fluids. The complex diagenetic responses of metastable framework components reflects variable patterns of fluid mixing, recycling, and geochemical evolution. The burial diagenetic zone corresponds to the mesogenetic zone commonly discussed in carbonate diagenesis.

(3) *Emergence and meteoric intrusion* (corresponding to telogenesis or supergene alteration of carbonate and ore petrology) subjects sediments or sedimentary rocks to flushing and re-equilibration with low-temperature meteoric water. Meteoric diagenesis may follow syndiagenesis directly in shallow sediments along the basin fringe, or it may follow burial diagenesis if deeply buried zones are uplifted into the zone of active meteoric circulation, or where deep intrusion of meteoric water can occur.

The following review of diagenesis in the basin sedimentary fill focusses primarily on the processes and products of burial diagenesis. Below depths of 3 – 5 km, burial diagenesis has produced rocks that are greatly modified relative to the sediment initially deposited in the basin. Among detrital components only quartz grains and very stable heavy minerals retain their primary compositions. Cementation and replacement in these deep rocks have shifted the bulk composition toward mineral assemblages resembling those of low-rank metasediments. The large sedimentary mass involved in these chemical changes implies a long-term, large-scale interaction of rocks and basinal fluids.

GEO THERMICS AND HYDRODYNAMICS OF THE SYSTEM

Introduction

Large-scale mass transport over geologic time has contributed to several different geologic processes including sandstone and limestone lithification, ore formation, and petroleum migration. Fluids transport mass via forced convection, free convection and diffusion. Heat is also an important factor in geochemical processes and is very closely linked to fluid transport, as it both influences and is influenced by fluid flow. Together, the thermal and hydrogeological environments largely control diagenetic processes in the Gulf Coast. A better understanding of heat and fluid transport should therefore result from an understanding of the diagenetic processes which have occurred.

Thermal regimes

Low geothermal gradients ($20^{\circ} - 30^{\circ}\text{C km}^{-1}$) prevail over most of the Gulf area. Generally, thermal gradients are highest in the thinner, onshore sediments and decrease toward areas of recent and/or rapid sediment deposition. Regionally, the lowest geothermal gradients are found offshore. In offshore Plio-Pleistocene sediments, the range is from 16° to $23^{\circ}\text{C km}^{-1}$. Temperatures and gradients gradually increase onshore. At the coastline, near-average gradients of $28.3^{\circ}\text{C km}^{-1}$ are found to a depth of about 2.5 km. Moving farther inland, gradients and temperatures generally increase (Bebout et al., 1982; Bodner et al., 1985; Bodner and Sharp, 1988). Gradients are highest (up to $55^{\circ}\text{C km}^{-1}$ at 2–4 km depth) in an arc-shaped region between 10 and 160 km inland and subparallel with the coast. This zone coincides with growth faulting of the Wilcox Formation where gradients can be as high as $50^{\circ}\text{C km}^{-1}$. Figure 1-6 demonstrates that thermal gradients are closely related to fault traces.

Geothermal gradients (shown in Fig. 1-7) tend to increase with depth. This pattern is the result of rapid sediment accumulation and, secondarily, slow but long-term, thermal advection caused by fluids released during sediment compaction. The temperature distributions are in disequilibrium, and are evolving at geologic rates. This general trend is modified by local conditions. Some of the factors causing variations are: (1) sediments with thermal conductivities that are either anomalously low (undercompacted, overpressured shales) or anomalously high (salt domes); (2) high rates of advection by meteoric or compactional pore fluids; (3) rapid rates of sedimentation; (4) an increase in gradients toward the northern Mexico igneous province; and (5) the possible occurrence of free convection.

There is currently no definitive model explaining the observed thermal patterns in the Gulf, and there are probably several mechanisms involved. For example, the trend toward cooler sediments offshore is perhaps best accounted for by a model proposed by Sharp and Domenico (1976). According to this model, if sediments ac-

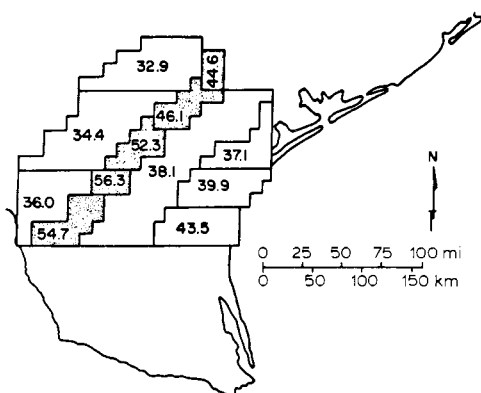


Fig. 1-6. Geothermal gradients ($^{\circ}\text{C km}^{-1}$) between 6000 and 15,000 ft below sea level for the South Texas Coastal Plain. Stippled area encompasses the Wilcox growth fault trend. (Data are from Bodner et al., 1985.)

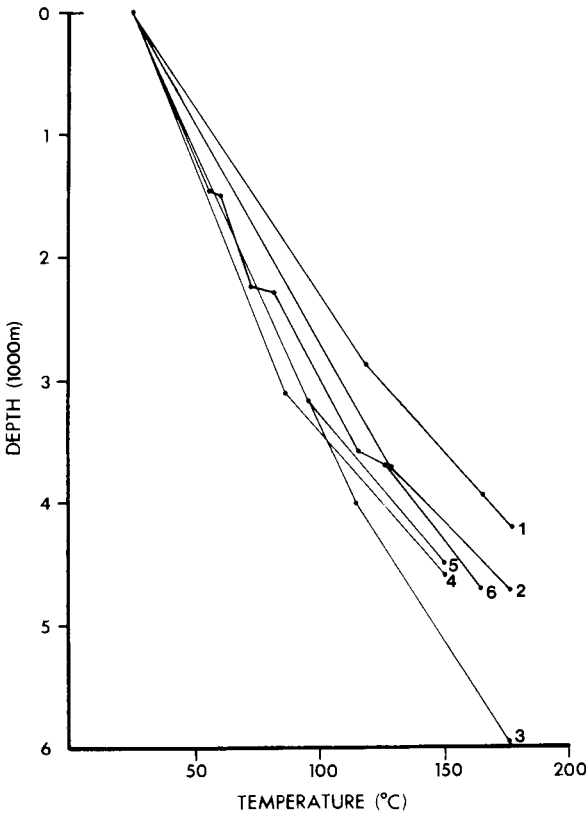


Fig. 1-7. Observed nearshore – near-offshore temperatures ($^{\circ}\text{C}$) as a function of depth (m): 1 = south Texas; 2 = Texas coast; 3 = Louisiana (after Kharaka et al., 1985); 4 = Texas coast (after Sharp, 1976); 5 = Louisiana (after Schmidt, 1973); and 6 = near-offshore Texas (after Lewis and Rose, 1970).

cumulate rapidly enough, they are cool relative to their burial depth. These sediments will eventually equilibrate, but not until deposition ceases and subsidence slows. The model successfully reproduces the low temperatures and gradients observed offshore.

The high gradients measured in the Wilcox growth-fault zone (Bodner et al., 1985) probably result from a different mechanism, one in which the hydrologic system seems to dominate. Heat is rapidly transported by moving pore fluids. When these fluids move at sufficient velocity, heat transport via convection can be important relative to heat transport via conduction. The observed thermal patterns of the Wilcox fault zone suggest this type of vertical flow: heat is transported from the deep basin into the overlying sediments and is manifested as higher-than-normal temperatures and thermal gradients.

There are many other mechanisms that might be involved in the Gulf thermal regime. For instance, the thermal regime is commonly perturbed around salt domes and fault zones. Because salt is a good heat conductor, gradients and temperatures

near the top of the dome and around their perimeter are higher than average (O'Brien and Lerche, 1987). Significant local thermal variations are also found in fault zones, where gradients can vary markedly from one fault block to another, probably due to hydrologic isolation. The effects of overpressure on thermal profiles are almost certainly important. Zones of transitional overpressure, where pore-fluid pressures exceed hydrostatic pressures, feature high thermal gradients, with normal gradients above in the hydrostatic zone and below in zones of high overpressure. Bebout et al., (1982) published temperature–depth curves for several areas within the “hot” growth-fault trend. These curves compare favorably with the theoretical curves from Lewis and Rose (1970), although Bodner (1985) has demonstrated that advecting fluids significantly affect these thermal patterns.

Hydrodynamics

General comment

The type and extent of rock–water interaction in Gulf Coast sediments is controlled, in part, by the character of fluid flow. For example, various investigators have postulated that large-scale mass transport and large numbers of pore-volume exchanges must have occurred to account for observed diagenetic changes. The writers can begin to evaluate possible mechanisms for mass transport by understanding the hydrodynamics of the basin. Three types of hydrodynamic systems coexist here: the meteoric, the overpressure–compactional, and the thermobaric (metamorphic), as shown in Fig. 1-8.

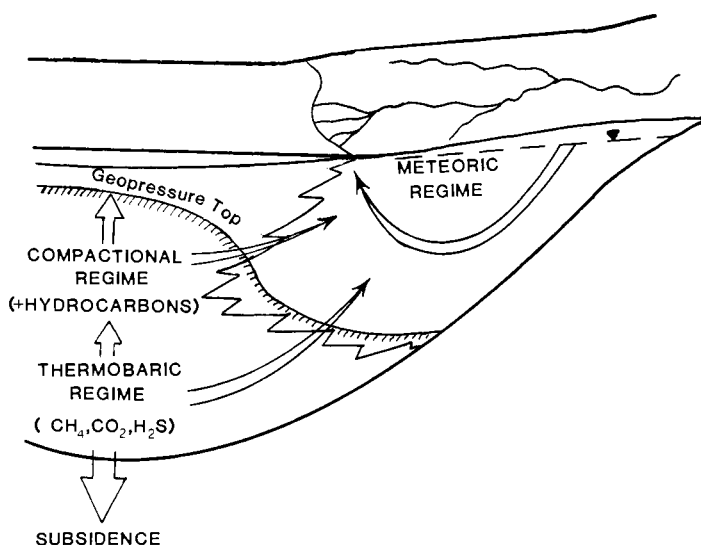


Fig. 1-8. Hydrodynamic regimes. (Modified from Galloway and Hobday, 1983.)

Meteoric regime

The meteoric regime encompasses sediments whose pore fluids are driven by the topography of the water table. Water includes both truly meteoric water and saline, evolved water. The latter can be “connate” (original formation waters not yet displaced) or can be waters expelled from much deeper formations. Contrary to popular opinion, flow in the meteoric zone is not solely downdip toward the Gulf. In gravity-driven flow systems, water recharges on topographic highs and discharges to the major river systems, similar to the flow pattern shown by Back (1966) for the Atlantic Coastal plain. Topographically driven meteoric flow has been documented in the Oakville aquifer of Texas (Smith et al., 1982) and the East Texas Basin (Fogg and Kreitler, 1982). Only where virtually no topographic gradient exists (usually near the coast) and/or in deeper, more stagnant portions of the meteoric zone, is the flow downdip to the coast. Gravity-driven flow approaching the Gulf discharges by diffuse, upward, cross-formational flow in the general vicinity of the shoreline. Concentrated discharge may, however, occur along fault zones.

The meteoric regime does not imply that the ground water is potable. There is a transition zone between meteoric and overpressured systems. The transition zone is geologically complex, but contains a mixture of meteoric and upward-expelled diagenetic fluids and possesses zones of overpressured rocks. It is within this transitional rock zone that most liquid hydrocarbons are concentrated.

Compactional – overpressured regime

The compactional regime, where fluids flow in response to pressure gradients induced by sediment consolidation, has frequently been subdivided into hydropressed and overpressured (or geopressed) sections. A fluid is considered to be overpressured if the pressure is “significantly” greater than hydrostatic. The compactional system thus includes most of the offshore sediments and overpressured regions onshore. Figure 1-5, a typical plot of fluid pressure versus depth for the Gulf Coast, shows a zone where fluid pressure sharply increases. The region beneath this sharp increase is considered to be overpressured.

Many theories have been suggested for the formation of overpressures in sedimentary basins. In the Gulf Coast Basin, the most viable theories are: (a) compaction disequilibrium (Magara, 1976; Sharp, 1976; Keith and Rimstidt, 1985); (b) aquathermal pressuring (Barker, 1972); (c) mineral-phase transformations (Burst, 1969; Bruce, 1984); and (d) hydrocarbon maturation (Hedberg, 1980).

All these mechanisms require the presence of low-permeability sediment to prevent rapid dissipation of excess pressure. The writers discussed the first three mechanisms listed above because they have been investigated quantitatively. The fourth mechanism, formation of hydrocarbon fluids from solid kerogen, could create pressures (Barker, 1987), but because solid kerogen constitutes less than 0.5% by weight of Gulf Coast sediments it seems doubtful that this mechanism is of major importance.

The term compaction disequilibrium implies that the sediments are being deposited too rapidly for the fluids to be squeezed out. These concepts are embodied in the principle of effective stress, written mathematically:

$$\text{total stress } (\sigma) = \text{effective stress } (\sigma') + \text{fluid pressure } (p)$$

where effective stress is that portion of the total stress borne by grain-to-grain pressure, and fluid pressure includes both hydrostatic and excess pressures. Total stress is created by the weight of all sediments and fluids above the point in question. On increasing the total stress by depositing more sediment, the increased load is initially carried by the trapped fluid as an excess pore pressure. As the fluid escapes from the sediment due to this pressure, the sediment compacts and the load is transferred to the grains as increased effective stress. An analytical solution for a one-dimensional, continuous sedimentation problem was developed by Gibson (1958). Bredehoeft and Hanshaw (1968) used this solution to demonstrate that compaction disequilibrium could lead to very significant overpressures in the Gulf Coast. A similar conclusion was reached by Sharp and Domenico (1976), who utilized a numerical solution which coupled the fluid flow and energy transport equations and allowed for variation of the parameters with temperature and degree of compaction.

Aquathermal pressuring is caused by the thermal expansion of fluid against a less expansive sediment or rock matrix. In other words, when expansion is limited, then the fluid pressure will increase. The feasibility of this mechanism has been greatly debated; aquathermal pressuring alone probably cannot account for observed overpressures. In combination with compaction disequilibrium, however, this may be an important, secondary overpressuring mechanism (Domenico and Palciauskas, 1979; Sharp, 1983).

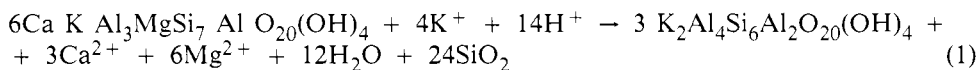
Mineral transformations, especially the smectite-to-illite transformation can, in theory, create overpressuring. This mechanism has often been suggested because of the circumstantial evidence that the mineralogic transformation takes place at the depth corresponding to the zone of transitional pressure. It should be noted, however, that overpressures are present in locations which never had significant quantities of smectite. Furthermore, the quantity of water released during this transformation has been widely debated. Bruce (1984) concluded that the quantities of water released are significant and are important in the development of overpressures, petroleum migration, and diagenesis.

As noted above, all overpressuring mechanisms depend upon permeability being low enough to retard the release of fluid pressure. None of the mechanisms precludes the possible occurrence of the other mechanisms and several may contribute. One result of a combination of mechanisms is that fluid pressure could exceed lithostatic pressure. In reality this does not occur, and fluid pressure rarely exceeds 0.9 times the lithostatic pressure (Fig. 1-5). This upper limit can be explained by the process of microfracturing. When the fluid pressure exceeds the least principal stress by an amount equal to the tensile strength of the rocks, microfractures develop which increase the porosity and permeability (Kortenhof, 1982). In addition to microfracturing, another possible mechanism for pressure reduction is fluid flow along more permeable zones. These zones may include intercalated sandstone beds, faults, or the flanks of salt domes. Numerical studies of Bodner et al. (1985) and Bodner and Sharp (1988) indicate that zones of upward-moving fluids near the Wilcox growth-fault trend (Fig. 1-6) create anomalously high temperatures. Thus, the possibility exists that certain broad zones occur which serve as pathways for the escape of geopressured fluids.

Once sediment deposition ceases, overpressures will decrease over time. The analytical error-function solution presented by Bredehoeft and Hanshaw (1968) shows that this depletion will require long times if permeabilities are low. Finally, the possible influence of encroaching meteoric systems during this overpressure depletion is unknown, but the fact that overpressures exist below meteoric systems indicates that meteoric processes do not significantly affect deep (> 5 km), low-permeability strata in the Gulf Coast.

Thermobaric regime

The thermobaric regime underlies the compactional regime. It is defined as the zone where the release of metamorphic fluids is the major hydrologic process. The importance of the fluids and fluid pressures produced in the thermobaric regime to the diagenesis and hydrology of the basin is unknown because this portion of the basin has not yet been sampled. However, temperatures and pressures in the deep basin, extrapolated from known temperature and pressure gradients, should be sufficient to cause low-grade metamorphism. Metamorphism is certainly occurring in rocks below and possibly even above the Louann Salt. These prograde metamorphic reactions may produce large quantities of water and carbon dioxide by, for example, conversion of mixed illite – smectite to muscovite. As written by Beach (1979), the reaction is:



As written above, this reaction consumes acid and produces water and silica.

Many studies have suggested that tremendous volumes of rock may be lost during metamorphism and that the fluid:rock ratio may be very high. This implies that metamorphic systems may be relatively open during the course of the reaction, and extrapolated pressure gradients suggest that the rocks may be extensively microfractured. Norris and Henley (1976) determined that aquathermal pressures would cause microfracturing during burial metamorphism if the geothermal gradient was greater than 12°C km^{-1} . Ethridge et al. (1983) concluded that microfracturing due to devolatilization reactions in metamorphic sequences is sufficient to increase the permeability to the point that free convection can account for the high fluid:rock ratio. The volume of fluid and amounts of dissolved species leaking out of that connecting system are not known.

Free convection

The possibility of free convection in sedimentary basins is suggested by the vast numbers of pore volumes of water required for some observed products of diagenesis in sandstones. Land (1984) calculated that a quantity in the order of 10^4 pore volumes is necessary to cement Frio sandstones. Neither meteoric nor compactional waters could supply this much water, but recirculation could provide a way to expose sediments to many volumes of water.

Free convection occurs when the buoyancy which results from density differences exceeds the viscous forces resisting motion. The major causes of density differences

are heating, with consequent expansion of the fluid, and salinity changes, which result from salt dissolution or reactions which release water. The feasibility of convection in porous media can be evaluated (Combarnous and Bories, 1975) with a stability criterion known as the Rayleigh number (Ra), where:

$$Ra = \frac{g \rho \alpha (\rho c)_f k \Delta T H}{\mu \gamma_*} \quad (2)$$

where g = gravity, ρ = density, $(\rho c)_f$ = volumetric heat capacity of the fluid, α = thermal expansivity, k = intrinsic permeability, H = layer thickness, T = temperature difference across layer, μ = fluid viscosity, and γ_* = thermal conductivity of the porous medium.

In a horizontal layer with isothermal, impermeable, upper and lower boundaries, the critical Rayleigh number (minimum to allow free convection) is $4\pi^2$. Critical values for other boundary conditions have also been determined (Nield, 1968). Rayleigh numbers of $12 - 4\pi^2$ correspond to the most reasonable boundary conditions for geologic settings (Aziz et al., 1973) involving nearly horizontal strata. Studies to date on sloping layers (e.g., Bories and Combarnous, 1973) have assumed that the boundaries are isothermal. In this case there is no stability criterion because the temperature and gravity vectors are not coincident, and convection should always occur in sloping layers. This is not true if the boundaries are not isothermal. If the isotherms are not horizontal in a formation, however, there should be convective movement.

The organization of convective cells depends on the slope of the layer and how much the Rayleigh number exceeds the critical value. The most reasonable cell configurations in a sedimentary basin are the polyhedral cell, and, in the infrequent areas of higher dip, unicellular flow. To evaluate the feasibility of convection, one can substitute reasonable parameters into the Rayleigh number equation (eq. 2). As noted by Straus and Schubert (1977), the fluid viscosity and thermal expansivity change a great deal with increasing temperature. A conservative approach sets the thermal values at the middle of the layer under consideration. The parameter of interest is the intrinsic permeability. Solving eq. 2 for intrinsic permeability, assuming a constant thermal gradient all the way to the surface, yields:

$$k_c = \frac{Ra_c \mu \gamma}{g \rho \alpha (\rho c)_f G H^2} \quad (3)$$

where G is the geothermal gradient. Using eq. 3, critical permeabilities of strata have been determined for a variety of thicknesses and depths as shown in Fig. 1-9. If strata are very thick, the calculated permeabilities correspond to the high end of the permeability range for shales (Freeze and Cherry, 1979, table 2.2), indicating the possibility of large-scale convection in thick, low-permeability sediments. The possibility of convection occurring in shales is increased if: (a) the shales are somewhat fractured; (b) the shales are interlayered with higher-permeability sands; or (c) when less restrictive boundary conditions are appropriate.

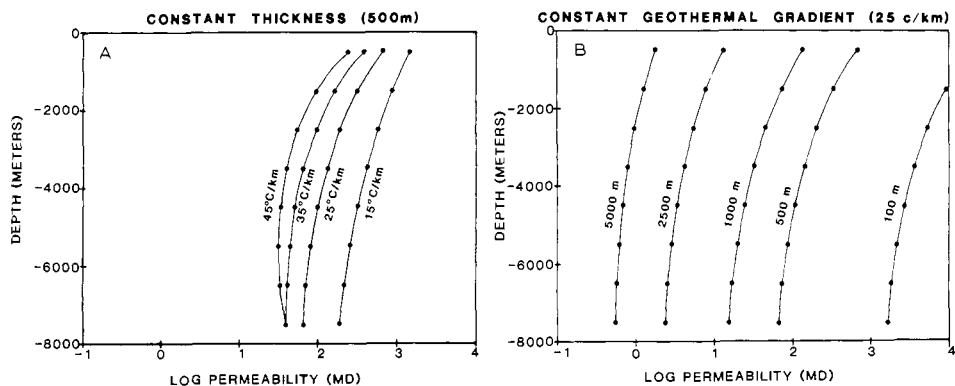


Fig. 1-9. Critical permeabilities for various strata thicknesses, A, and geothermal gradients, B. (After Blanchard and Sharp, 1985.) When critical permeabilities are exceeded, free convection should occur.

If free convection is occurring in the Gulf Coast basin, a likely location would be in the thick barrier bar – strandplain sandstones of the Frio Formation. Evidence presented by Blanchard and Sharp (1985) indicates the feasibility of convection in this setting.

Summary

The hydrodynamic and thermal settings are coupled. Together they largely control diagenetic processes in the Gulf of Mexico Basin. Low geothermal gradients ($20-30^{\circ}\text{C km}^{-1}$) are typical of the Gulf of Mexico basin. Generally, geothermal gradients decrease in an offshore direction and increase south towards the Texas–Mexico volcanic province. Local variations are created by high-thermal-conductivity salt diapirs and by sporadic plumes of upwelling pore fluids, especially along growth fault zones. The three basic hydrogeological regimes, depicted in Fig. 1-8, are: (1) meteoric; (2) compactional; and (3) thermobaric. Figure 1-10 depicts a generalized flow chart for hydrologic system development in an evolving sedimentary basin.

(1) Meteoric flow systems are controlled by topography. The fluids are chiefly meteoric in origin, but may mix with upward-moving diagenetic fluids with depth or above fault-zone conduits. Flow is directed toward major river systems and toward the coast.

(2) The compactional system expels connate and diagenetic fluids upward. Heat buildup and restricted fluid flow are associated with overpressured sediments, which dominate the compactional system. Overpressured zones near growth faults are associated with temperature plumes which probably result from upwelling fluids.

(3) High temperatures and pressures result in near-lithostatic pressures and metamorphic reactions which take place progressively in the thermobaric regime. Fluids produced from these reactions must eventually rise through the thermobaric zone and eventually enter the overlying hydrodynamic systems.

(4) Free convection may occur in any of the above hydrogeologic regimes.

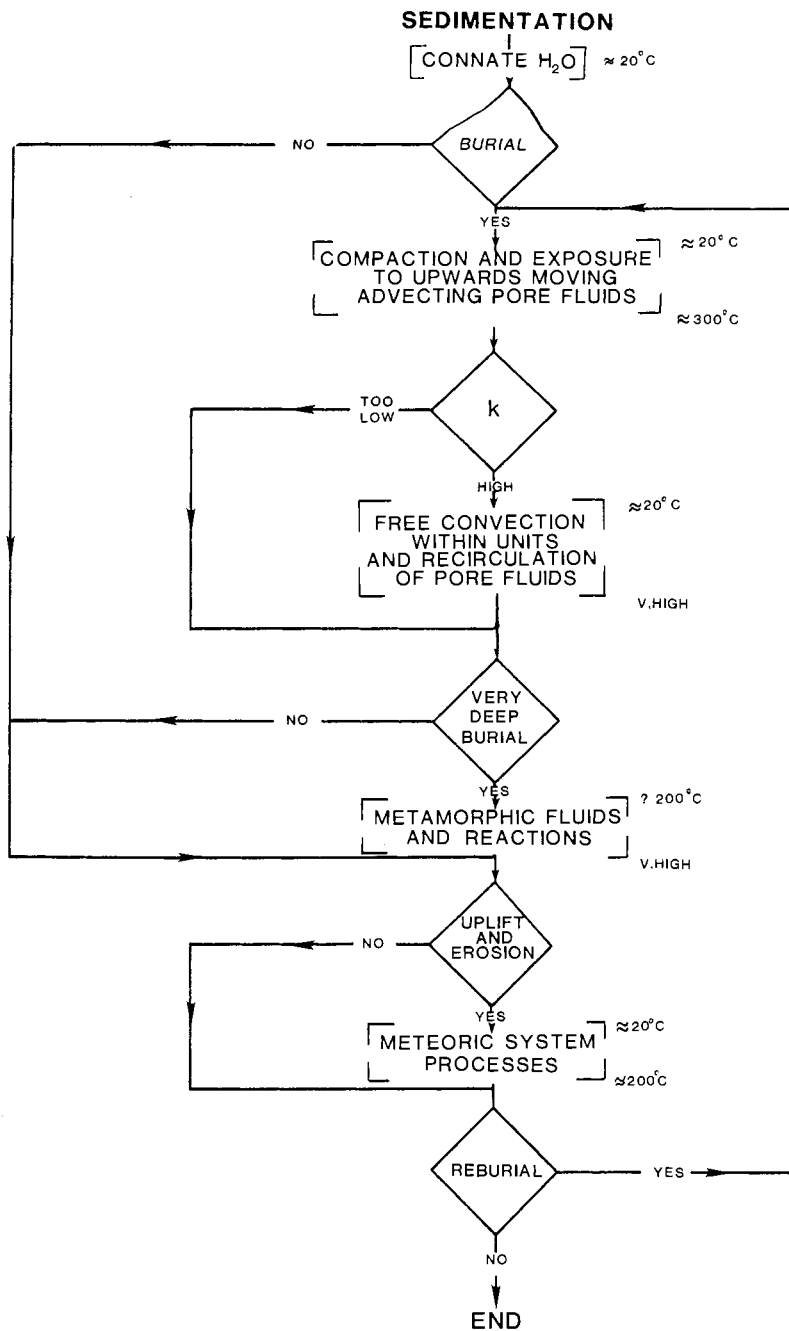


Fig. 1-10. Flow chart of possible hydrodynamic regimes for a sedimentary basin. Estimated temperature limits for each regime are given.

Water in Mesozoic rocks

Formation waters from units of Mesozoic age are very saline, dominated by sodium, calcium and chloride, as is typical of many sedimentary basins. Because many of these fluids approach halite saturation, it is implicit that they have evolved directly from interaction with evaporites rather than from any other postulated process of salt concentration (such as reverse osmosis). In many areas, the fluids are found in close proximity to presently existing evaporites, and few "shale membranes" exist in the Mesozoic section.

Three theories have been advanced to explain the composition of these waters. Carpenter (1978) noted that the ionic composition of these very saline brines resembles sea water modified by evaporation to or past halite saturation. He proposed that burial of the pore fluids from which evaporites form, with subsequent modification (primarily by dolomitization), can yield water of the observed composition. Carpenter placed strong emphasis on the conservative behavior of Br during the evaporation of sea water to account for the Cl/Br ratio of the brines.

Land and Prezbindowski (1981) advanced an alternative hypothesis, namely continuous generation of brines in the subsurface by the dissolution and recrystallization of halite, coupled with the reaction of anorthite (as a component in detrital plagioclase) to form albite and account for the calcium. Br-rich halite has been shown experimentally to recrystallize to a low-Br salt and a Br-rich solution (reverse partitioning), casting doubt on the use of Br as a conservative component (Wilson and Long, 1984; Stoessell, 1984; Stoessell and Carpenter, 1986). Land and Prezbindowski (1985) subsequently emphasized that the volume of highly saline brine presently in the subsurface appeared to be much larger than the volume which could have been buried with the Louann salt. This is especially true when losses due to uranium mineralization (Goldhaber et al., 1978), heavy-metal sulfide deposition (Price et al., 1983), and losses of ions such as Cl^- to the surficial hydrologic system (Feth, 1981) were taken into account.

Morton and Land (1987) proposed a third hypothesis, namely that acid metamorphic fluids are locally discharged into the sedimentary section from the underlying basement. Dilute acids are generated during low-grade metamorphism, as "reverse weathering" reactions release the protons bound in clay minerals (Krauskopf, 1979, p. 535). For example, the sodium/hydrogen and potassium/hydrogen ratios of a fluid in equilibrium with albite, microcline, and clay minerals decrease between two and three log units between 25° and 300°C (Helgeson, 1974, fig. 15). Neutralization of the dilute hydrochloric acid generated in underlying metamorphic rocks, basal limestones in the Gulf coupled with halite dissolution and recrystallization, results in Na–Ca–Cl brines which are extremely impoverished in magnesium.

Carpenter's hypothesis (espoused by Stoessell and Moore, 1983), treats the basin simply as a compacting one. Brines, which precipitated the Louann salt, are buried, later modified by extensive dolomitization (the locus of which is unknown in the Gulf), and then dispersed throughout the section. Land and Prezbindowski (1981) and Morton and Land (1987) proposed a dynamic system in which halite is con-

tinually dissolved in the subsurface with brines discharged vertically and laterally. No specific source for the water involved in the latter two hypotheses has been proposed. However, extensive rock – water interactions are evidenced in all cases by hydrogen, oxygen (Land and Prezbindowski, 1981), and strontium (Stueber et al., 1984) isotopic modification of the water.

In addition to typical Na – Ca – Cl brines, Br-rich brines associated with interior salt basins are known in the Gulf. Land and Prezbindowski's (1981) hypothesis of halite recrystallization is inadequate to explain these extremely Br-rich fluids. Similarly, Carpenter (1978) was unable to satisfactorily explain such high Br concentrations. It seems likely that dissolution and/or recrystallization of bittern salts may be involved in these local but interesting fluids. The fact that bromide contents of these fluids cannot be satisfactorily explained is further reason to exert caution in treating bromide as a conservative component.

Waters in Tertiary rocks

The chemistry of water in the predominantly clastic Tertiary section is highly variable. Chloride is the dominant anion in all cases, ranging in concentration from about 8000 ppm to near halite saturation. Sodium and calcium are the dominant cations, but there is considerable variation in the Na/Ca ratio. Generally, the most saline waters are found in the salt-dome provinces of east Texas and south Texas (Kharaka et al., 1977, 1985; Morton and Land, 1987) where water with nearly equal sodium and chloride exists. Figure 1-11 contrasts the sodium, chloride, and bromide contents of Mesozoic formation waters, exemplified by the Cretaceous Edwards Formation in Texas and Jurassic formations in the Mississippi salt basin (Carpenter and Trout, 1978), with Tertiary formation water. Unfortunately, bromide data on water from the Wilcox Formation are unavailable. Water from Mesozoic formations is generally more saline than water from Tertiary formations and has a Na/Cl (molal) ratio much less than one (simple halite dissolution) because of high calcium content. Water from Tertiary formations has Na/Cl ratios falling between those of water characteristic of Mesozoic formations and a ratio somewhat greater than one. Chlorinities much higher than that of sea water coupled with Na/Cl ratios of nearly one, and low bromide content, clearly support salt dissolution as being a major control in the ionic composition of some Tertiary formation waters. The lowest-salinity waters generally exhibit Na/Cl ratios in excess of one (Fig. 1-11). The excess positive charge is balanced by high alkalinity, caused primarily by high concentrations of dissolved acetate (Carothers and Kharaka, 1978).

Although the chloride/bromide ratio of formation waters is complicated by halite dissolution and recrystallization, its conservative behavior in the absence of contact with halite makes it a useful parameter. The Cl/Br (molar) ratio in water from Jurassic rocks in the Mississippi salt basin is much less than the ratio in sea water (654), and generally less than in water from other Mesozoic units for which data are available. In contrast, the Cl/Br ratio of Tertiary water ranges from low values typical of Mesozoic brines to approximately 2500. High Cl/Br ratios, which most often are characteristic of water with molar Na/Cl ratios near one, have been interpreted by most authors to be diagnostic of salt dissolution. But dissolution of a first-

cycle halite containing approximately 75 ppm Br should result in a solution with a Cl/Br near 18,000. Because Cl/Br ratios in excess of approximately 2500 are unknown in Gulf Coast formation waters, recrystallization of diapiric salt and reverse partitioning of bromide into the resultant brine are indicated (Land and Kupecz, 1987).

Four kinds of water appear to exist in the Tertiary section (Fig. 1-11). Ca-rich water (low Na/Cl ratios), also rich in bromide, is similar to water in Mesozoic units and appears to be derived from them by vertical leakage. Water having Na/Cl ratios greater than one is characterized by relatively low salinity and high organic acid content. Such "acetate-type" water is common within the overpressured zone, especial-

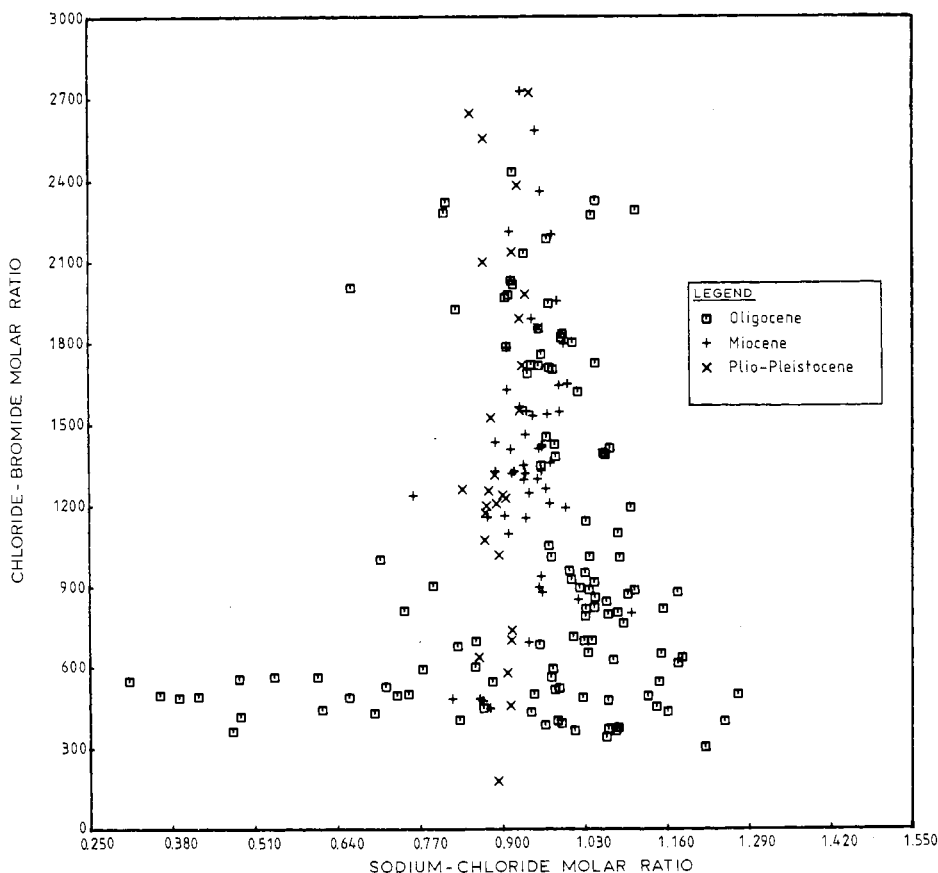


Fig. 1-11. Molar Cl/Br versus molar Na/Cl ratios of Gulf Coast formation waters. Four kinds of water can be defined. Brines in Mesozoic units (which also penetrate the Tertiary section) are bromide- and calcium-rich. Low-salinity brines have a Br/Cl ratio near sea water and a Na/Cl ratio greater than one due to significant concentrations of organic acid anions, and are commonly associated with shale-rich sections. Brines having Na/Cl ratios near one are derived by halite dissolution. Some are evolving toward Ca-rich brines by albitization (as evidenced by $^{87}\text{Sr}/^{86}\text{Sr}$ data), but retain their high Cl/Br ratios.

ly in shale-rich sections. Water having high Cl/Br ratios is derived from salt solution and recrystallization, and in some cases water of this type is evolving into a Ca-rich type as a result of albitization. This minor water type, characterized by high Cl/Br ratio and low Na/Cl ratio, typically contains very radiogenic Sr, consistent with extensive reaction with feldspars.

Many authors (e.g., De Sitter, 1947; Bredehoeft et al., 1963) have invoked reverse osmosis (shale membrane filtration) as a mechanism of modifying the salinity of connate sea water initially present in the pores of the sediments. Although this process cannot be dismissed, few authors support reverse osmosis as a process that can account for the very saline fluids present in the Tertiary rocks. The fact that observed ion ratios (and isotopic ratios) do not vary systematically, as might be predicted if reverse osmosis were to operate, and that the shale "membranes" are highly

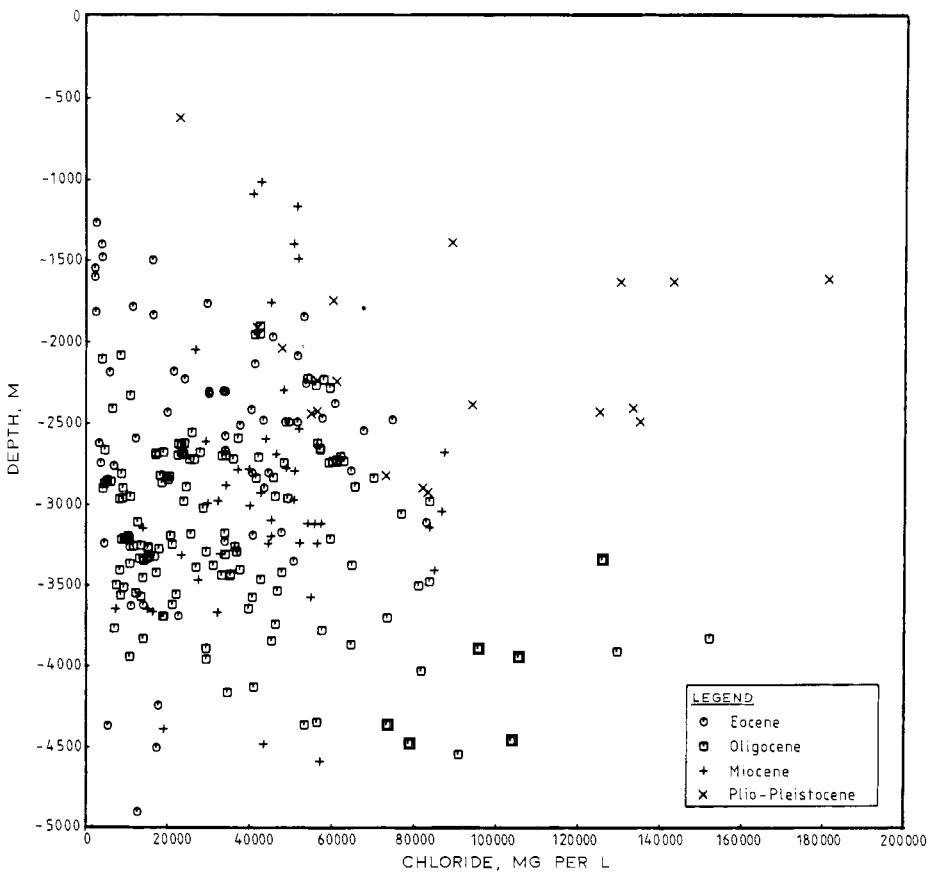
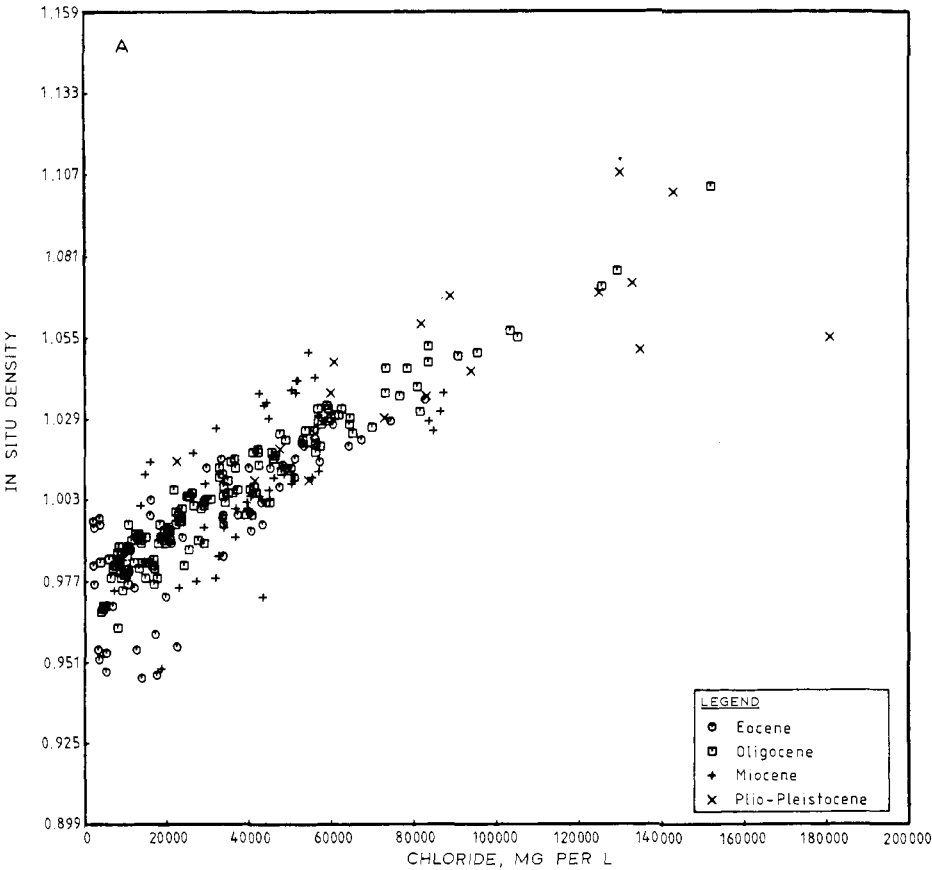


Fig. 1-12. Salinities of formation waters from thick shale-rich sections. Depth versus chloride content for brines from Tertiary formations. Very saline brines are either of the Ca-rich type, and are found relatively deep on the section, or of the NaCl type. Although restricted data sets commonly document lowest-salinity brines near the top of hard overpressure (pressure approximately 85% of the lithostatic), this large data set shows no relation of salinity to overpressure.

faulted and possibly microfractured, indicates that this process probably does not occur on a wide scale. With active fluid flow in the subsurface, large salinity differences are more easily explained by salt dissolution, mineral dehydration, and mineral – water interaction.

Formation waters sampled from within thick shale-rich sections, such as those generally associated with the San Marcos arch, commonly have salinities less than seawater, and as low as about 8000 ppm Cl (Fig. 1-12). Low salinities are not artifacts of the sampling process because the water often has dissolved silica concentrations in excess of quartz saturation under in situ temperatures and normal δD and $\delta^{18}O$ values. Because many of these waters are produced from within the over-pressured zone, meteoric water cannot be involved. It is also unlikely, based on the depositional environment of the rocks, that brackish water could have been buried with the predominantly marine deltaic deposits. Loss of smectite interlayer water, together with mineral dehydration reactions, can account for salinities lower than



sea water. Evolving water in this way requires entrapment within the overpressured zone and subsequent burial because these brines often have temperatures higher than required for the smectite-to-illite transformation.

The problem of formation water circulation is critical to understanding the origin of the waters and their effect on diagenesis of rocks. Most previous studies have not considered long-distance transport in trying to account for formation-water chemistry. It is important to note that the most important parameter controlling density of formation waters and, in turn, hydraulic potential is salinity and not temperature (Fig. 1-13). The presence of low-salinity water at relatively great depths within the geopressed zone, and high-salinity water both at relatively shallow depths and relatively great depths, must be considered when attempting to interpret

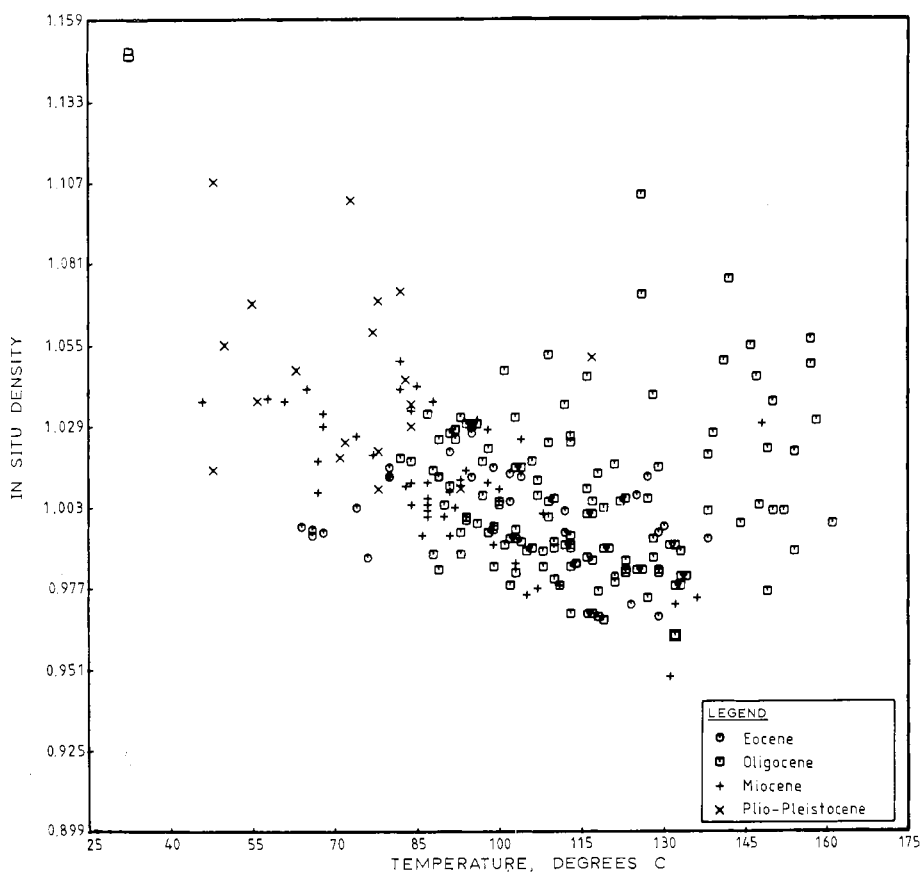


Fig. 1-13. Effect of salinity and temperature on in situ density of Gulf Coast formation waters. The in situ density of water is most strongly controlled by salinity (A) and less strongly by temperature (B). Salinity-induced density variations have not been adequately taken into account in current hydrologic models.

basin-wide fluid movement. Unlike many older basins, which are essentially density (salinity) stratified (Land, 1987), the Gulf Coast Tertiary basin exhibits tremendous local salinity differences.

The quantitative interpretation of formation water compositions is still uncertain. Water with chloride in excess of about 1 molal (about twice as high in concentration as seawater) cannot now be considered rigorously in equilibrium calculations, even at near-Earth-surface temperatures. Some interpretations based on the thermodynamic approach (e.g., Stoessell and Moore, 1983; Kaiser, 1984) exhibit both the highly scattered nature of the data set and the problems of this approach. It is not surprising that, on a gross basis, most water is in near-equilibrium with phases like illite, quartz and calcite. What is important is how the chemistry varies along flow paths which, in concert with material transport, causes the diagenesis of the rocks. Integration of diagenesis and formation water chemistry data, coupled with hydrologic constraints, remains a future goal.

“Recent” meteoric ground water

Rocks older than Cretaceous do not crop out along the Texas Gulf margin and do not contain fresh ground water. The major aquifers in the Gulf Coast region include the Travis Peak or Hosston Formations (basal Cretaceous sandstone), the Edwards Formation (limestone and dolomite), and four Tertiary sandstones or sandstone pairs (Carrizo–Wilcox, Catahoula–Frio, Oakville, and Beaumont–Lissie). Many other formations act as minor aquifers, but their chemistry is not significantly different from the major aquifers.

The fresh-water aquifers extend from the outcrop into the subsurface to the south and southeast (basinward). They crop out in an arcuate belt which approximately replicates the shape of the present Gulf margin (Fig. 1-14). The downdip extent of fresh water is controlled by recharge rates, rock type and permeability, and out-of-basin flux of saline water; thus, there is a great deal of variation in the maximum depth of fresh water. Aquifers consisting of relatively stable minerals contain potable water to relatively great depths (e.g., the Carrizo, to ~1.5 km; Hamlin, 1984), whereas lower-permeability units with unstable minerals may contain relatively saline water at fairly shallow depths.

Hydrochemical facies

The hydrochemical facies, distinguished by major-ion chemistry, in general reflect the host rock type and mineralogic maturity. Piper diagrams (Fig. 1-15) illustrate the various chemical facies.

Ground waters in nearly all the clastic aquifers change from calcium-rich to sodium-rich with increasing total solids content. The most commonly cited source for this relative increase in sodium is exchange of calcium for sodium on clay minerals (Fogg and Kreitler, 1982; Kaiser and Ambrose, 1984; Macpherson, 1984). In order to increase sodium concentration with time or along a groundwater flow path, calcium ions must be continuously supplied by dissolution of calcite. Calcite dissolution occurs initially because of relatively high partial pressure of CO_2 in the

unsaturated zone of the aquifer. Further dissolution occurs because exchange of dissolved calcium on clays results in undersaturation of the ground water with respect to calcite (Fig. 1-16). In some instances, upward leakage of sodium-chloride brines along faults into fresh-water aquifers also raises the sodium content of ground water (Clement and Sharp, 1988). The accompanying increase in chloride and other ions characteristic of brines provides the easiest way to identify this mixing. Finally, sodium may be supplied by dissolution of evaporite minerals within the aquifer itself (Henry et al., 1982).

Variations in the anion composition of the aquifers are more complicated. The

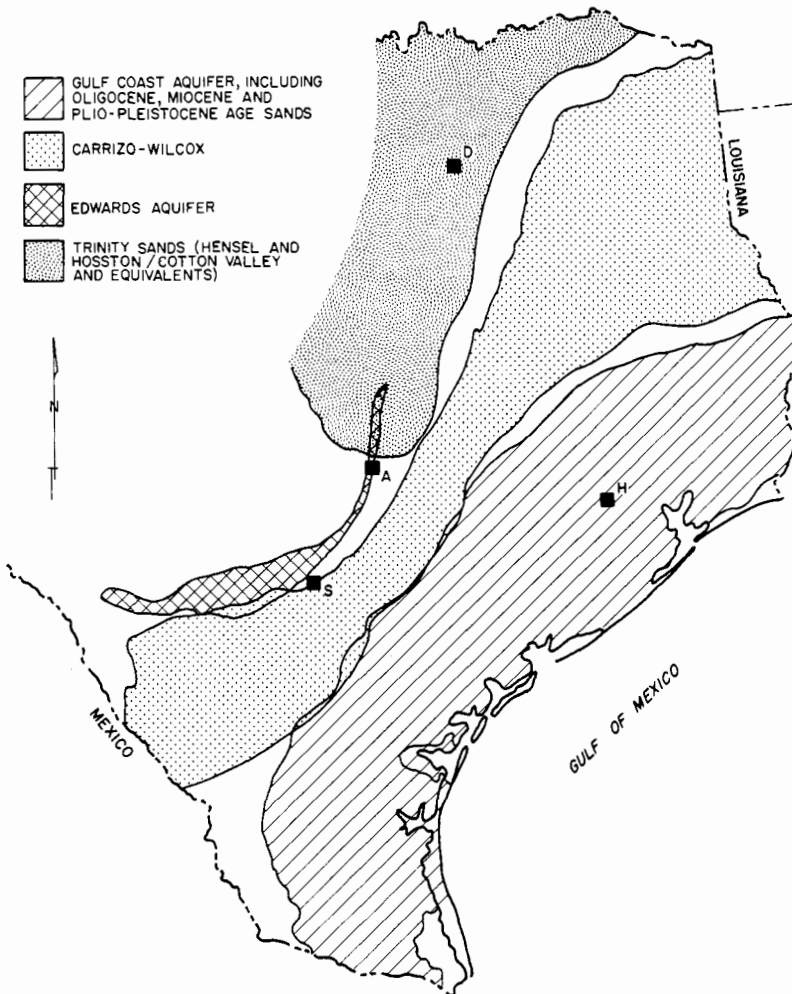
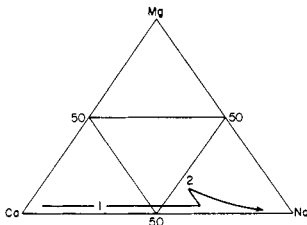
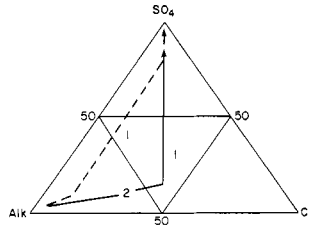


Fig. 1-14. Distribution and extent of major fresh-water regions of aquifers in Texas. Major cities (Austin, Dallas, Houston, and San Antonio) are shown for reference.

A. HOSSTON / TRAVIS PEAK (Lower Cretaceous)

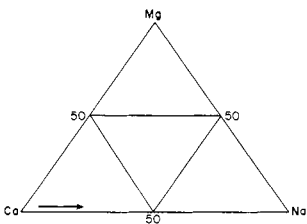


1. $\text{Na}_2\text{-clay} + \text{Ca}^{2+} \rightarrow \text{Ca-clay} + 2\text{Na}^+$
2. Calcite + acid $\rightarrow \text{Ca}^{2+}$ + alkalinity

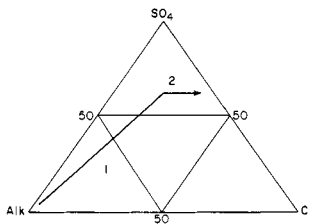


1. $\text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{acid}$
2. Addition of Na-Cl brine

B. EDWARDS FORMATION (Cretaceous)

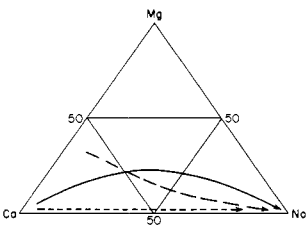


Addition of Na-Cl brine



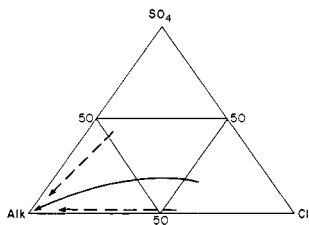
1. $\text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{acid}$
2. Addition of Na-Cl brine

C. WILCOX GROUP (Eocene)



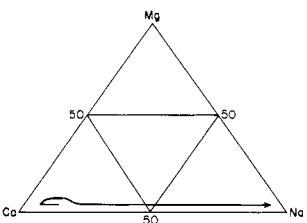
Both shallow and deep paths -- E. Tx. Basin:
 $\text{Ca} + \text{Na}_2\text{-clay} = 2\text{Na} + \text{Ca-clay}$

Deep path has higher Na from residual sea water (?) discharge from low-permeability units

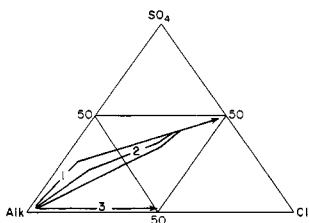


ETB water -- $\text{SO}_4 + \text{org.} = \text{H}_2\text{S} + \text{CO}_2$

D. CARRIZO SANDSTONE (Eocene)

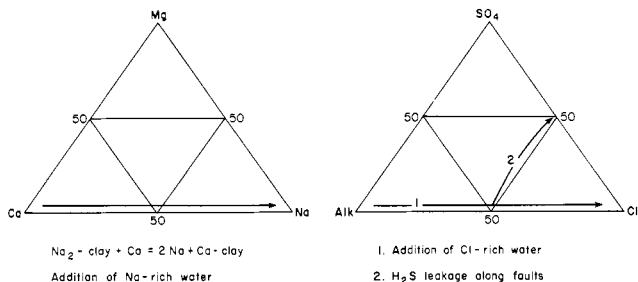


$\text{Na}_2\text{-clay} + \text{Ca} = 2\text{Na} + \text{Ca-clay}$
 or addition of Na brine

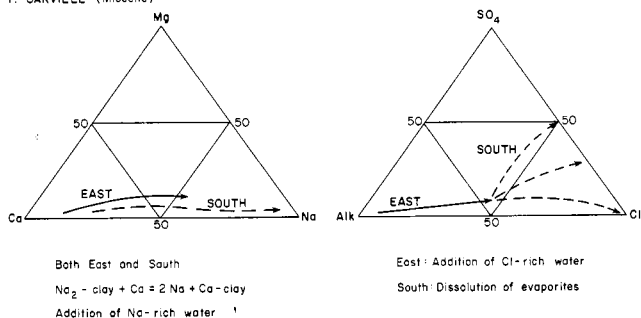


1. $\text{H}_2\text{S} + \text{org.} = \text{SO}_4 + \text{CO}_2$
2. Addition of SO_4 -Cl water
3. Addition of Cl water

E. CATAHOULA - FRIO (Oligocene)



F. OAKVILLE (Miocene)



G. BEAUMONT (Pleistocene)

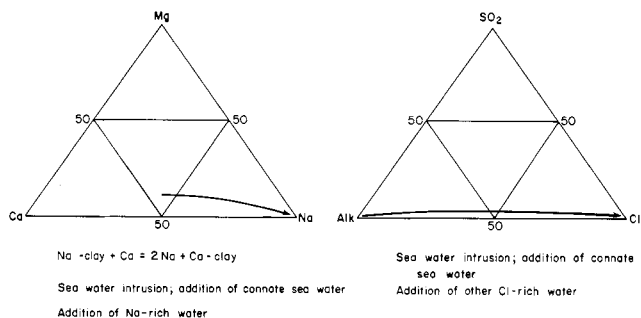


Fig. 1-15. Piper diagrams with percent equivalents of major cations and anions for the major aquifers in the Texas Gulf Coast region. Arrows show direction of increasing dissolved solids. Probable causes for the change in dominant cation or anion are listed below each triangle. The depositional facies (not shown) is a strong controlling factor on the chemical facies of the ground water. Wilcox waters are shown for the East Texas Basin (ETB) region as well as South Texas. In the ETB, Carrizo waters are commonly undifferentiated from Wilcox waters. Carrizo triangular plots represent South Texas water only.

most abundant anion in many ground waters is bicarbonate, even at relatively high salinities. Processes which have been suggested to be responsible for the high concentration of bicarbonate ions include: (1) cation exchange, and thus, ultimately, calcite dissolution; (2) coalification of organic matter; and (3) infiltration of CO_2 from external sources (such as deeper natural gas).

In some ground waters, sulfate is the major anion. In the more saline portions of aquifers or in down-flow zones, significant concentrations of sulfate have been attributed to one of the following mechanisms: (1) addition of H_2S or other reduced sulfur species by leakage along faults, with subsequent oxidation to sulfate (Catahoula Formation – Galloway and Kaiser, 1980); (2) oxidation of H_2S or other reduced sulfide species at the interface between basinward-moving fresh water and saline water (or gas) moving out of the basin (Edwards Formation – Rye et al., 1981; Land and Prezbindowski, 1981; Hosston – Travis Peak – Macpherson, 1984); and (3) evaporite dissolution within the aquifer. In the Wilcox Formation (East Texas Basin area), sulfate concentrations are higher near the recharge areas than basinward. This distribution probably represents shallow dissolution and oxidation of pyrite, followed by sulfate reduction, as ground water moves basinward.

Some aquifers have a high chloride ion content, which can be attributed to mixing with sodium-chloride brines found downdip in these units, leakage of deeper brines along faults, or, rarely, flushing of connate (i.e., syndepositionally trapped) fluids (e.g., Wilcox – Dutton, 1982; Beaumont – Lissie – L.C. Dwyer, pers. commun., 1984), or seawater intrusion (Beaumont – Kreitler et al., 1977).

In the Carrizo – Wilcox aquifer, the silicic acid content is significantly higher in recharge areas than in discharge areas, suggesting that feldspars, other silicates, or opal phytoliths are dissolving near the outcrop, and authigenic quartz or clay minerals are precipitating along the flow path (Fogg and Kreitler, 1982; Kaiser and Ambrose, 1984; Macpherson, 1984).

Very few analyses of stable isotope ratios of fresh ground water in the Gulf Coast

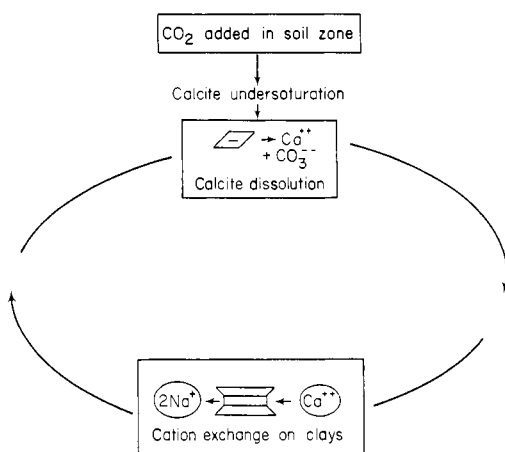


Fig. 1-16. Calcite-undersaturated waters created by base exchange of calcium on clays.

region are available, but initial studies indicate that the $\delta^{18}\text{O}$ contents are similar to the local meteoric water (e.g., Hosston – Travis Peak – Macpherson, 1982) or altered to be in equilibration with hosting carbonate rocks. The $\delta^{13}\text{C}$ values also reflect interaction of the water with the hosting rock (e.g., Wilcox – Dutton, 1982), casting doubt that coalification of organic matter is a significant process.

In summary, modest rock – water interaction controls the water chemistry of aquifers in the Gulf Coast region. Diagenetic changes include: (1) alteration of Na-clay minerals to Ca-clays; (2) dissolution of calcite and, where present, evaporites, as well as minor dissolution of silicate minerals (e.g., feldspars); and (3) precipitation of authigenic silica or clay minerals (Fig. 1-17). The stable isotopic signature of the ground water and its relatively low dissolved solids content are suitable for identifying penetration of relatively recharged ground water into the deeper parts of the Gulf Coast basin where saline waters dominate.

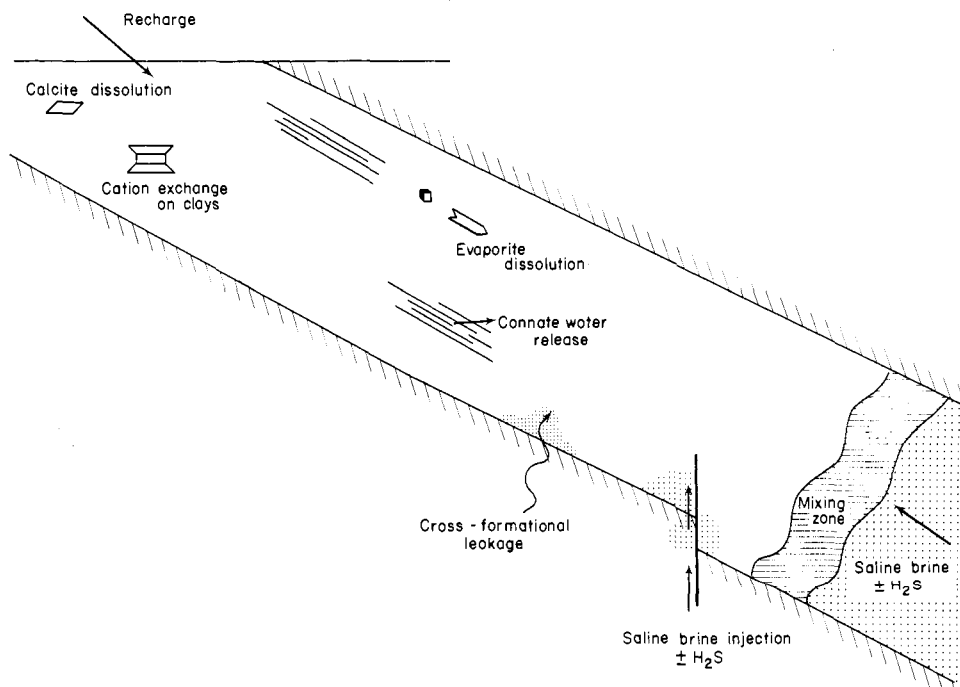


Fig. 1-17. Authigenic silica and clay minerals. Summary of simple geochemical reactions in mixing, which influence shallow ground-water chemistry. Calcite dissolution and cation exchange on clay minerals lead to sodium- and bicarbonate-rich ground water. Evaporite dissolution may add sodium, chloride, calcium, and sulfide ions. Cross-formational leakage along faults and simple mixing at the deepest penetration of meteoric ground water can add several varieties of brines to shallow ground water.

EVAPORITES

Introduction

Evaporites comprise a small proportion of the total volume of sedimentary rocks in the Gulf Coast basin, but they have an important influence on the compositional evolution of deep basinal fluids and, consequently, on diagenesis.

The most important of the evaporite units is the Middle Jurassic sequence of halite-rich rocks collectively known in the northern Gulf region as the Louann Salt. The Louann overlies, interfingers with, and is overlain by numerous anhydrite-bearing units which occur primarily along the margin of the Gulf Basin. These units include probable continental evaporites such as the Werner Anhydrite, which underlies the Louann Salt, as well as overlying shallow, subtidal to supratidal, anhydrite- (rarely halite-) bearing marine units such as the Upper Jurassic Buckner Formation and the Lower Cretaceous Ferry Lake Formation in the northern Gulf, and the Upper Jurassic Olvido Formation in northeastern Mexico.

According to Kupfer (1974) and Salvador (1987), evaporite deposition began in the late Middle Jurassic, when continental rifting allowed the sea to enter from the west. Subtidal halite deposition occurred primarily in localized deep graben basins throughout the region, while shallow subtidal to supratidal calcium-sulfate deposition occurred at basin margins. As spreading continued, carbonate deposition dominated throughout the region except for a few isolated basins in the southern part of the region where halite deposition continued.

Although there are few continuous cores through significant thicknesses of Louann Salt, the unit is believed to be dominantly halite, with less than 20% anhydrite, carbonates, and siliclastic rocks. There have only been three reported occurrences of bittern salt deposits within the Louann Salt (Kupfer, 1974). It is probable that these bittern minerals were deposited during early diagenesis of the Louann and not as primary precipitates during Louann deposition.

*Diagenesis of the Louann Salt**Stages of diagenesis*

Diagenetic modification of the Louann Salt can be divided into processes occurring prior to diapirism, during diapirism, and after diapirism. The paragenetic sequence of diagenetic processes occurring within each of these stages is illustrated in Fig. 1-18.

Pre-diapir stage

Pre-diapir stage of diagenesis begins with initial burial of the evaporitic sediments and ends with the transition from salt pillowing to salt diapirism and extensive withdrawal of underlying halite (e.g., Seni and Jackson, 1983a). Initial porosity of the evaporites is typically as high as 50%. Expulsion of interstitial connate brine occupying this porosity goes to completion within approximately 1 km of burial. The composition of this fluid depends on the stage of evaporite mineral precipitation at the time of burial. Because the occurrence of bittern salts within the Gulf basin is

extremely rare, it is likely that the composition of these connate brines was within the composition range of a marine brine at halite precipitation stage, that is, a Na – Cl – Mg – K – Br brine.

Within the Gulf Basin, gypsum should theoretically revert to anhydrite at depths of burial ranging from 1.1 to 2.4 km depending on the salinity of the pore fluids and the geothermal gradient. In fact, gypsum is seldom observed below 0.6 km because of the combined effects of high-salinity fluids and the unequal pressure on liquid and solid, both of which decrease the effective temperature of transformation (Graf and Anderson, 1981). Anhydrite typically has a higher trace-element concentration than gypsum; therefore, during burial the transformation of any primary gypsum which might have been deposited releases CaSO_4 -saturated water of dehydration into adjacent pore space.

Highly soluble halite dissolves as soon as less saline fluids enter the system. Less saline water derives from early perched meteoric lenses, as well as water derived from the dehydration of minerals (gypsum, iron hydroxides), and the transformation of smectite to illite. With the development of salt pillows (Seni and Jackson, 1983a), halite begins to move upward with respect to overlying sediments, and extensive recrystallization and dissolution begin. Dissolution of halite releases Na^+ and Cl^- as well as important trace elements such as K^+ , Br^- , I^- , and Mg^{2+} (Fig. 1-18). Recrystallization preferentially releases the trace elements such as Br^- to

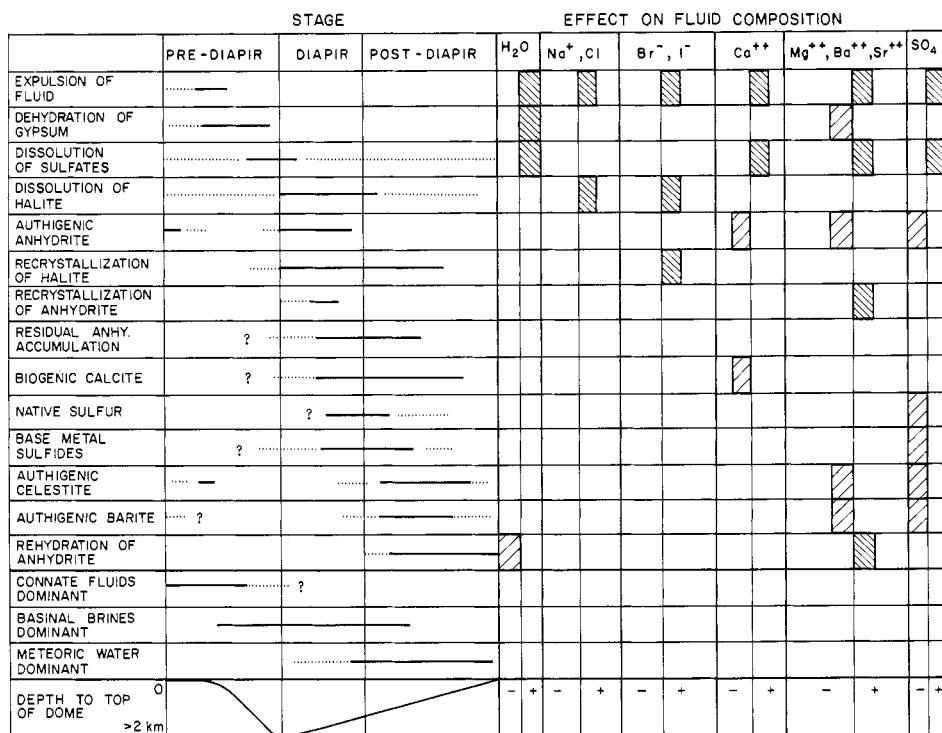


Fig. 1-18. Paragenetic sequence of diagenesis of Louann Salt and effect on fluid composition.

solution due to reverse partitioning (Land and Prezbindowski, 1981; Stoessel and Carpenter, 1986). As a result of this process, as well as important siliciclastic diagenetic processes such as albitization, host fluids begin to evolve from connate sea water and brines to high-salinity, high-temperature, Na – Ca – Cl basinal brines.

Diapir stage

The bulk of halite dissolution and recrystallization occurs during the main stage of diapirism. Seni and Jackson (1983a) estimated that in the East Texas basin, 76% of the total Louann Salt had been removed from a region of salt diapirism, whereas only 16% had been removed from an area with pillow development. The focus of diagenesis in this stage as well as the later post-diapiric stage is at the top of the salt diapir.

The degree of salt dissolution depends to a great extent on the timing and extent of cap-rock formation because the cap rock retards halite dissolution at the top of the diapir. Murray (1966) proposed the following sequence for the development of cap rock in Gulf Coast salt diapirs (Fig. 1-19): (1) intrusion of the salt plug into a

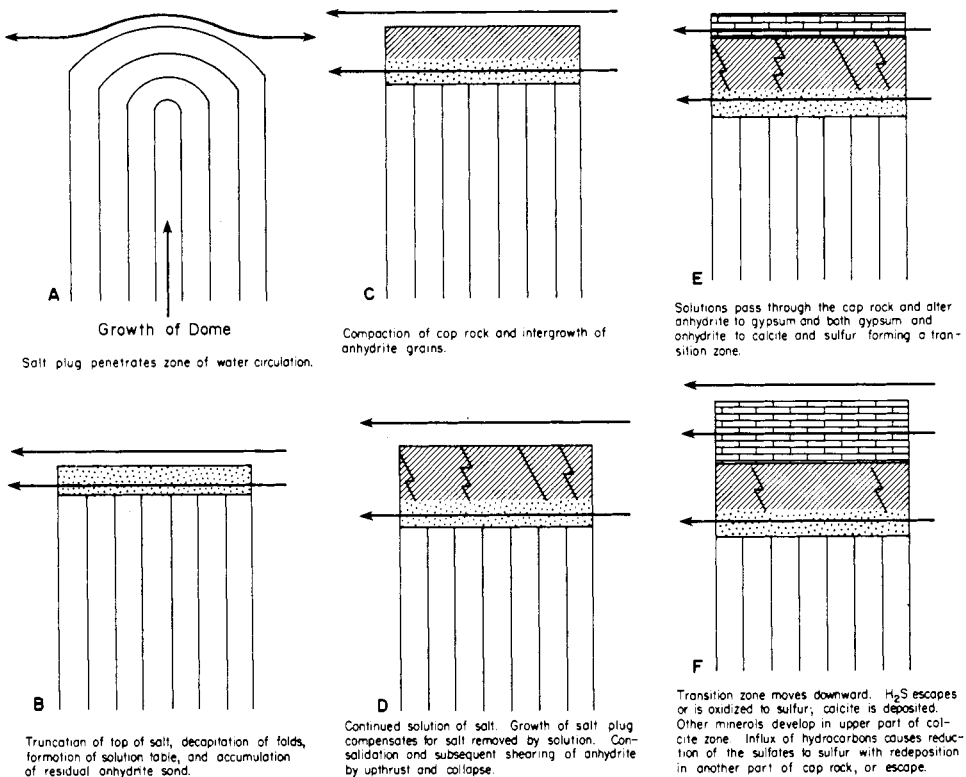


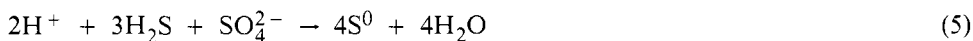
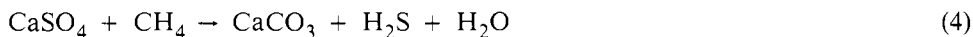
Fig. 1-19. Schematic diagram of cap-rock formation. (After Kreitler and Dutton, 1983.) Horizontal arrows show water flow. Figure courtesy of Texas Bureau of Economic Geology.

zone of active water flow; (2) gradual truncation of the top of the salt diapir by dissolution; (3) compaction of the diapir top with accumulation of residual anhydrite and intergrowth of anhydrite grains; (4) repetition of steps 2 and 3 to develop the banding observed in anhydrite cap rock; (5) influx of hydrocarbon-rich solutions that hydrate anhydrite to gypsum, reduce SO_4^{2-} to S^0 , and produce calcite, and (6) influx of oxidizing solutions that (a) oxidize H_2S or FeS_2 to native sulfur, and (b) form secondary calcite.

To this scenario can be added the precipitation of authigenic base-metal sulfides and sulfates in the cap rock in stage 5 (Price et al., 1983) from basinal fluids discharged along the flanks of the diapirs.

As shown in Fig. 1-19, the residual accumulation of anhydrite, which provides the framework for cap rock, may begin early in the diapiric stage. The effective development of residual anhydrite depends upon the rate and duration of diapirism and hence halite dissolution, the position of the top of the diapir with respect to the stability field of gypsum, as well as the degree of saturation of the surrounding fluids with respect to anhydrite.

Calcite and native sulfur are precipitated in the upper portion of cap rock by the bacterial reactions (Price et al., 1983):



These stages are not universally present in cap rocks and their appearance reflects the exposure of the anhydrite cap rock to hydrocarbon-rich fluids (the source of energy for the bacteria) and the development of appropriate conditions for sulfur-oxidizing bacteria to oxidize the sulfide species. Kreidler and Dutton (1983) have shown that the process of biogenic calcite formation from anhydrite involves a volume reduction and, therefore, produces porosity and collapse breccias within the cap rock. This porosity is important for channeling the fluids responsible for precipitating sulfate and sulfide minerals.

Base-metal sulfide deposits within the cap rocks of salt domes in the Gulf Coast basin can be considered a subtype of Mississippi Valley-type (MVT) lead-zinc deposits. As in MVT deposits, the base metals derived from siliciclastics within (or beneath) the basin are carried to the site of mineralization within hypersaline basinal brines. Precipitation of sulfide occurs as a result of the metal-rich brines encountering a source of reduced sulfur. In the case of salt dome deposits, the reduced sulfur is probably H_2S derived from bacterial reduction of SO_4^{2-} from anhydrite. These deposits differ from classic MVT deposits in that they are relatively young and occur within short-lived host rocks. Unlike other MVT deposits, the conduits for the mineralizing brines are fractures along the margins of the salt diapirs.

The most important example of these salt dome deposits is within the Hockley Dome of southeastern Texas. It consists of an annular zone containing marcasite, pyrite, sphalerite, galena, hauerite, and acanthite within both anhydrite and calcite zones of the cap rock (Fig. 1-20). The most nearly economic accumulations are porous infillings within the calcite zone, which reach concentrations of 7 wt.% Pb

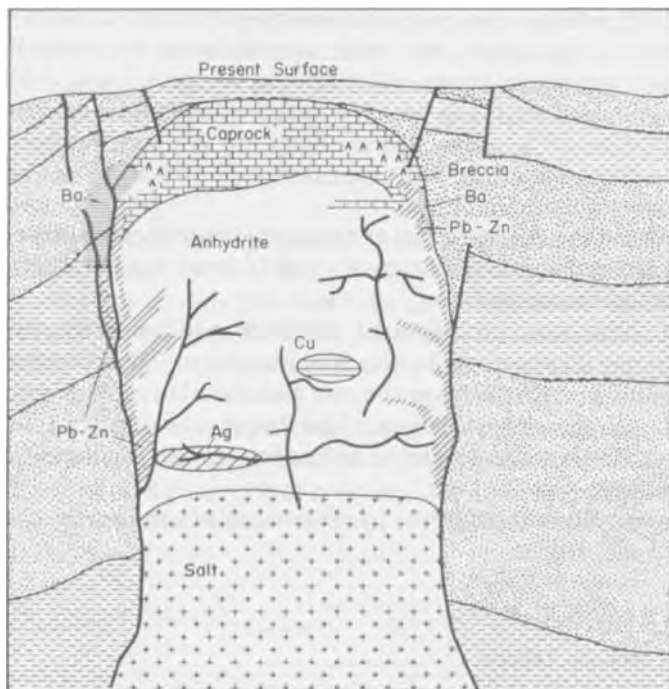


Fig. 1-20. Schematic diagram showing location of lead – zinc, copper, barium, and silver mineralization, and structural patterns, Hockley salt dome, Harris County, Texas. (Modified from Price et al., 1983.)

and Zn over 6 m intervals with total sulfide content as high as 50 wt.% (Price et al., 1983). Sulfides, barite, celestite, sulfur and other exotic minerals have been reported from 13 other domes (Kyle and Price, 1986).

Post-diapir stage

Once the diapir reaches depths less than approximately 600 m, there is no further upward movement due to buoyancy (e.g., Seni and Jackson, 1983a). During this period of relative tectonic stability, the diapir may undergo continued dissolution of halite by ambient meteoric fluids if the cap rock remains permeable (e.g., Knauth et al., 1980). Processes which are important during this stage include the hydration of anhydrite to gypsum, which should release trace elements such as Sr^{2+} and Ba^{2+} (Fig. 1-18).

Kreitler and Dutton (1983) suggested that there are two end members of salt domes within the Gulf and East Texas basins based on timing and type of cap rock which they contain. One end member, typified by the Gyp Hill dome in south Texas, consists of a gypsum-rich cap rock which contains no calcite. Non-deformed residual anhydrite developed relatively late in the diapiric stage by a low-temperature, low-salinity fluid. Soon after this accumulation of anhydrite, the cap rock was infiltrated by meteoric fluids which were within the gypsum stability field and anhydrite was rehydrated to gypsum. Because of the relatively poor anhydrite

zone developed late in the history of diapirism, extensive dissolution of halite is still occurring at the anhydrite – halite boundary.

In contrast to Gyp Hill, the Oakwood salt dome in the East Texas basin developed a residual anhydrite cap rock very early in its diapiric stage, within a hot, saline, high-pressure environment. Extensive calcite within the upper part of the cap rock developed in two stages, as hydrocarbon-rich, saline, deep basinal brines migrated through the upper zone of anhydrite and converted anhydrite to calcite. Recent meteoric groundwater has precipitated gypsum within the transition zone of the cap rock. Because of the early development of cap rock, however, there is no evidence of active halite dissolution by meteoric fluids.

Differences in the diagenetic histories of salt diapirs in different parts of the Gulf basin may be extremely important in explaining the regional differences in the composition of both basinal brines and meteoric fluids.

Diagenesis of anhydrite- and gypsum-bearing units

Anhydrite- and gypsum-bearing Mesozoic units other than the Louann Salt have undergone a number of diagenetic reactions including: (1) gypsum – anhydrite transformation; (2) dissolution of gypsum and anhydrite; (3) deformation and recrystallization of anhydrite and gypsum; (4) reprecipitation of sulfate minerals; and (5) rehydration of anhydrite to form gypsum.

Throughout their burial history, anhydrite and gypsum within these units have undergone dissolution. Because these sediments were deposited within very shallow subtidal and supratidal environments, some have been subjected to meteoric diagenesis during early eustatic lowering of sea level. Extensive dissolution of evaporites is evidenced by the development of large zones of solution – collapse breccias within Cretaceous units, such as the Fort Terrett Formation (Rose, 1972) and Jurassic evaporites in northeastern Mexico.

Precipitation of anhydrite within these units is an effective mechanism for sealing hydrocarbon reservoirs in the Smackover and Buckner formations. Harris and Dodman (1982) distinguished two stages of anhydrite cementation. They attributed early anhydrite cements to lateral movement of brines from the anhydrite-rich Buckner Formation into the Smackover Formation. The later stage of anhydrite precipitation in the Smackover was attributed to brines moving up fracture conduits from the underlying Louann Formation.

MESOZOIC ROCKS

Facies and diagenesis of carbonate rocks

Following Louann Salt deposition, carbonate deposits accumulated in the basin throughout most of Mesozoic time. Late Jurassic and lower Cretaceous shelf- and shallow-ramp deposits were periodically interrupted by relatively mature clastic wedges, especially concentrated in the East Texas embayment. Restricted conditions on the shelves resulted in minor evaporite deposition and moderately extensive (but

not pervasive) dolomitization. Basinal facies include organic-rich (anoxic?) units and variable amounts of fine-grained terrigenous detritus. Following exposure in the mid-Cretaceous, chalks and marls exceeding 1 km thickness in the basin center draped the previous deposits.

Because of economic potential, the Jurassic Smackover and Cretaceous Pearsall – Glen Rose – Edwards formations have received the most extensive study. The Austin Chalk has also been studied to some extent.

The diagenesis of the Mesozoic units proceeded in three stages, all of which may not have affected all formations at all locations. Nearly all the up-dip, shelf deposits experienced extensive meteoric diagenesis following a marine and/or hypersaline depositional and early diagenetic phase. In places, meteoric recharge occurred essentially contemporaneously with deposition as shoaling-upward cycles prograded across the subsiding shelf (e.g., Mueller, 1975). Early meteoric influx also dissolved previously deposited evaporites, creating solution – collapse breccias, and induced the replacement of evaporite-related dolomite by more stable, limpid phases. Extensive meteoric diagenesis may also have taken place during the mid-Cretaceous sea-level lowering, when the shelf and shelf margin were extensively exposed. It is not clear for all stratigraphic units whether contemporaneous, local, meteoric processes or regional alteration at the time of mid-Cretaceous sea-level lowering dominated the diagenesis of the rocks. The depth of penetration of meteoric diagenesis during the Lower Cretaceous lowstand is unknown. Rocks known to have been affected by early meteoric processes include the updip Smackover Formation (Moore and Druckman, 1981) and Lower Cretaceous shelf- and shelf-margin deposits (Loucks, 1976; Lohman and Moldovany, 1984; Prezbindowski, 1985).

Most of the less permeable units and the down-dip ramp facies did not experience extensive, dynamic, meteoric alteration. Most authors have attributed the diagenesis of these rocks to alteration in predominately marine-pore fluids, similar to the alteration observed by Saller (1984) in the borings of Enewetak atoll. Moore and Druckman (1981) presented the most compelling case for extensive burial alteration in the absence of meteoric water, although Wagner and Matthews (1984) do not agree. Limestones which had previously experienced meteoric diagenesis also continued to be altered (stylolitized and cemented) during early burial, and Prezbindowski (1985) estimated that ~20% of the alteration of the Stuart City shelf margin took place during early burial in a partly closed, “rock-dominated” system.

The final diagenetic event, which in part is probably still active, affects virtually all the subsurface units irrespective of lithology. Because no uplift has occurred in the Gulf, the late diagenetic assemblage of processes is restricted to the subsurface. Late cements include Fe-calcite, ankerite (rarely Fe-dolomite), anhydrite, quartz, kaolinite, barite, celestite, albite, and rarely galena and sphalerite (Moore and Druckman, 1981; Woronick and Land, 1985). These phases have clearly been emplaced by fluids not too different from the fluids present in some of the Mesozoic formations today. “Out-of-the-basin” fluid movement is implied, with the precipitation of cements being driven not only by temperature decrease but by CO₂ loss and sulfate reduction as well (Woronick and Land, 1985; Lundegard and Land, 1986). Replacement reactions such as dedolomitization, albitization, and kaolinization also occur as the sodium-rich, magnesium-depleted, acid fluids move progressively updip.

In some respects, the late-stage burial diagenesis of the carbonates resembles that of the sandstones, reflecting the fact that less stratigraphic control is exerted on fluid movement as the rock section becomes less permeable and more homogeneous. Because carbonate units lose permeability early in their history as a result of early meteoric alteration and early burial solution – compaction, they do not exhibit the massive clay and carbonate cementation seen in the sandstones which had higher permeabilities during early burial. Although late-burial diagenesis of both sandstones and carbonates involves similar phases, late-burial cementation is a relatively minor volumetric process in the Gulf Coast carbonates which have been studied. Most Gulf Coast carbonates were altered diagenetically early in their burial history when meteoric water was able to affect them, and during early solution – compaction in nearly static, marine-derived, pore fluids.

Facies and diagenesis of sandstone

Diagenetic studies of Mesozoic sandstones in the Gulf Coast have focussed primarily on three stratigraphic units: (1) the Middle Jurassic Norphlet Formation; (2) the Upper Jurassic and Lower Cretaceous Cotton Valley (Schuler) and Travis Peak (Hosston) formations; and (3) the Upper Cretaceous Woodbine and Tuscaloosa formations. The oldest of these sandstones, the Norphlet, was deposited on the Louann Salt and is thickest in the northeastern Gulf Coast from Louisiana to Florida; it is overlain by dolomite and evaporites of the Smackover Formation. The Norphlet Formation includes eolian, fluvial, and marine facies. It has an average composition of 77% quartz, 16% feldspar, and 7% rock fragments in Mississippi (McBride, 1981), but contains more rock fragments in Alabama (Pepper, 1982). According to McBride (1981) and Honda and McBride (1981), the earliest diagenetic events in the Norphlet sandstone were the formation of illite grain coatings followed by the precipitation of calcite, anhydrite, and quartz cements at a shallow depth of burial. Halite cement formed upon deeper burial, and, subsequently, feldspar grains (chiefly plagioclase), volcanic rock fragments, and some of the anhydrite and calcite cements were dissolved. Unlike deeply buried Cenozoic sandstones in the Gulf basin, however, K-feldspar has resisted wholesale dissolution, probably because of the stabilizing influence of K-rich brines. The dissolution stage was probably related to oil generation and the production of organic acids and CO₂ (Honda and McBride, 1981). Dolomitization and precipitation of abundant authigenic illite followed de-cementation. The latest diagenetic events were continued precipitation of illite, the formation of ankerite, and stylolitization. The Norphlet Formation locally retains porosities of 10–14% despite burial to depths up to 5600 m. Much of this porosity is microporosity within illite cement; thus, permeability is relatively low, 0.1–5.0 mD.

The Cotton Valley and Travis Peak sandstones form a thick siliciclastic section of shallow marine and fluvial-to-deltaic deposits that accumulated during the time interval that spanned the Jurassic – Cretaceous boundary. Cotton Valley sandstones have an average composition of 81% quartz, 8% feldspar, and 11% rock fragments (Bailey, 1983), and Travis Peak sandstones have a composition of approximately 95% quartz, 4% feldspar, and 1% rock fragments (Dutton, 1985, 1986). Wescott

(1983) has described the following diagenetic sequence in the very fine-grained quartzarenites and subarkoses of the Cotton Valley sandstones in the East Texas basin: (1) development of clay coats on detrital grains; (2) precipitation of quartz overgrowths; (3) dissolution of unstable grains, primarily feldspars, and precipitation of illite and chlorite; and (4) precipitation of calcite pore-filling and grain-replacing cements. Ankerite also formed as a late-stage cement in Cotton Valley sandstones described by Hall et al. (1984). Plagioclase feldspars have been albitized to varying degrees (Dunay, 1981).

Bailey (1983) reported a similar diagenetic history in Cotton Valley sandstones in East Texas, with the following differences: (1) the earliest cement in many sandstones is poikilotopic calcite; (2) plagioclase overgrowths developed prior to quartz cementation; (3) dolomite and ferroan calcite precipitated after quartz; and (4) following carbonate precipitation, pressure solution dissolved quartz grains and formed illite-lined stylolites. Dissolution of carbonate cement created secondary porosity within the Cotton Valley sandstones. Present porosity averages 7% but ranges from 2 to 16% (porosimeter values; Bailey, 1983).

All of the authigenic phases that occur in the Cotton Valley sandstones have also been observed in the overlying Travis Peak Formation in the East Texas basin (Dutton, 1985). Quartz cementation has been extensive, and ankerite, illite and chlorite cements are common. Much of the pore space is lined or filled by solid bitumen. Thomson (1978) and Fielder et al. (1985) described the Hosston Formation (Travis Peak equivalent) in Mississippi as a quartz-rich sandstone with little feldspar (all plagioclase) and few or no rock fragments. The diagenetic sequence reported by Fielder et al. (1985) is facies-dependent, but quartz and calcite are dominant cements. Thomson (1978) interpreted quartz cement to have formed at depths of 1800 m or more.

The third Mesozoic sandstone the diagenetic history of which has been studied is the Upper Cretaceous Tuscaloosa sandstone in Louisiana and Mississippi. The Tuscaloosa is a sublitharenite and litharenite that contains sedimentary, volcanic, and metamorphic rock fragments (Thomson, 1979; Dahl, 1984). Chlorite rims, the earliest cement, formed as a result of intrastratal solution of volcanic and basic igneous rock fragments (Thomson, 1979; Dahl, 1984; Larese et al., 1984). Chlorite $\delta^{18}\text{O}$ ranges from +12.2 to +15.4 ‰ and chlorite δD ranges from -54 to -36 ‰; these isotopic values are interpreted to indicate that chlorite precipitated from a mixed solution of sea water and fresh water in a cool, shallow-burial environment (Suchecki, 1983, 1984). Porosity in the Tuscaloosa sandstone is as high as 25% at depths of 6100 m, and the preservation of abundant primary porosity has been attributed to the presence of the thick, early chlorite rims (Thomson, 1979; Dahl, 1984; Larese et al., 1984). The importance of secondary porosity is emphasized by Smith (1985).

Calcite and then kaolinite cements precipitated after chlorite. In the shallow Mississippi Salt Province, the kaolinite precipitated from water derived from meteoric sources, but kaolinite in the deep Tuscaloosa Trend precipitated from water derived from shales following the smectite-to-illite transformation (Suchecki, 1984). Increasing burial resulted in pressure solution and quartz cementation (Dahl, 1984). Ankerite formed as a late-stage, pore-filling cement and also replaced calcite.

Summary

Following deposition of the Louann Salt, carbonate deposits accumulated throughout most of Mesozoic time. Late Jurassic and Early Cretaceous shelf- and shallow-ramp deposits (extensively dolomitized) were periodically interrupted by clastic wedges with relatively mature sandstones. Following exposure in the mid-Cretaceous, chalks and marls draped the earlier deposits. Diagenesis of the carbonates proceeded in three stages: (1) marine and/or hypersaline diagenesis; (2) meteoric diagenesis soon after deposition; and (3) late burial diagenesis that includes the formation of Fe-calcite, ankerite, anhydrite, quartz, kaolinite, barite, celestite, albite, and rarely galena and sphalerite cements and replacement minerals. During stage 2, evaporites were lost by dissolution and collapse breccias developed.

Three major sandstone units have somewhat diverse diagenetic histories. Brines from the Louann Salt invaded the overlying Middle Jurassic Norphlet sandstones to preserve K-feldspar even to depths greater than 5000 m and form local halite cement. The Upper Jurassic and Lower Cretaceous Cotton Valley sandstones show complex diagenetic histories but are dominated by quartz, dolomite, and ferroan calcite cements. The Upper Cretaceous Tuscaloosa sandstone in Louisiana and Mississippi has exceptionally thick and locally abundant chlorite coats that probably inhibited cementation by quartz. Porosity as high as 25% is present at depths of 6100 m. Calcite and kaolinite are other diagenetic phases. Isotopic data on quartz cement from all three formations have been interpreted as evidence of hydrothermal circulation of meteoric water during early burial, probably driven by heat flow in the recently rifted basin (Dutton, 1986; McBride et al., 1987; Suchecki, 1983).

CENOZOIC SEDIMENTS AND ROCKS

Composition of sands and sandstones

In general, Cenozoic sands and sandstones in the Gulf of Mexico Basin are lithic arkoses and feldspathic litharenites (classification of Folk, 1980). Figure 1-21 sum-

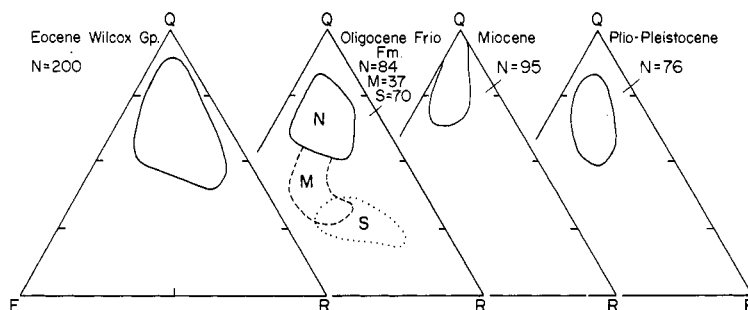


Fig. 1-21. QFR plot for four stratigraphic units of the Gulf Coast Tertiary. Wilcox data are from Loucks et al. (1979), Frio data are from Bebout et al. (1978), Miocene data are from Gold (1984), and Plio-Pleistocene data are from Milliken (1985). For the Frio Plot, N, M and S refer to the number of samples in the northern part, middle part, and southern part of the Texas Gulf Coast, respectively.

marizes the quartz – feldspar – rock fragment proportions that have been reported for subsurface Cenozoic units along the Texas – Louisiana coastal area. Except for very quartz-poor compositions of Oligocene sandstones in southern Texas and of some quartz-rich Miocene sandstones in southeastern Louisiana, most samples in all units contain between 50 and 75% quartz and nearly equal proportions of rock fragments and feldspar. Volcanic rock fragments dominate in central and southern Texas, and metamorphic fragments increase in dominance northeastward (Loucks et al., 1979), but the differences are not great. Thus, systematic differences in diagenesis between Cenozoic units cannot be ascribed solely to differences in primary detrital framework composition.

Syngenetic and telogenetic features

Burial diagenesis and its related features – physical compaction, cementation, grain and cement leaching, and grain alteration – have received the most attention in the Gulf basin. Nearly all Mesozoic and Cenozoic rocks lie at depths sufficient for burial-related diagenetic processes to have dominated their diagenetic history. A review of syndiagenetic and telogenetic features that have been recognized at least locally within the shallow, fringing sediments of the basin, however, is worthwhile. Examination of rocks which have never been deeply buried helps to complete the picture of diagenetic phenomena that determine the petrophysical properties and even bulk composition of the basin fill. Further, it is important to differentiate the early and/or meteoric features from the overprint of burial diagenesis.

Recent studies of mineralogy and diagenetic features of shallow Cenozoic rocks have focussed on alteration phenomena that are related to epigenetic sandstone uranium deposits (Galloway and Kaiser, 1980; Galloway, 1982). In addition, a variety of syndiagenetic features, similar to those documented by Walker et al. (1978), have been noted as follows:

(1) *Clay cutans*. Mechanically infiltrated clay particles and colloidal aluminosilicates may form discontinuous to continuous coats around framework sand grains (Fig. 1-22A, B). Cutans are formed primarily by downward percolation of clay and colloidal materials produced by the reactions of shallow ground water with unstable detritus. They are best developed within units such as the Catahoula – Frio, which contain abundant first-cycle volcanogenic sediment.

(2) *Authigenic clay rims and grain replacements*. Intensely weathered sandstones, particularly those associated with a humid paleoclimate, show replacement of feldspar and muscovite grains by kaolinite, commonly accompanied by the precipitation of kaolinite cement.

(3) *Limonite and pyrite*. Redox reactions involving iron result in locally abundant oxyhydroxide (which has dehydrated with age to form hematite). In reducing environments, minor amounts of early iron sulfide also form (cf. Reynolds et al., 1982).

(4) *Pedogenic carbonate*. Local redistribution or precipitation of carbonate in soil-forming environments (caliche) produces micritic cement, grain replacement, and sparry-calcite pore fill.

(5) *Shallow meteoric flux and pedogenesis*. Local leaching of feldspar, volcanic

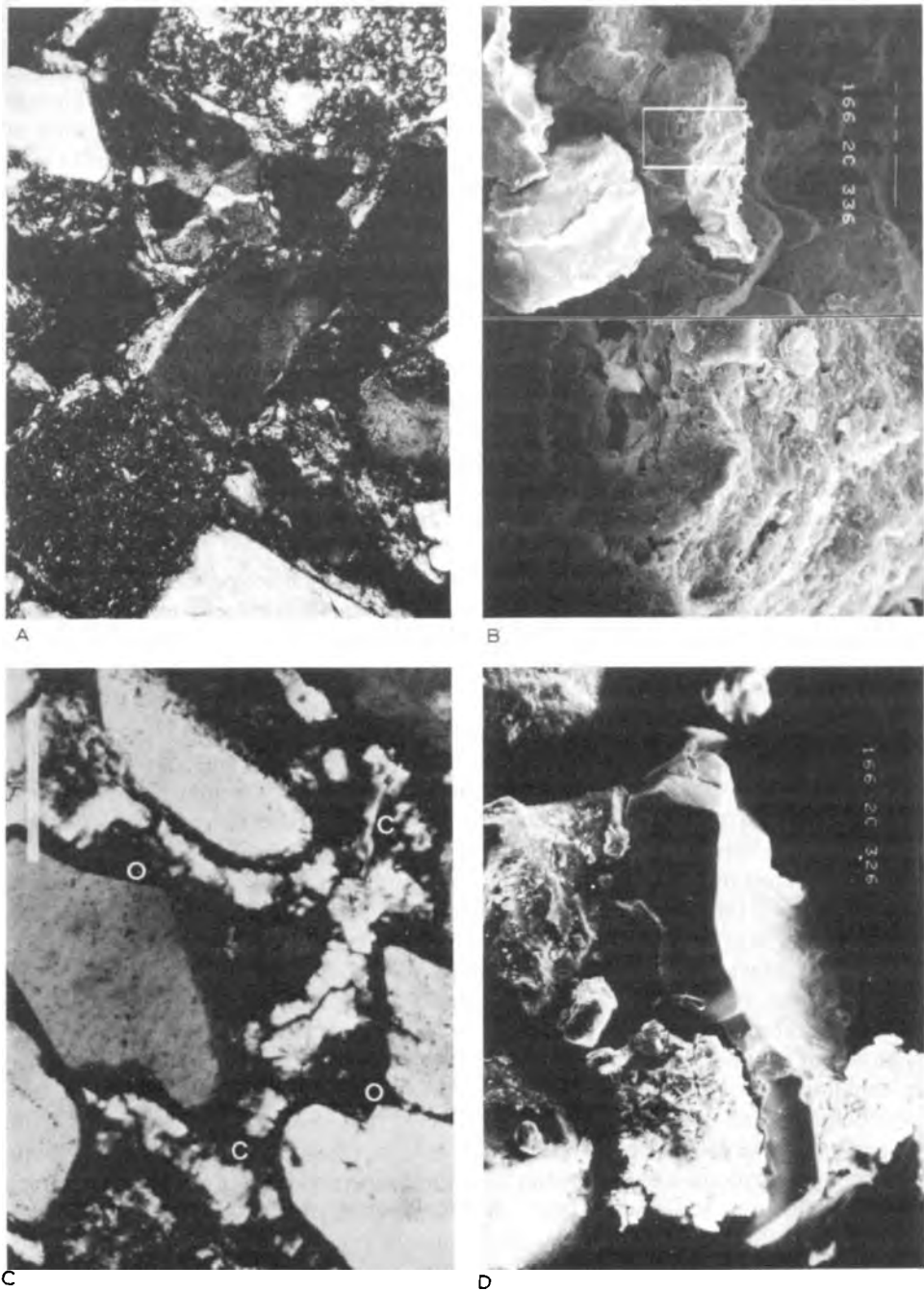


Fig. 1-22. Typical syngenetic (A and B) and telogenetic (C and D) features of Gulf Cenozoic sandstones. (A) Smectite cutans. Crossed polars. Catahoula Formation, Live Oak County. (B) Mechanically infiltrated clay coats and enlargement of partially leached feldspar. Oakville Sandstone, Live Oak County. (C) Opal rim and chalcedony pore fill. Oakville Sandstone, McMullen County. (D) Calcite spar pore fill. Clay coats are present on framework grains. Oakville Sandstone, Live Oak County.

rock fragments, micas, and possibly some heavy minerals occurs as a result of shallow meteoric flux and pedogenesis.

Telogenetic alteration of shallow, basin-fringing aquifers has also been well documented by uranium genesis studies (summarized in Galloway, 1982). Though primarily a shallow process, it is important to note that the active circulation of meteoric water extends to depths exceeding 1 km in the most permeable Gulf Coast aquifers, and that evidence exists for meteoric alteration of oil pools and formation waters to depths exceeding 2 km (Galloway et al., 1982a; Fisher, 1982). Recognized products of telogenesis include:

(1) *Surficial silicification*. Opal and chalcedony cements locally indurate Tertiary sandstones along their outcrop belt. A typical manifestation, consisting of opaline grain coats and pore-filling chalcedony, is shown in Fig. 1-22C. Silicification appears to be associated with outcrop silicretization in the semiarid western Gulf margin, and rarely, precipitation from high-pressure gas seeps (Lindemann, 1963).

(2) *Oxidation – reduction of iron minerals*. The interplay of oxidizing meteoric ground water with the syngenetic and post-depositional pyrite in reduced aquifers has produced volumetrically minor but economically important amounts of diagenetic limonite and pyrite – marcasite. Sulfide or iron oxyhydroxide content rarely exceeds 1% by volume (Galloway, 1982).

(3) *Sparry calcite pore fill*. Minor volumes of sandstone are pervasively cemented with pore-filling sparry calcite (Fig. 1-22D), which locally replaces framework grains and mud matrix. Some samples of the calcite are depleted in ^{13}C , suggesting oxidation of upward-migrating methane or liquid hydrocarbons as an important source of carbon (Galloway, 1982).

(4) *Grain leaching, locally accompanied by zeolite or kaolinite precipitation*. Active meteoric circulation resulted in leaching of silicate grains. In addition to feldspars, micas, rock fragments, and carbonate fossils, volcanic glass, which is locally abundant in parts of the Cenozoic section, is readily leached. Geochemical evolution of downward-flowing ground water in ash-rich aquifers leads to sequential precipitation of authigenic smectite coats and pore-filling clinoptilolite cement (McBride et al., 1968; Walton, 1975; Galloway and Kaiser, 1980). In eastern Texas, where rainfall is greater than in central and southern Texas, kaolinite is a common alteration product of feldspar and muscovite. Feldspars in places develop kaolinite pseudomorphs. Some replaced feldspars and all replaced micas, however, show grain expansion.

Although shallow syngenetic or telogenetic processes typically dominate only in the shallow Cenozoic section of the northwestern Gulf Coast Basin, they nonetheless define important diagenetic systems that should be distinguished from the pervasive overprint of burial diagenesis. Furthermore, the sequence of evolving and mixing hydrologic systems within the thin basin-rim aquifers has led to complex diagenetic histories (Galloway, 1982; Goldhaber et al., 1983). For example, Fig. 1-23 schematically illustrates the diagenetic history of a tuffaceous Oligocene sandstone that hosted a uranium deposit. Following deposition in a fluvial environment, pedogenic alteration of finest glass resulted in accumulation of colloidal aluminosilicates as clay coats. Recurrent flushing by meteoric and deep-formation waters caused repeated reduction and oxidation accompanied by uranium

mineralization. Calcite precipitation, leaching of coarse glass shards, and precipitation of clinoptilolite in primary and secondary pores in an open meteoric flow system completed the diagenetic scenario.

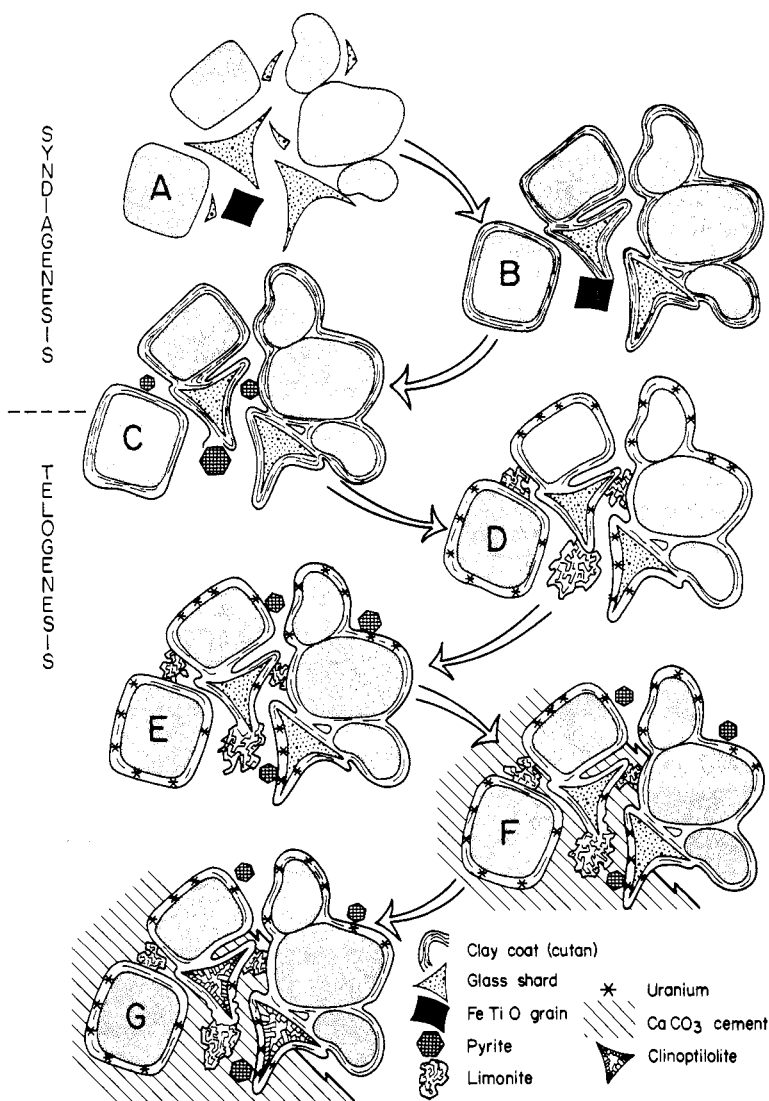


Fig. 1-23. Complex diagenetic history of a shallow, tuffaceous aquifer sandstone, Catahoula Formation, Live Oak County. (A) Deposition of framework grains. (B) Pedogenesis. (C) Reduction. (D) Uranium mineralization and oxidation. (E) Re-reduction. (F) Calcite precipitation. (G) Open-hydrologic-system leaching and zeolite authigenesis. (Modified from Galloway and Kaiser, 1980.)

Table 1-1

Summary of various diagenetic aspects of Gulf Coast sandstones

Age/unit	Q:F:R*	Major cements	Depth (ft) of impt. qtz cmt.	$\delta^{18}\text{O}$ qtz cmt.	Depth (ft) of impt. carb cmt.	Detrital plag. composition	Depth (ft) impt. albitization	Temp (°C) impt. albitization	Depth (ft) K-feld loss	Temp (°C) K-feld loss	Depth (ft) of impt. dissol'n
Plio-Pleistocene	65:18:17	(Cal, Qtz)	—	—	—	An ₂₅	>12,000	>100	>17,000	>120	?
Miocene	83:9:8 (variable)	Cal, Qtz, Kaol	>15,000	+34	variable	An ₁₅	12,000–20,000	100–150	>17,000	>120	12,000–17,000
Oligocene:	25:30:45	Cal, qtz,	8000–	+31	~7000	An ₂₃	7500–	110–150	>12,000	>130	10,000–
Frio Fm.	to 65:20:15	Kaol	10,000				14,000				12,000
Eocene	65:15:20	Ank, Qtz,	6000–	+25	~5000	An ₆₋₈	7500–	120–150	>7500	>100	6000–
Wilcox Fm.	(variable)	Kaol	8000				10,000				10,000
Cretaceous:	90:0:10	Qtz, Ank,	?	14–17	?	?	?	?	?	?	?
Tuscaloosa Fm.		Cal, Chl									
Jurassic:	84:8:8	Qtz, Dol,	<8000	+20	<6000	?	<8000	120	7000	80	<8000
Cotton Valley		Feld, Chl									
Jurassic:	75:15:10	Qtz, Hal	?	+18	?	None left	<16,000	?	No signif. loss		?
Norphlet (Miss.)		Anhy, Carb									

* Q = quartz, F = feldspar, R = rock fragments.

For sources of data: see references cited in text. Cements: Cal = calcite, Qtz = quartz, Kaol = kaolinite, Hal = halite, Dol = dolomite, Anhy = anhydrite, Carb = unspecified carbonates, Chl = chlorite; Anhy = anhydrite; cements underlined are dominant; cements in parentheses are minor. Other abbreviations: impt. = important; cmt. = cement; K-feld = K-feldspar; dissol'n = dissolution.

Burial diagenetic features

Introduction

Sandstones of the paralic depositional systems and continental margin depocenters are rapidly buried below the depths of surficial influence. Processes of burial diagenesis, operating in an environment of increasing temperature and pressure and of basinal fluid circulation systems, determine ultimate sandstone composition and physical properties.

Albitization

Incipient to complete replacement of Ca-plagioclase grains by authigenic albite has been documented in the deeper-buried part of each of the four major clastic wedges in the Gulf of Mexico Basin (Land and Milliken, 1981; Boles, 1982; Fisher, 1982; Land, 1984; Gold, 1984, 1987; Milliken, 1985). Table 1-1 summarizes depths, temperatures, and other conditions under which this volumetrically important reaction takes place. Although the depth to the first occurrence of albitized plagioclase differs significantly between units of different ages, the reaction nonetheless begins between 100° and 120°C in all units. Some albitization commences at lower



Fig. 1-24. Photomicrographs of albitization. Grain in center is a porous albitized plagioclase that has tiny euhedral overgrowths of albite (arrows) developed on parts of it. *Q* = quartz overgrowths. Miocene sandstone, Louisiana; depth = 6100 m.

temperatures in sands containing relatively more calcic detrital plagioclase. Temperature of albite formation, estimated by considering observed depths of albitization, together with albite oxygen isotopic compositions, suggests that albitization took place in water enriched in ^{18}O within the overpressured regime (Land and Milliken, 1981; Fisher, 1982; Gold, 1984).

Thin-section and SEM observations indicate that albitization proceeds through a dissolution–reprecipitation mechanism, and not by a solid-state diffusion process (Fig. 1-24). Petrographic information suggests that plagioclase is preferentially replaced by albite, whereas, in contrast, most potassium feldspar dissolves (Land and Milliken, 1981; Gold, 1984, 1985; Milliken, 1985).

Carbonate replacement

Replacement of grains, mostly feldspars but also rock fragments, by carbonate is observed over a wide range of depths in Eocene and Oligocene units of the Texas Gulf Coast (Lindquist, 1976; Stanton, 1977; Loucks et al., 1977, 1979, 1984). “Ghosts” marked by relict grain outlines and remnant portions of feldspar provide evidence that some large patches of carbonate (most commonly calcite) occupy spaces formerly filled by detrital grains. Alternatively, such textures could be interpreted as carbonate cement filling secondary intragranular pores within partially dissolved grains. It is, therefore, difficult to assess the importance of carbonate grain replacements in Gulf Coast Tertiary deposits except where “dust lines”, visible in thin section, outline replaced grains.

Kaolinite replacement

Kaolinite (and possibly its polymorph dickite) replaces parts of and, locally, entire grains of feldspar, muscovite, and biotite in some samples. Replacement is common in outcrop and at shallow depths, where it is related to meteoric-water alteration, but it is present throughout the section.

Grain dissolution

Feldspars. Both plagioclase and potassium feldspar have undergone dissolution in all Gulf Coast Cenozoic units (Lindquist, 1976; Stanton, 1977; McBride, 1977; Loucks et al., 1979; Land and Milliken, 1981; Fisher, 1982; Land, 1984; Milliken, 1985; Gold, 1987). At temperatures above 100°C , dissolution of potassium feldspar proceeds, with time, nearly to completion, leaving albite as the only feldspar. Dissolution of plagioclase, on the other hand, is generally minor though locally significant.

Other detrital grains. Opaque and nonopaque detrital heavy minerals also have undergone dissolution in Cenozoic sandstones of the Gulf Coast. Assemblages of detrital heavy minerals in subsurface Eocene and Oligocene units are generally quite simple (zircon + tourmaline) in comparison to those in equivalent sediments in outcrop and also in contrast to the more complex heavy-mineral associations observed in Miocene and younger rocks of the Louisiana shelf (amphibole + pyroxene + epidote + others). These differences result primarily from a progressive subsurface dissolution of the more unstable heavy minerals with increasing burial depth (Milliken, 1984).

Other grains that show partial to almost complete dissolution in some formations include carbonate skeletal grains, biotite, muscovite, glauconite, and volcanic and metamorphic rock fragments.

Pressure solution. In contrast with Mesozoic sandstones, Cenozoic sandstones show only minor pressure solution effects among silicate grains. Pressure solution begins at 2 km in the Wilcox Formation but at greater depths in younger rocks. Carbonate rock fragments and fossils show extensive pressure solution in some rocks at shallow depths. Megascopic stylolites are rare in Cenozoic units.

Pore-filling authigenic phases

Carbonates. Carbonate minerals comprise the most abundant cements in Gulf Coast Cenozoic rocks (e.g., Lindquist, 1977; Loucks et al., 1977, 1979; Fisher, 1982; Gold, 1984). Chemistry, abundance, and depth distribution of carbonate cements vary significantly in units of different age (Land, 1984; Land and Fisher, 1987), but carbonate cement averages less than 5% of sandstones by volume.

Quartz. Quartz is the second most abundant cement in Gulf Coast Cenozoic rocks (e.g., Lindquist, 1977; Loucks et al., 1979, 1984; Fisher, 1982; Gold, 1984, 1985). In places, beds are tightly cemented by quartz, which averages less than 5% by volume. It everywhere occurs as optically continuous overgrowths on detrital quartz. Abrupt increases in the volume of quartz cement correlate strongly with the top of hard overpressure in the Tertiary section. Typically, quartz cement is found only in Cenozoic rocks hotter than 100°C, although it is common in Mesozoic sands at lower temperatures. Clays in mudrocks associated with quartz-cemented sandstones commonly show evidence of conversion of smectite to illite.

Clay minerals. Kaolinite and chlorite are the most abundant authigenic clays observed in Cenozoic sandstones of the Gulf Coast (Lindquist, 1977; Loucks et al., 1979, 1984; Fisher, 1982; Gold, 1984). Chlorite may precede or post-date quartz cement. Kaolinite typically post-dates authigenic quartz and fills secondary pores. No clear correlation exists, however, between the volume of porosity generated by framework grain dissolution and the volume of authigenic clay in a particular sample. Some kaolinite within the hydro pressured zone formed from water with a significant meteoric component.

Minor cements. Other cements and minor authigenic phases in Cenozoic sandstones include: analcite, laumontite, albite, potassium feldspar, illite, mixed-layer clay, sphalerite, sphene, barite, pyrite, and tourmaline. These cements are localized in their occurrence and, with the exception of laumontite, are also present in amounts much less than one percent by volume of the rock. Sphalerite, sphene, barite, and pyrite locally replace detrital grains in addition to filling pores. In general, these "exotic" phases are present in deeper, hotter portions of the section, typically below 3 km.

Summary

Cenozoic sandstones are, in general, fairly similar in composition. Most contain between 50 and 75% quartz and nearly equal amounts of feldspar and rock fragments. Differences in diagenesis cannot be ascribed solely to differences in detrital framework composition.

Syngenetic processes that are recognized in some sandstones include the development of clay cutans, authigenic clay rims and grain replacements (chiefly by kaolinite), limonite and pyrite, pedogenic calcite (caliche), and dissolution of feldspar, volcanic rock fragments, feldspar, and heavy minerals. Telogenetic processes that locally are important include surficial silicification (opal and chalcedony), oxidation/reduction of iron minerals, precipitation of sparry calcite with carbon derived from methane, grain dissolution, and precipitation of authigenic zeolite and kaolinite.

Burial diagenetic features are more widespread in the sandstones and include the following: (a) albitization at temperatures beginning at 100° – 120°C and within the overpressured regime; (b) replacement of feldspars and rock fragments by carbonate over a wide range of depths in Eocene and Oligocene units; (c) replacement of feldspar, muscovite, and biotite by kaolinite; (d) dissolution of feldspar at temperatures above 100°C – dissolution of K-feldspar proceeds essentially to completion; dissolution of plagioclase is generally minor but locally significant; (e) dissolution to various degrees of heavy minerals, skeletal grains, biotite, muscovite, glauconite, and volcanic and metamorphic rock fragments; (f) pressure solution is relatively minor, but it develops at a depth of 2 km in Wilcox sandstones and at greater depths in other rocks; and (g) pore-filling and pore-lining authigenic minerals in order of average abundance are carbonate (< 6%), quartz (< 5%), kaolinite and chlorite (both < 2%), and lesser mixed-layer clay, illite, K-feldspar, albite, pyrite, laumontite, analcite, sphene, sphalerite, barite, and tourmaline.

Organic matter

Type and abundance

Because few data are available on organic matter in Mesozoic rocks, the discussion here is restricted to the Tertiary rocks and formation waters.

Available data on the sequence of Tertiary rocks in the Gulf Coast basin indicate that the mudrocks generally contain little organic matter. Galloway et al. (1982a) reported an average of 0.28 wt.% for 140 analyses of mudrocks from the Frio Formation in Texas. The low content of organic matter in Tertiary shales is understandable in terms of their environment and rate of deposition. Most of the mudrocks sampled were deposited in prodelta or shallow-shelf environments. High sedimentation rates and oxygenated water in these settings masked and inhibited the accumulation of organic matter. While typically low, organic content of the mudrocks correlates with sedimentary facies (Fig. 1-25). Dow and Pearson (1974) showed that the lowest organic contents are in nearshore rocks, whereas the highest contents are in rocks deposited in offshore slope and rise environments.

As with the abundance of organic matter, the type of organic matter varies with sedimentary facies. In prodelta and shallow shelf mudrocks, structured terrestrial organic matter predominates. Slope and rise mudrocks contain more amorphous marine organic matter. Terrestrial organic matter is oxygen-rich and produces mainly gas, whereas marine organic matter is hydrogen-rich and is more oil-prone. Considerations of organic matter type and composition are important in studies of hydrocarbon sources and the generation of organic compounds that may interact with mineral deposits.

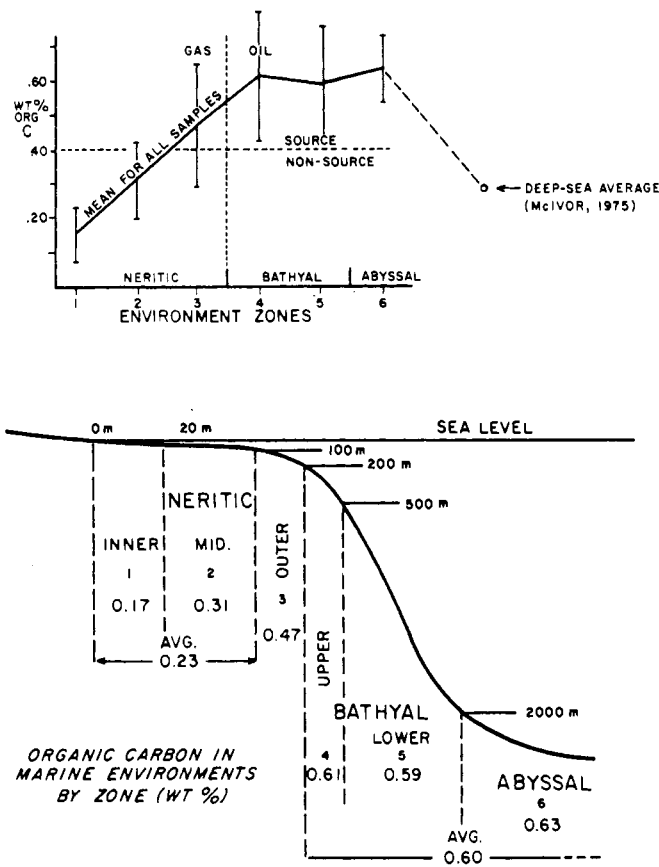


Fig. 1-25. Mean organic carbon content by environmental depth zones in the Louisiana Gulf Coast Tertiary section. (Adapted from Dow and Pearson, 1974; from Galloway et al., 1982b, fig. 20.) Figure courtesy of Texas Bureau of Economic Geology.

Maturation and migration

A strong relationship among time, temperature, and organic maturation is well displayed in the Gulf Coast Basin. Dow's (1978) classic study of organic matter maturation in offshore Louisiana shows that younger rocks must be buried to higher temperatures to achieve the same level of organic maturity as older rocks (Fig. 1-26). As a result, iso-maturity lines dip Gulfward, in the direction of sediment offlapping (Fig. 1-27).

Few studies of oil migration in the Gulf Coast Basin have been made but they have provided a useful line of evidence as to the direction and extent of fluid migration. Mapping of the top of the "oil window", the level of organic maturity at which significant oil generation begins, demonstrates clearly that vertical migration of oil has occurred. Most oil reservoirs in the Gulf are found at or above the top

of the oil window. Young et al. (1977), in a study of oil ages in the Gulf, concluded that oil has migrated a vertical distance of up to 3300 m from source rock to reservoir. Prezbindowski (1985) cited organic geochemical evidence that oil in Lower Cretaceous reservoirs of the Stuart City Trend was derived from Jurassic source rocks. If one accepts the hypothesis that oil migration depends on the movement of pore water, it is clear that further oil-source rock correlation studies will be a fruitful means of refining hydrologic and diagenetic models of the Gulf Coast Basin, especially where the timing of diagenetic events relative to hydrocarbon migration can be established.

Organic matter and rock diagenesis

Organic compounds may be involved in rock diagenesis in a variety of ways. Maturation of kerogen or oil may produce products such as carbon dioxide and organic acids that can be important proton sources for diagenetic reactions (Carothers and Kharaka, 1978, 1980; Lundegard and Land, 1986). Organic acids or

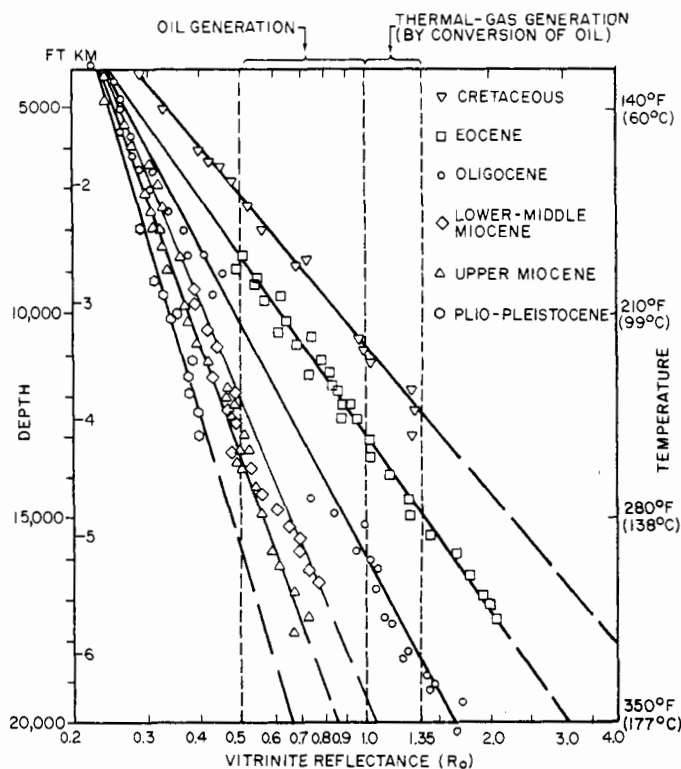


Fig. 1-26. Composite maturation profiles of two representative wells in age-defined Gulf Coast producing trends. All wells display uniform geothermal gradients close to 1.4°F per 100 ft (2.54°C per 100 m). Higher temperatures are required to achieve equivalent maturities in younger rocks compared to older ones. (Revised from Dow, 1978; from Galloway et al., 1982b, fig. 23.) Figure courtesy of Texas Bureau of Economic Geology.

other types of organic ligand may be involved in metal complexing and transport (Surdam et al., 1984; Siebert et al., 1984).

Efficient production of secondary porosity requires acid, the amount of which depends on the composition of the mineral being dissolved and, in some rocks, on the fate of the mineral's components once in solution (Lundegard and Land, 1986). Both carbon dioxide and organic acids (principally acetic) are produced during ther-

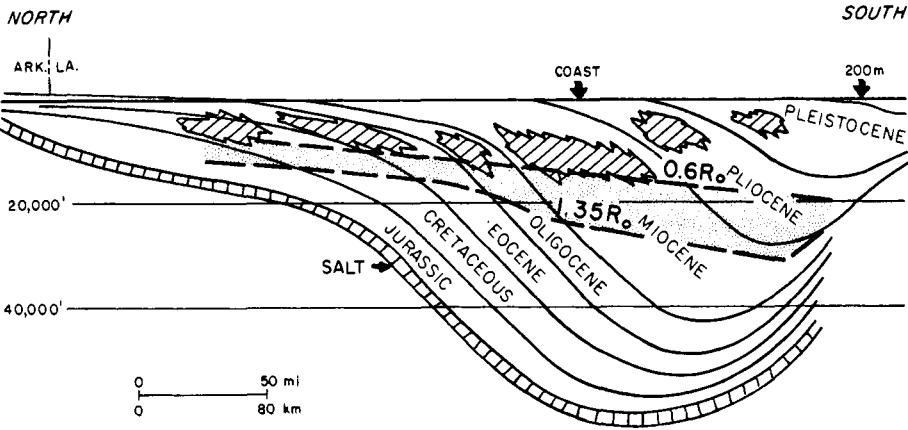


Fig. 1-27. Cross-section of the Louisiana Gulf Coast Basin showing distribution of productive intervals for oil (hachured areas) and most probable oil generation zone [measured vitrinite reflectance (R_o) between 0.6 and 1.35%]. (Modified from Dow, 1978; from Galloway et al., 1982b, fig. 16.) Figure courtesy of Texas Bureau of Economic Geology.

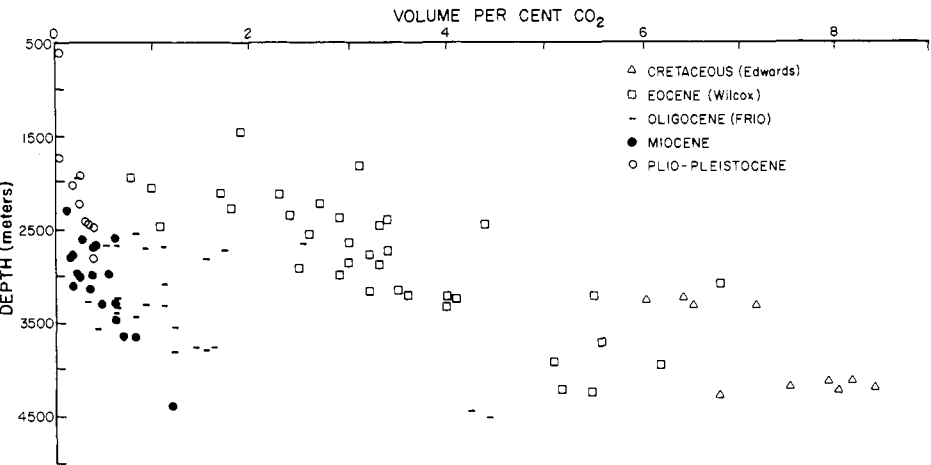


Fig. 1-28. Volume % CO₂ in natural gas from reservoirs of Cretaceous through Plio-Pleistocene age. CO₂ content increases exponentially with increasing depth in formation of all ages, and older units contain more CO₂-rich gas.

mal maturation of organic matter (Carothers and Kharaka, 1978, 1980; Lundegard, 1985), and are the most likely sources of protons for dissolution reactions (Kharaka et al., 1985; Lundegard and Land, 1986). The CO_2 content of natural gas from Gulf Coast reservoirs of Tertiary age increases with both the depth and the age of reservoirs (Fig. 1-28). Molar percentages of CO_2 range up to 15 or more in gas from some deep Wilcox reservoirs. Organic acids have maximum concentrations (up to 2500 mg l^{-1} acetate) in waters produced from reservoirs with temperatures of $80 - 100^\circ\text{C}$ (Fig. 1-29), irrespective of age.

Whereas carbon dioxide and organic acids are the most obvious proton sources for diagenetic reactions, severe material-balance problems exist if these are the only source of acid. Carbon dioxide and organic acids are produced in part by the elimination of carboxyl groups in kerogen. Estimates of the volume of porosity generated in Tertiary sandstones and shales by subsurface dissolution, however, far

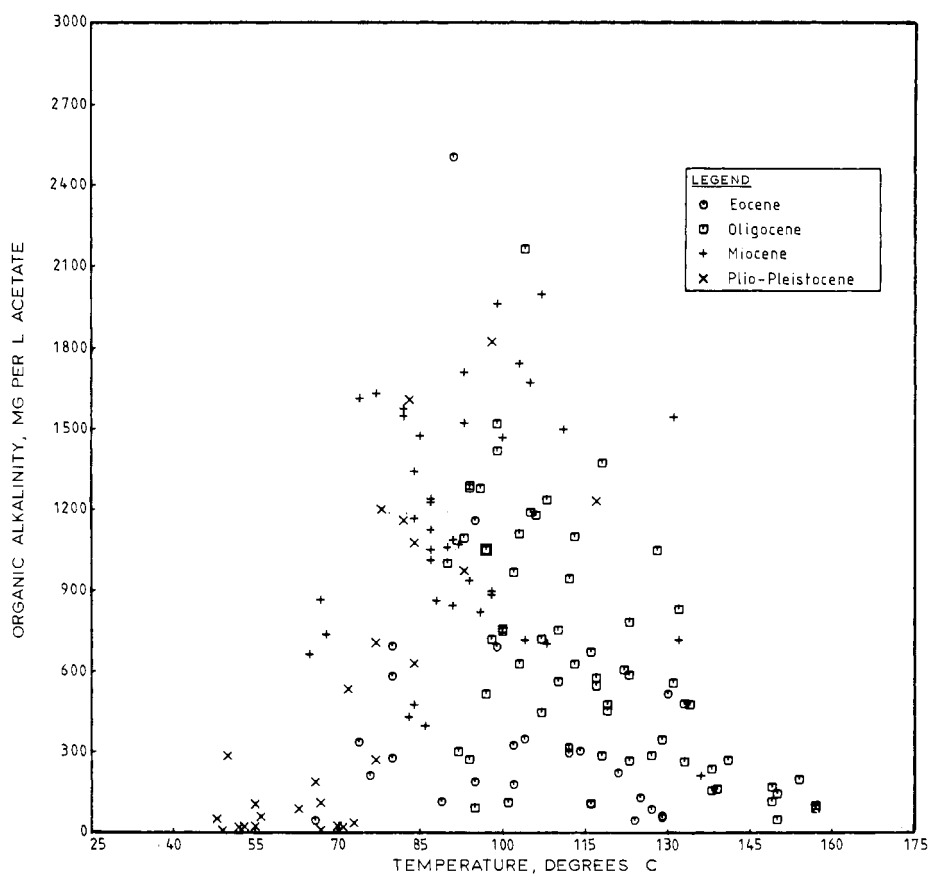


Fig. 1-29. Organic-acid concentrations in pore fluids. Organic alkalinity versus temperature for all Tertiary units. Maximum organic alkalinity in all units occurs at approximately 100°C , corresponding very closely to the maximum occurrence of liquid hydrocarbons.

exceeds that which can be explained by the elimination of carboxyl groups from the ambient kerogen to serve as acids (Lundegard et al., 1984; Lundegard and Land, 1986). Additional sources of protons by inorganic reactions are elusive. Shale diagenesis may actually consume protons (see following section). Lundegard and Land have suggested "hydrous pyrolysis" reactions between organic carbon and H_2O as a possible means of producing additional carbon dioxide or organic acids, and Morton and Land (1987) suggested that acid metamorphic fluids may be locally important.

Several water-soluble organic compounds have been suggested as being important to complex aluminum and silica in subsurface waters (Seibert et al., 1984; Surdam et al., 1984). Difunctional organic acids, particularly oxalate (Surdam et al., 1984), are known to effectively complex aluminum, but field evidence has provided virtually no support for the suggestion that these or other species are important in increasing the solubility of aluminum in the subsurface. Measurements of dissolved aluminum in Gulf Coast brines rarely exceed 1 mg l^{-1} (Kharaka et al., 1977; Morton et al., 1981), and oxalate is present only in very small concentrations (Kharaka et al., 1985). Computer modelling of aqueous ion associations suggests that organo-metallic complexes are of minor importance in metal transport by brines due to the predominance of competitive inorganic (primarily Cl^-) complexes (Kharaka et al., 1985). While invoking complexing agents to increase aluminum (or silica) solubility may be appealing because it reduces the amount of water required for diagenesis, it is not supported by available data. There is good evidence, however, that hydrocarbons may affect diagenesis by inhibiting fluid – rock interactions once they are emplaced in a reservoir.

TABLE 1-2

Average shale bulk-rock mineralogy (carbonates not included)

Wells	Anahuac and Frio fms.			Frio and Vicksburg fms.	
	CWRU No. 6	P.B. No. 2	Tx.state No. 2	D.M.L. No. 1	A.A.M. No. 3
Quartz	28	15	12	14	12
K-feldspar	2	3	1	2	1
Plagioclase	5	5	4	8	5
Total clay	65	77	83	76	82
Total	100	100	100	100	100
Illite – smectite	48	55	53	56	60
Chlorite	4	0	0	0	1
Kaolinite	12	14	23	10	9
Illite and mica	1	8	7	10	12
Total clay	65	77	83	76	82
Carbonate	3	10	7	13	13

Based on data from Hower et al. (1976) and Freed (1980a, b). See Table 1-3 for more complete well designations.

Shale diagenesis

General comments

Tertiary shales in the Gulf Coast basin typically contain 50–60% mixed-layer illite–smectite (Table 1-2). The reaction of mixed-layer clays to form ordered, slightly expandable illite–smectite is a very important diagenetic reaction, but very little is known about its exact nature, for several reasons. First, there are few published analyses of the chemistry of the clay minerals involved. Second, the thermodynamics properties of the mixed-layer clays are not accurately known. Third, variations in shale mineralogy can also be controlled by deposition. And finally, analytical errors are difficult to assess. It is difficult to unequivocally and quantitatively determine what other minerals participate in the mixed-layer clay reactions.

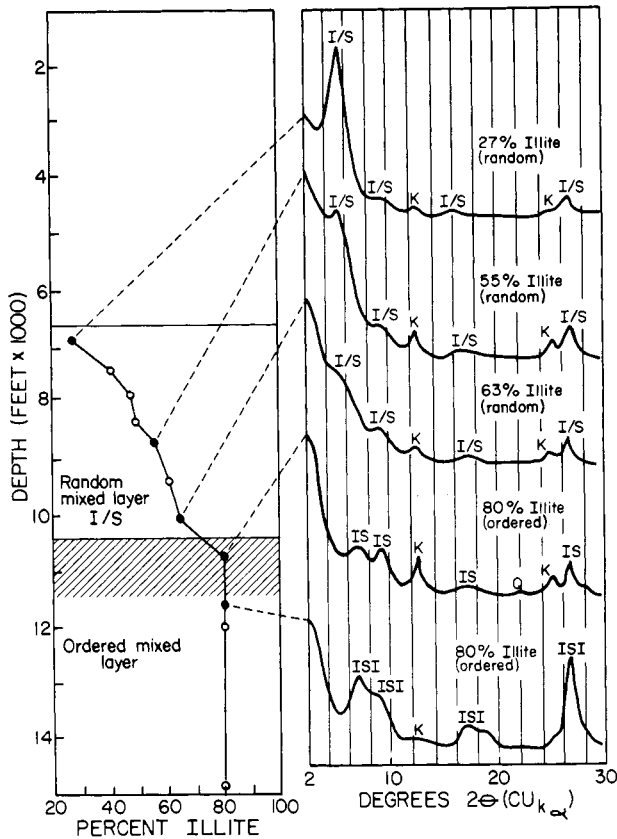


Fig. 1-30. Example of illite–smectite diagenesis. (From Perry and Hower, 1970; Well E, southeast Texas.)

Zone of illite – smectite diagenesis

Every Gulf Coast Tertiary shale sequence which has been examined displays a zone of illite – smectite diagenesis: a range of depth (and temperature) over which the nonexpandable component (“illite”) of the mixed-layer clay increases from less than 30% to more than 70%. This zone can be divided into two stages (Fig. 1-30). In the first stage, there is a gradual increase in the nonexpandable illite component at the expense of the smectite component, though the structural interlayering remains random. Once the illite component reaches about 66%, ordering of illite – smectite is evident, marking the top of the second stage. Ordering seems to take place over a relatively narrow range of depth and temperature and is recognized in X-ray diffraction patterns by the occurrence of IS or ISI superlattice peaks. After ordering develops, the clay structure may continue to change by a further increase in the illite component from 66 to 80 or even 90% along with the development of larger superlattices of the ISII type. Eventually, a depth is reached where the clay structure appears to stabilize, marking the base of the zone of illite – smectite diagenesis, though metamorphic changes must certainly occur at greater depths.

The zone of illite – smectite diagenesis and its two stages were first recognized by Burst (1969) and Perry and Hower (1970, 1972). Perry and Hower discovered that the zone spanned different depths and temperatures in different wells. As more se-

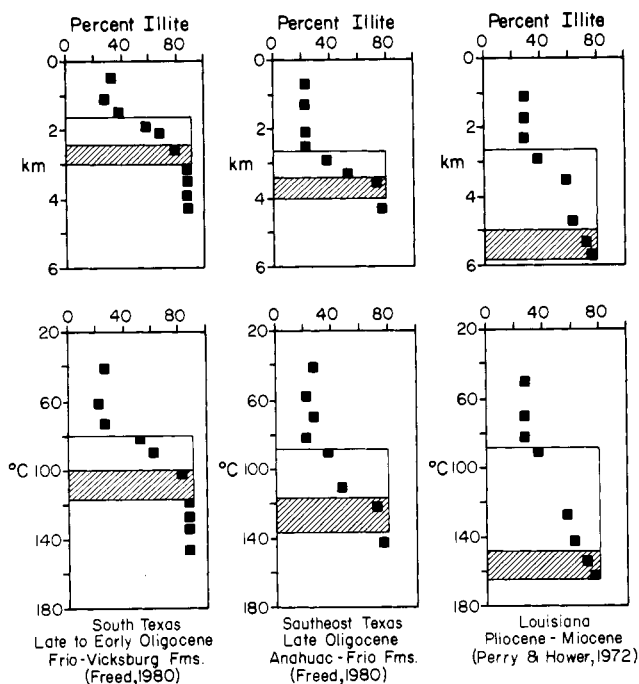


Fig. 1-31. Plots of illite content (%) in $< 0.5 \mu\text{m}$ illite – smectite versus depth and temperature. Zones of illite – smectite diagenesis are indicated by the boxes: Open box indicates random mixed-layer clay; cross-hatched box indicates ordering. (Data from Freed, 1980a, b, and Perry and Hower, 1972.)

quences were examined, further variations were discovered. The work of Foster and Custard (1980) and Bruce (1984) revealed a geographic pattern to these variations. From east to southwest along the arc of the northern Gulf Coast, the zone of illite – smectite diagenesis is found to span different temperature ranges, and ordering is found to occur at successively lower temperatures (Fig. 1-31). Two explanations for this pattern have been suggested: first, that reaction kinetics is responsible (Perry and Hower, 1972); and, second, that the pattern is due to variations in detrital mineralogy (Bruce, 1984). These two explanations are not incompatible, because the bulk chemistry of a system can affect reaction rates. Sampling to date, however, has been biased toward younger rocks in Louisiana and older rocks in Texas. Because few bulk-shale chemical data are available to compare rocks of similar age in the different areas, it is not yet possible to rigorously separate the effects of primary mineralogy differences from differences in reaction kinetics.

Nadeau et al. (1985) have shown that randomly interlayered illite – smectite is a physical mixture of smectite and illite, whereas ordered illite – smectite is, in fact, a physical mixture of extremely thin illite crystals. The size of the ordered superlattice depends on the size (along the C-axis dimension) of the illite crystals. STEM lattice images published by Lee et al. (1985) support this model. Thus, the transition from random to ordered illite – smectite appears to represent the temperature at which the smectite-stability field vanishes under the conditions of the bulk rock chemistry of the Tertiary shales of the Gulf Coast.

Bulk rock chemistry

Existing information on the bulk-rock chemistry of shale from the Gulf Coast is generally expressed as ratios to aluminum and then is averaged above and below the illite – smectite reaction zones (as defined above). These ratios are listed in Table 1-3. With reference to the Frio Formation in southeast Texas, the Fe/, Mg/, Ca/, Na/ and K/Al ratios in the CWRU No. 6 well are all larger than those in the other three wells. These differences may not be real, but could be the result of a systematic error in the Al and Si analyses of Hower et al. (1976): the reported Al_2O_3 is too low and the reported SiO_2 is too high. Although this is not important for comparing changes in the ratios above and below the illite – smectite reaction zone for that well, comparison with other wells is not possible.

Published semi-quantitative estimates of bulk-rock mineralogy above and below the illite – smectite reaction zone are summarized in Table 1-4. The data were obtained by Schultz's (1964) method on the data of Hower et al. (1976) using Freed's (1980a) method of estimating weight percent from X-ray diffraction data.

Above the illite – smectite reaction zone, the bulk rock mineralogy of the Anahuac – Frio sequences is quite similar (Table 1-4). In all wells in this area, a large decrease in calcite is observed across the reaction zone. Hower et al. (1976) argued that, because the finest fraction of calcite decreases at a shallower depth than the coarser calcite, the decrease is probably due to dissolution, and not to primary differences in sedimentary composition. If so, then such a large amount of dissolution requires a large amount of acid. The loss of calcite with depth is reflected in the decrease of Ca/Al ratios in all four wells (Table 1-3).

All similarity between the three wells ends here. With the exception of calcite, the

TABLE 1-3

Bulk-rock chemistry as ratios to Al_2O_3 averaged above and below the I-S reaction zones

	Anahuac and Frio fms. — southeast Texas									Frio and Vicksburg fms. — south Texas								
	Well E (Perry and Hower, 1970)			CWRU No. 6 Well (Hower et al., 1976)			Pleasant Bayou No. 1 Well (Freed, 1980a, b)			Texas State No. 2 Well (Freed, 1980a, b)			Dick Mortgage Loan No. 1 Well (Freed, 1980a, b)			A.A. McAllen No. 3 Well (Freed, 1980a, b)		
	above	below	Δ	above	below	Δ	above	below	Δ	above	below	Δ	above	below	Δ	above	below	Δ
SiO_2	3.74	3.45	0.29	5.12	5.19	+0.07	N.A.	N.A.		N.A.	N.A.		N.A.	N.A.		N.A.	N.A.	
Fe_2O_3	0.35	0.27	-0.08	0.44	0.39	+0.05	0.30	0.30	+0.00	0.32	0.32	+0.00	0.37	0.31	-0.06	0.37	0.37	+0.00
MgO	0.09	0.04	0.05	0.20	0.16	-0.04	0.10	0.08	-0.02	0.10	0.09	-0.01	0.15	0.15	+0.00	0.15	0.15	+0.00
CaO	0.50	0.13	-0.37	0.81	0.28	-0.67	1.20	0.10	-1.10	0.60	0.20	-0.40	0.60	0.60	+0.00	0.80	0.60	+0.20
Na_2O	0.13	0.07	-0.06	0.14	0.07	-0.07	0.12	0.10	-0.02	0.11	0.11	+0.00	0.12	0.12	+0.00	0.11	0.11	+0.00
K_2O	0.16	0.18	+0.02	0.20	0.24	+0.04	0.15	0.20	+0.05	0.16	0.16	+0.00	0.20	0.27	+0.07	0.21	0.26	+0.06

changes (or lack of changes) with depth in the mineralogy and bulk rock chemistry are distinctly different in each well.

In the CWRU No. 6 well, illite – smectite content decreases about 15% or more across the reaction zone (a loss referred to as “cannibalization” by Boles and Franks, 1979). This is balanced by a 16% increase in quartz, which appears to be diagenetic because it is not accompanied by any increase in the bulk rock Si/Al ratio. Isotopic data on the quartz (Yeh and Savin, 1977) support this conclusion. Likewise, chlorite content increases with depth by about 3%, and Fe and Mg actually decrease relative to aluminum, also suggesting that the chlorite is diagenetic. K-feldspar and coarse mica both disappear with depth. Kaolinite shows a 6% increase, which Hower et al. (1976) ascribed to deposition.

Across the reaction zone, averaged bulk-rock chemistry shows that Mg, Fe, Ca and Na contents all decrease relative to Al, suggesting that the soluble products of eq. 1 are released from the shales. The K/Al ratio increases, however, and Hower et al. (1976) suggested that this apparent increase in K content is due primarily to the decrease of detrital kaolinite, which is offset by a relative increase in detrital illite – smectite and mica. This would produce little change in the bulk rock Al and Si contents, but would cause the Mg, Ca, Na and K to increase relative to aluminum. Thus, the decreases in contents of illite – smectite and soluble cations across the reaction zone may be even greater than is apparent in Tables 1-2 and 1-3.

TABLE 1-4

Bulk-rock mineralogy of shales averaged above and below the illite – smectite reaction zones. Calcite was excluded from the averages. Data were obtained by using semiquantitative XRD techniques

	Anahuac and Frio fms. – southeast Texas						Frio and Vicksburg fms. – south Texas			
	CWRU No. 6 (Hower et al., 1976)		Pleasant Bayou No. 2 (Freed, 1980a, b)		Texas State No. 2 (Freed, 1980a, b)		Dixie Mortgage Loan No. 1 (Freed, 1980a, b)		A.A. McAllen No. 3 (Freed, 1980a, b)	
	above	below	above	below	above	below	above	below	above	below
Quartz	20	35	14	15	11	14	13	15	11	13
K-feldspar	4	0	2	3	3	1	3	2	1	1
Plagioclase	4	7	4	4	3	4	6	10	5	6
Clay	72	58	79	76	82	82	79	73	83	80
I/S	53	42	52	58	61	38	60	48	63	52
Illite	3	0	11	5	7	7	15	7	18	6
I + I/S	55	42	63	63	68	45	75	55	81	58
Chlorite	3	8	0	0	0	0	0	0	0	3
Kaolinite	14	9	15	14	14	37	3	18	3	20
Carbonate	5	0	18	2	9	3	12	14	15	12

A second Anahuac – Frio sequence (in the Texas State No. 3 well) displays a very large decrease in the percentage of illite – smectite balanced by an increase, not of quartz, but of kaolinite (Table 1-4). A 22% increase in detrital kaolinite causes a 9% increase in bulk-rock Al content, an increase large enough to make a significant reduction in the ratios of Fe, Mg, Na, and K to Al. But, except for a minor decrease in Mg content, these elements show no change relative to Al. The ratios of Mg/Al and Ca/Al decrease less than in the other two wells, indicating that the shales in the Texas State No. 2 Well are acting as a more nearly closed system.

The Pleasant Bayou No. 1 Well is very different. Quartz does not significantly change with depth, *nor are there any changes in K-feldspar*, illite – smectite, or kaolinite contents. Chlorite is not present in detectable amounts. Only discrete illite and/or mica shows any significant decrease (besides calcite), and this could be the source for the K required for the illite – smectite reaction. The bulk-rock chemistry shows an increase in K and a decrease in Mg, Ca, and Na contents relative to aluminum (silicon data are not available in Freed, 1980b), again suggesting the loss from the shales of the more soluble products of the illite – smectite reaction.

Frio – Vicksburg claystone “diagenesis” (south Texas)

Because of a difference in provenance, sediments in south Texas contain greater quantities of unstable minerals (plagioclase, carbonate rock fragments, and volcanic rock fragments) than Tertiary sediments in southeast Texas (Loucks et al., 1980). Hence the Frio – Vicksburg shales, while containing about the same proportions of quartz, K-feldspar, total clay, and illite – smectite as the Anahuac – Frio shales in southeast Texas, have a larger component of plagioclase and mica – discrete illite and a smaller amount of kaolinite. Comparing the bulk-rock chemistry of the shales from these two regions reveals that the Vicksburg claystones contain more Fe, Mg, and K relative to aluminum than the Anahuac – Frio shales, due to the greater amount of mica and discrete illite in these rocks, and perhaps due to a more montmorillonitic illite – smectite.

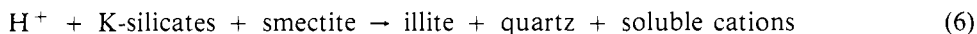
Across the Vicksburg claystone illite – smectite reaction zone (Table 1-3), potassium increases relative to aluminum in both wells, but the other elements are generally conserved. This increase in potassium, however, also corresponds to the contact between the Frio and Vicksburg formations (Freed, 1981). Below this contact, the weight percent of illite – smectite decreases by 11%, and mica and/or discrete illite decreases by 10%. A slight increase in quartz content of 3% and a large increase in kaolinite of 16% balances the decrease in illite – smectite and quartz contents. Chlorite appears in both wells below the reaction zone and is possibly a reaction product (Freed, 1980a and b). Calcite increases slightly in both wells, but not significantly, and K-feldspar shows no change, even up to temperatures of 170°C.

Discussion

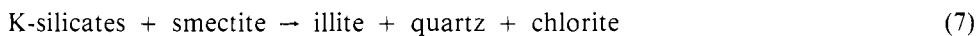
Are there really major variations in shale diagenetic reactions, or are there problems with the data? There are two reasons for believing that a major problem exists with the data. First, the bulk-rock mineralogy determined by semi-quantitative X-ray diffraction is not consistent with the bulk-rock chemistry. For example, it is difficult to believe that a large increase in kaolinite, in the wells which have been

studied, has no effect on the ratios of Fe, Mg, and Na to Al. Second, each of the sequences studied in southeast and south Texas are from single wells, and thus each sequence spans a variety of formations and depositional facies, making it impossible to determine whether mineralogic and chemical changes are the result of diagenesis or deposition.

There is no question that illite – smectite undergoes both structural and chemical changes during shale diagenesis. This reaction has the potential to release large amounts of Mg, Fe, Ca, Na and Si into the shale pore fluids. Whether these elements precipitate to form authigenic minerals in the shales, or escape into the surrounding sandstones, is a question that remains unanswered. Also unanswered is the question of how charge balance in both the solution and solid are maintained if cations such as magnesium and iron are released to the pore fluid. Boles and Franks (1979) achieved a balanced reaction by invoking O^{2-} , which is formally correct but not feasible. Because K^+ appears to be consumed in quantities less than the amount of total cations released from smectite, then a significant quantity of another cation, presumably H^+ , must be consumed as well:



Alternatively, significant amounts of cations are not released to the pore fluids, and the “closed system” reaction proposed by Hower et al. (1976) applies:



CONCLUDING STATEMENT

This review of the current state of knowledge about diagenetic processes in the northwestern Gulf of Mexico considers many aspects – the origin of the basin, its geothermics and hydrodynamics, water chemistries and the evolving lithologies, including evaporites, carbonates, sands and sandstones, clay and shales, and organic matter. Brief summations are presented at the end of each of these subsections. Nevertheless, certain broader implications are apparent. These implications include:

(1) The evolution of the northwestern Gulf of Mexico Basin and diagenesis of its sediment is perhaps the best documented example of the accretionary growth stage of continental crust.

(2) All evidence (physical, chemical, and lithologic) demonstrates the impact of major fluxes of matter and energy. Clearly, the basin and its sediment are geologically open systems. Pore fluids circulate on a vast scale; are a paramount factor in diagenesis; and apparently are active in the deepest sections of the basin.

(3) The sediments and rocks have undergone prodigious changes in both their fabrics and mineral compositions. This is true for mudrocks, sandstones, and carbonates.

(4) The nature and extent of organic matter reactions on diagenesis are not well understood, but they appear to be very important.

The northwestern Gulf of Mexico is one of the world's most intensively studied basins. Data are abundant, and yet are completely lacking in many respects. A number of exciting research directions are evident. These include investigation of the extent and interaction of deep-seated metamorphic processes; quantitative analysis of the evolving fluid and heat-flow systems; better definition of the role of organic matter and clay diagenesis; evaluation of hydrochemical evolution and the factors which control it; and the three-dimensional description of the sediments and rocks which record, however surreptitiously, these geologic processes.

The degree of interaction between sandstones and organic compounds derived from kerogen or oil remains unclear. Both carbon dioxide and organic acids are produced during thermal maturation of organic matter and are likely sources of protons for dissolution reactions. In addition, organic acids can form complexes with aluminum and dissolve feldspars. Water analyses and mass-balance calculations, however, indicate that there is a shortage of acids and organic complexes necessary to account for the amount of dissolution observed in the sandstones. Hydrocarbons do affect diagenesis by inhibiting fluid – rock interactions, once they are emplaced in a reservoir.

The most important diagenetic reaction that shales undergo with depth is the increase of mixed-layer clay with from 30% nonexpandable component (illite) to more than 70%. In the first step of this process, there is a gradual increase in the nonexpandable illite component at the expense of the smectite component. The second step is the ordering of the structural interlayering once the illite component reaches 66%. The smectite-to-illite transformation has potential to release large amounts of Mg, Fe, Ca, Na and Si into pore fluids. Whether these elements precipitate to form authigenic minerals in the shales or escape into the surrounding sandstones is a major question that remains unanswered.

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*Chapter 2***FERROMAGNESIAN AND METALLIFEROUS PELAGIC CLAY MINERALS IN OCEANIC SEDIMENTS**

SATOSHI YAMAMOTO

INTRODUCTION

A universally accepted definition of the term diagenesis does not exist. Singer and Müller (1983), for example, prefer to apply the term to “all changes which take place in a freshly deposited sediment until it reaches the stage of metamorphism”. According to Friedman and Sanders (1978), diagenesis involves, among other things: (1) compaction; (2) addition of new materials; (3) removal and transformation of materials by; (4) change of mineral phase; and (5) replacement of one mineral phase by another. The present author prefers to apply the term diagenesis to the processes operating during sedimentation as well as the processes occurring after the deposition and during burial.

Mineralogical changes during sedimentation originated from the interaction of sedimentary particles or particulates with the water column in relation to the movements concerning deposition and transportation. The various environments of the sedimentation in which diagenetic changes occur include: non-marine, nearshore coastal, offshore to open-sea marine, and deep-sea. The types of sediments and sedimentation are differentiated or characterized for each type of depositional environment, although several problems are involved in the characterization. Among the unsolved problems, the characterization of pelagic sediments or pelagic environments is not well understood.

The term “pelagic” refers to “of the open sea” (Cook and Egbert, 1983). Although sediments deposited in the pelagic environments may involve a long-distance transportation from the source area (Gorsline, 1985), the transformed features of sediment during transportation are very ambiguously recognized in comparison to the terrigenous sediments near the source area (Sugisaki et al., 1982). The aim of this chapter, therefore, is to differentiate the pelagic sediments from the terrigenous ones in terms of geochemical and mineralogical characterization of oceanic sediments, because the diagenetic processes may produce some geochemical and mineralogical features characteristic to the pelagic environments and sediments.

The pelagic (deep-sea) sediments can be generally considered as metalliferous, owing to occasional enrichments of manganese (Mn), zinc (Zn), copper (Cu), nickel (Ni), and other economically important heavy metals (Goldberg and Arrhenius, 1958; Boström and Fisher, 1969; Piper, 1973; Cronan, 1974; Edmond et al., 1979; Yamamoto, 1981, 1982; Sugisaki et al., 1982; Walter and Stoffers, 1985). This is explainable partly by the active volcanic emanation of heavy metals from the deep-sea floors, and partly by the sinking processes during which sedimenting material may extract and become enriched in heavy metallic elements from the water column.

In this respect, the concentration processes of heavy metals constitute an important aspect in the diagenesis of deep-sea sediments.

MINERALOGY AND CHEMISTRY OF OCEANIC SEDIMENTS

The sediments in the modern ocean have been classified into several types by various workers (e.g., Friedman and Sanders, 1978; Seibold and Berger, 1982). The most important categories of the sediment composition may belong to either the biological or geological (chemical products are also included in this category) products. Several important compositions of the modern oceanic sediments are listed in Table 2.1. All of the sediment components listed there vary greatly in grain size, texture, and sedimentary structure, but the present text discusses preferentially their mineralogy and chemistry in relation to the depositional environments.

Biogenous components are variable in their biofacies, but they are simple in mineralogical compositions and usually occur as calcite, high-Mg calcite, and aragonite of calcareous minerals or as opaline minerals (Table 2.1). The organic carbon is also derived from various kinds of combustible organic matter. The sediments rich in biogenous constituents are often called *calcareous ooze* or *siliceous ooze*.

Lithogenous materials are fragments of various rock types as detrital mineral grains and lithic fragments. The mineral fragments $< 4 \mu\text{m}$ can be termed as clay-sized minerals and clay minerals per se. The degree of fragmentation is a combined effect of mechanical destruction and of water on rocks. In addition to the lithogenous origin, several inorganic minerals are formed by diagenetic reactions

TABLE 2-1

Compositions of oceanic sediments

1. Biogenous components	
Organic matter (hydrocarbons)	
Calcareous organic remains (calcitic minerals)	
Siliceous organic remains (opaline minerals)	
2. Lithogenous components (detrital mineral components)	
Quartz	
Feldspars	
Silicate minerals	
Clay minerals	
Lithic fragments	
3. Authigenic – diagenetic mineral components	
(1) Silica minerals	(6) Barite (BaSO_4)
(2) Zeolite	(7) Gypsum (CaSO_4)
(3) Pyrite	(8) Halite (NaCl)
(4) Iron oxide – hydroxide	(9) Dolomite [$\text{CaMg}(\text{CO}_3)_2$]
(5) Manganese oxide – hydroxide	
4. Other components	
Volcanic ash	
Cosmogenic minerals	

after deposition, as indicated in Table 2.1 by authigenic–diagenetic products. Volcanic ash and extraterrestrial material are only very minor constituents of oceanic sediments.

The quantity of these mineral components can be measured readily by chemical and other analytical methods. Although it is popular to determine the chemical composition of the sediments, the meaningful interpretation of these chemical data in regard to the exact mineralogy is usually very difficult. Important chemical phases in the oceanic sediments are organic matter, carbonates, silicates, oxides, and occasionally sulphides and others. The metallic elements combined with carbonates are Ca, Mg, Sr, and very rarely Mn and Fe. The metallic elements (including alkali and alkaline earth metals) combined with silicates and oxides are the most common and abundant elements in the Earth's crust. They are Al, Fe, Mg, Ca, K, Na, Ti and Mn, and also Si and oxygen as non-metallic elements. Most of the transition metals, such as V, Cr, Co, Ni, Cu, Zn, Pd, Ag, Cd, Pt, Au and Hg, are suspected to occur as silicate – oxide forms, but they can be present as pure metals, or can be associated with carbonate or sulphide minerals. The bound state of the transitional metals can be rarely determined, because these transitional metals are usually present in trace amounts only.

Several analytical methods are available, depending on the purpose of analysis, type of elements, and quantity. The aspects discussed here are mainly concerned with the major and minor metallic elements and their distribution patterns in the carbonate and silicate minerals. The concentration of metallic elements was determined by the atomic absorption spectrometry either after the elements were digested from the bulk sample or after the elements were leached from the carbonate fraction (Yamamoto, 1977, 1981, 1982, 1984, 1985b). Special attention was placed on the relationship between Fe and Mg and the concentrations of transitional metals in oceanic sediments. In other words, a possible discrimination between the pelagic sediments and non-pelagic terrigenous sediments in terms of the relationship be-

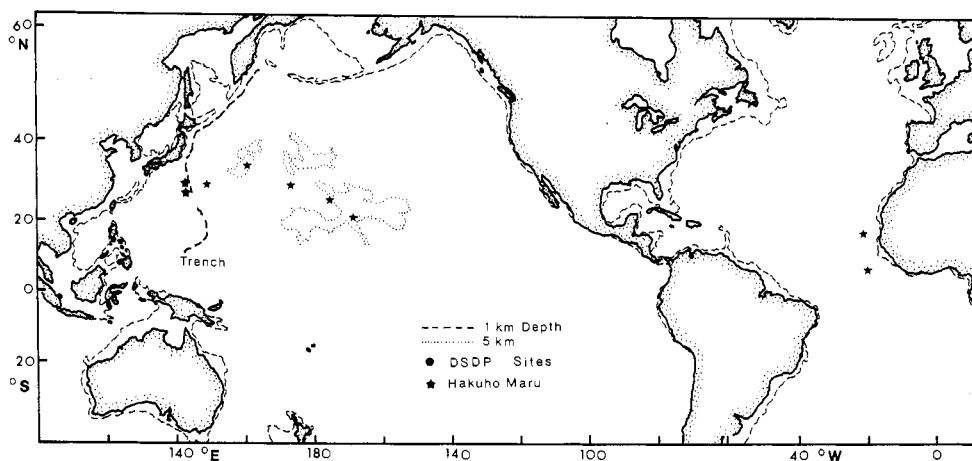


Fig. 2-1. Site locations of core-samples in the Pacific and Atlantic Oceans.

tween Fe and Mg and the concentrations of transition heavy metals was attempted with success. In the foregoing sections, the correlations between Fe and Mg are examined for various types of oceanic sediments from several parts of the modern ocean floors (including the deep-sea floors of the Pacific and Atlantic Oceans and the shallower seafloors of the East China Sea and nearshore bays) to demonstrate that the presence of correlation between Fe and Mg is a fundamentally important characteristic of pelagic sediments.

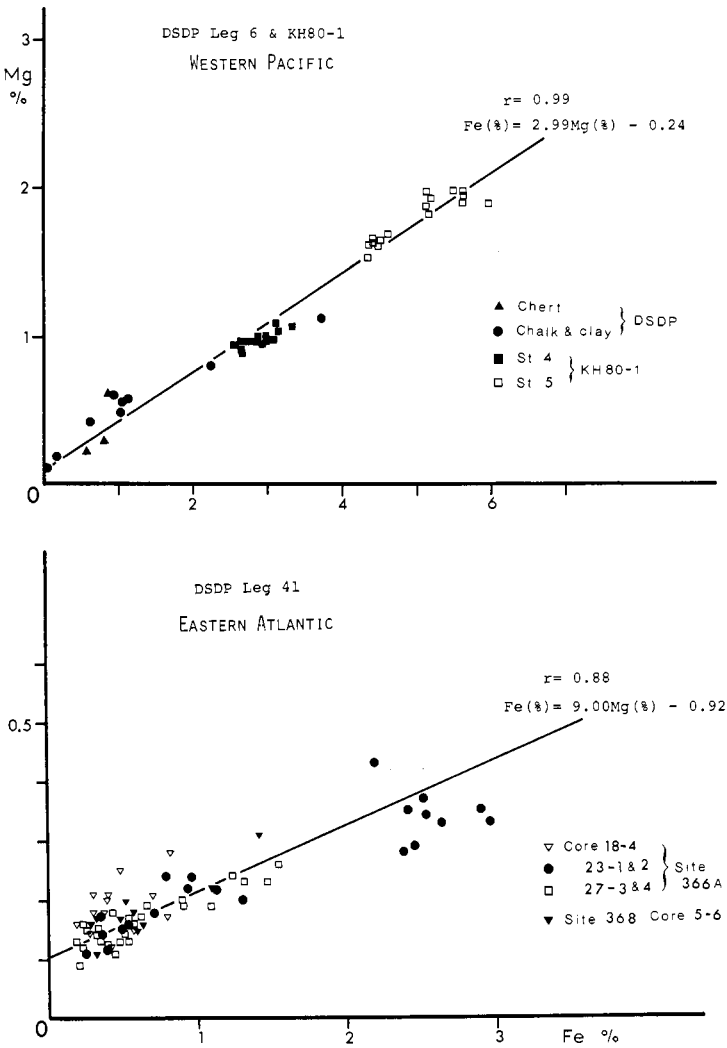


Fig. 2-2. Correlations between Fe and Mg for the western Pacific and eastern Atlantic core-samples. Total numbers of core samples are 83 for the Atlantic and 45 for the Pacific. Iron and Mg concentrations are expressed as those in whole fraction of sediments. Correlation coefficients (r) and equations of regression lines (Fe as dependent and Mg as independent variables) are shown in figures. (From Yamamoto, 1982.)

CORRELATION BETWEEN Fe AND Mg IN DEEP-SEA SEDIMENTS

Pelagic sediments and cherts

Although the value of the $\text{Fe}(\%) / \text{Mg}(\%)$ molar ratio is different for the Atlantic and Pacific deep-sea sediments, the correlation coefficients between Fe and Mg contents are significantly high for both the Atlantic and Pacific sediments (Figs. 2-1 and 2-2). Various types of sediments were used in this correlation study: the Atlantic sediments are semiconsolidated clays or chalks of Miocene and Pliocene age; whereas the Pacific sediments are surface clays or calcareous oozes, and some are Cretaceous and Eocene radiolarian mudstones (Yamamoto, 1982). The ranges of Fe and Mg concentrations vary from 0 to 6%, forming a rather continuous spectrum, and the fluctuations of the Fe and Mg concentrations are influenced mainly by the concentrations of CaCO_3 in sediments, because the Fe and Mg concentrations are diluted with the CaCO_3 fractions.

The correlations between Fe and Mg are significantly high for both the Pacific Ocean chert samples and the deep-sea origin cherts derived from land (Figs. 2-3 and 2-4). The Pacific cherts include several nodular flints derived from the Cretaceous to Paleocene chalks as well as some radiolarian mudstone beds in reddish clay (Yamamoto, 1986b). Their sampling sites cover the entire region of the western

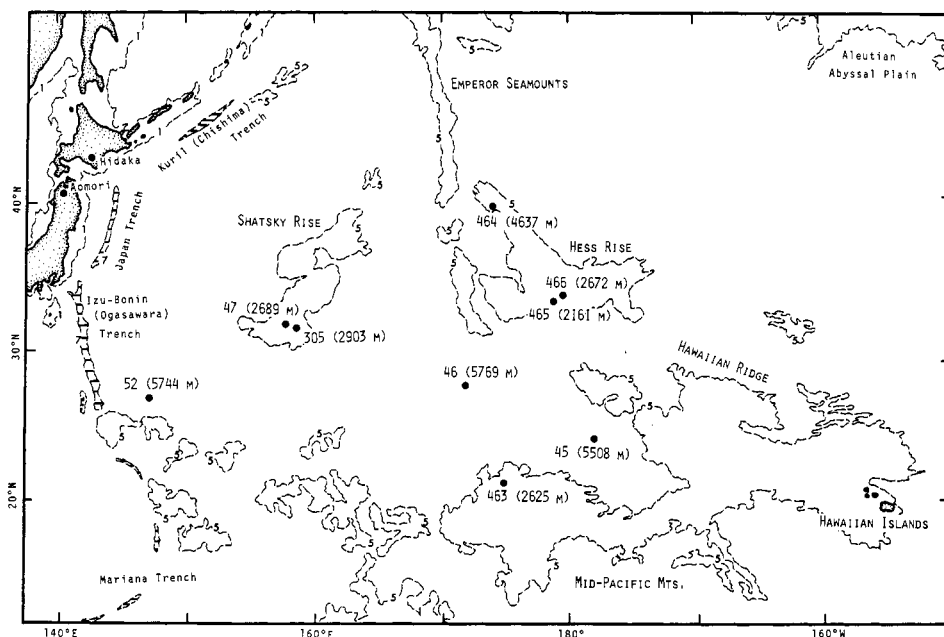


Fig. 2-3. Locations of sampling sites of deep-sea cherts. Site numbers are identical with those of the Deep Sea Drilling Project and water depths of sites are indicated in parentheses. Major bathymetric contours are given in km.

Pacific. The cherts of deep-sea origin derived from land include the bedded jaspers of the Hidaka Group, Hokkaido, and some samples of varicolored radiolarites in Aomori, Japan (Yamamoto, 1986b). Although the nodular flints contain very small amounts of clayey minerals with Fe and Mg, the relationship between Fe and Mg in these flint nodules may be considered as a linear regression plot passing through the zero point. The clayey matter in the flinty nodules or in the cherty beds is generally fine-grained and may be responsible for the color variations in the specimens (Yamamoto, 1981, 1986b).

The $\text{Fe}(\%) / \text{Mg}(\%)$ ratios of the Pacific deep-sea sediments are equal to those of the Pacific cherts, judging from the regression equations of the correlations. In comparison to the correlated plots, the Fe-rich chert samples may be recognized as

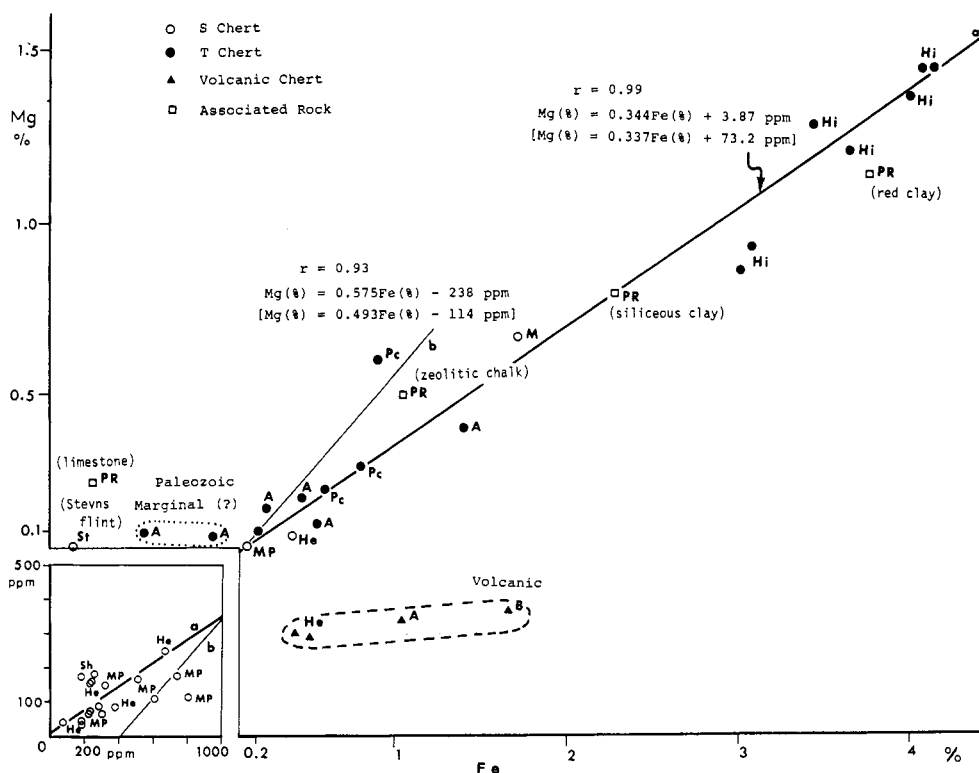


Fig. 2-4. Correlation between Fe and Mg in chert samples. Correlation coefficient (r) is 0.93 for all chert samples from the Pacific ($N = 25$) and increases to 0.99 ($N = 37$) by adding Hidaka jaspers and Aomori radiolarites (two samples indicated as "Paleozoic marginal" are excluded). On regression lines by these samples, PR and M points are plotted and compared. Magnesium as dependent and Fe as independent variables, but regression equations in parentheses will be obtained by reversing these variables.

Labels beside plots are abbreviated: MP = Mid-Pacific Mountain; He = Hess Rise; Sh = Shatsky Rise; B = flinty chert near the Bonin Trench; Pc = radiolarian mudstone in the Pacific; PR = associated rock/sediment in the Pacific; St = Stevens Klint, Denmark; M = Moorehouse Member, New York; Hi = Hidaka Group, Hokkaido; A = unnamed formation of pre-Neogene (possibly Paleozoic age), Aomori. (From Yamamoto, 1986b.)

volcanogenic because they are enriched with the hydrothermal Fe products such as goethite and Fe-oxides. The reason for the higher values of $\text{Fe}(\%)/\text{Mg}(\%)$ ratio in the Atlantic sediments than in the Pacific sediments is unknown, but the ratio should be re-examined for samples from more widespread sites, particularly for samples in the Atlantic Ocean. The compositional differences between the Pacific and Atlantic basalts (Thompson et al., 1976) or the differences in the processes involved in the production of clayey sediment from the oceanic basalt could account for the different $\text{Fe}(\%)/\text{Mg}(\%)$ ratios of the Pacific and Atlantic sediments.

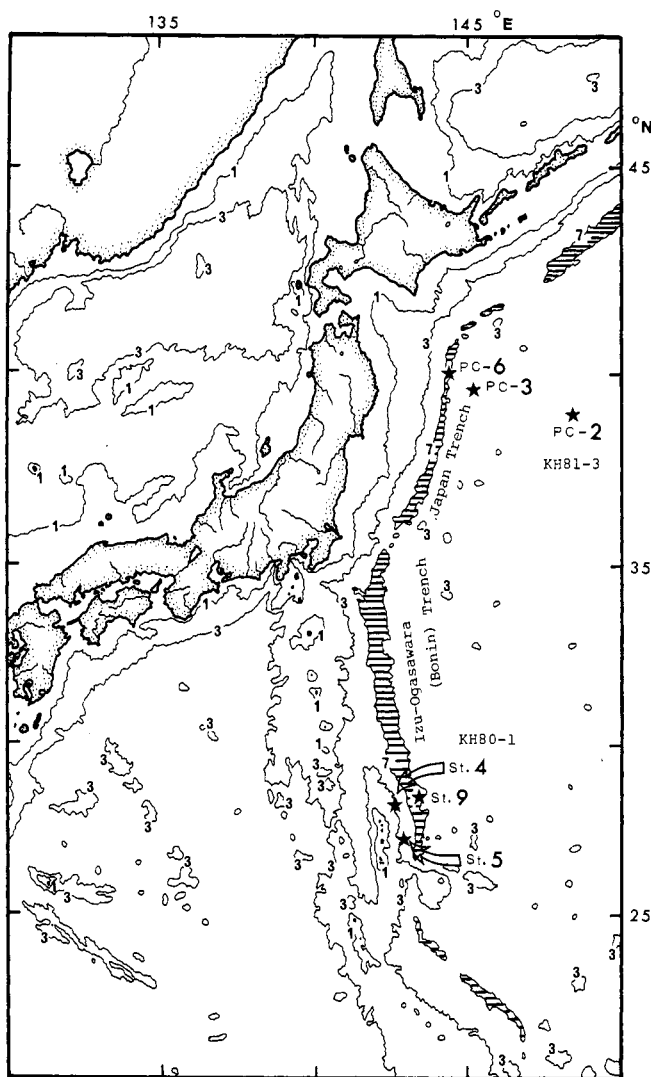


Fig. 2-5. Site locations of piston and box core-samples in the Japan Trench region. Bathymetric contours are in km, and trench basins are shaded.

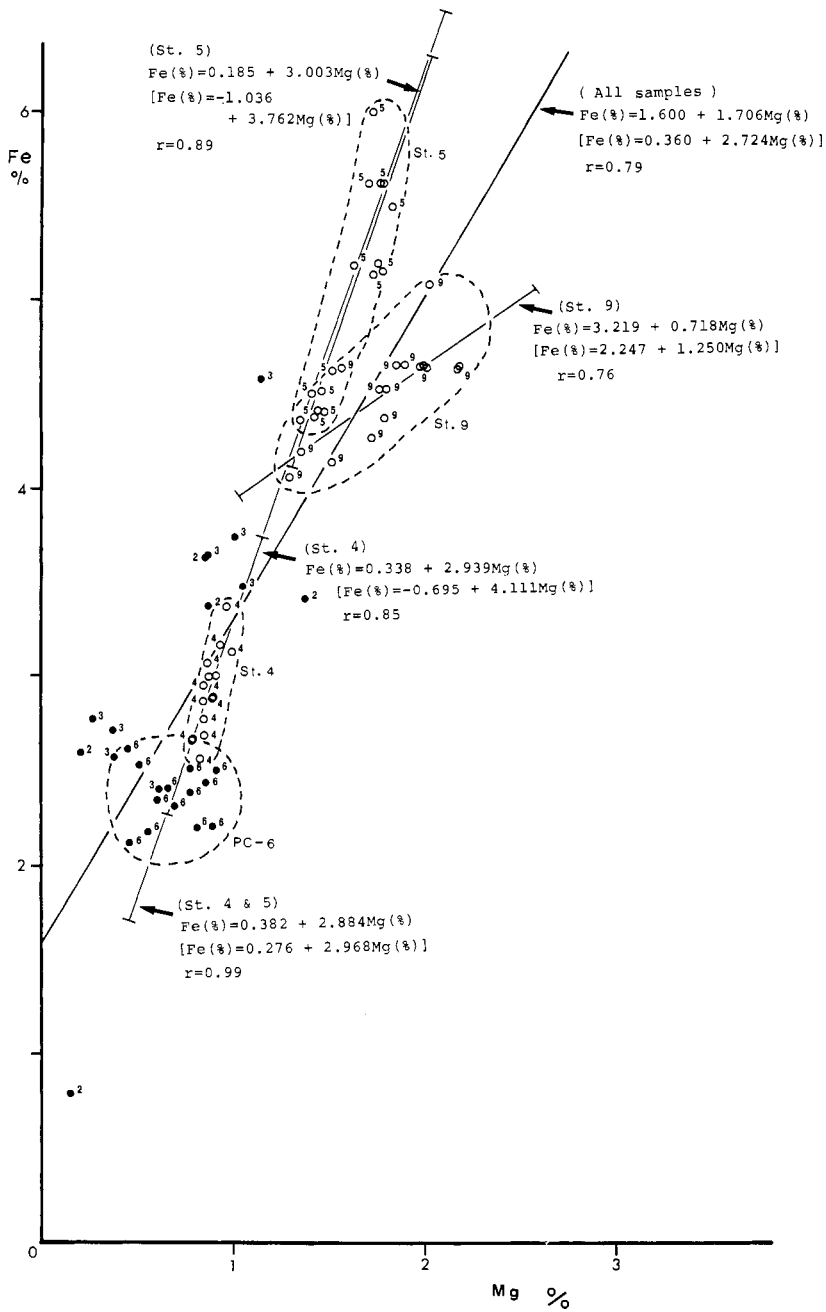


Fig. 2-6. Correlation between Fe and Mg of noncalcareous fraction of sediments. Regression equations (Fe as dependent and Mg as independent variables) and correlation coefficients (r) are indicated for clustered groups and all combined samples. Numbers beside plotted points indicate site numbers. (From Yamamoto, unpubl. data.)

Inasmuch as Fe and Mg are elements which can be present (1) in interstitial water, (2) as exchangeable cations, (3) in the carbonate minerals (Siever et al., 1965; Friedman et al., 1968; Masuzawa and Kitano, 1983), and (4) in the silicate fraction, samples should be fractionated by using the ammonium – acetic acid of pH 5.2 in order to determine their concentrations in the silicate fraction (Wangersky and Joensuu, 1964, 1967). Such an attempt was achieved for surface sediments from the Japan Trench and adjacent abyssal floors (Yamamoto, 1984), and the summarized results are shown in Figs. 2-5 and 2-6. Roughly speaking, no major difference is apparent between Fe – Mg relationships in the bulk sediment fraction and those in the ammonium – acetic acid (AA) insoluble fraction. This may be due largely to the low concentration of high-Mg calcite in the deep-sea sediments (Yamamoto, 1984).

The correlation between Fe and Mg becomes weaker when sediment samples from the trench floors are included into the statistical comparison (Fig. 2.6). The association between Fe and Mg in the PC-6 samples of the Japan Trench floor (water depth 7260 m) does not show a linear correlation. On the other hand, their relationship in the St. 9 samples of the Ogasawara Trench floor (water depth 8260 m) is different from that of other groups, although a rather high correlation-coefficient is indicated. The poor correlation in the Japan Trench may be due to the terrigenous supply to the trench basin, and the unique association in the Ogasawara Trench

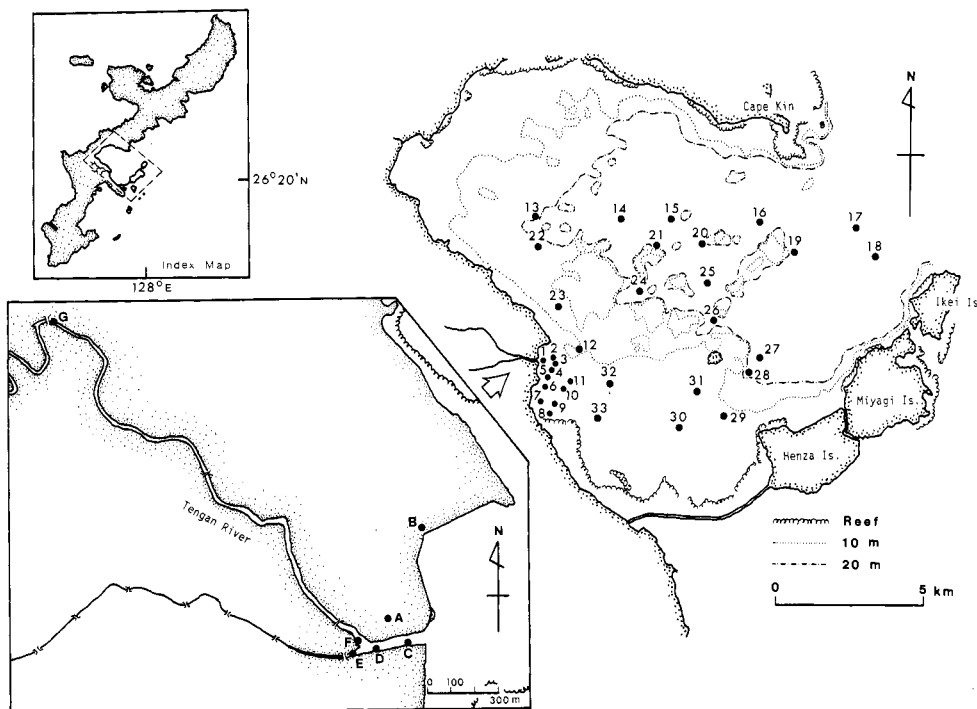


Fig. 2-7. Surface sediments from the Kin Bay and Tengan River estuary regions, Okinawa. Site numbers are identical with those of Fig. 2-8.

might be related to the geochemical condition of the basement igneous complex or the deposition of a large amount of Fe-oxides on the basin floor (Yamamoto, 1984; Yamamoto and Oomori, 1984).

Comparison with shallow-water sediments

Some examples of the Fe – Mg correlation for the shallow-water marine sediments are presented here and compared with the Fe – Mg relationship in the pelagic deep-sea sediments. Calcareous sediments with a very small admixture of siliciclastic mud do not show any significant correlation between Fe and Mg, because considerable amounts of Mg are contained in high-Mg calcite as well as in the siliciclastic mud (Ujiié et al., 1983; Yamamoto and Ujiié, 1983; Yamamoto and Yuine, 1985). When the Mg in the high-Mg calcite and other calcareous minerals is fractionated by the AA and the relationship between Fe and Mg is compared for the AA-insoluble

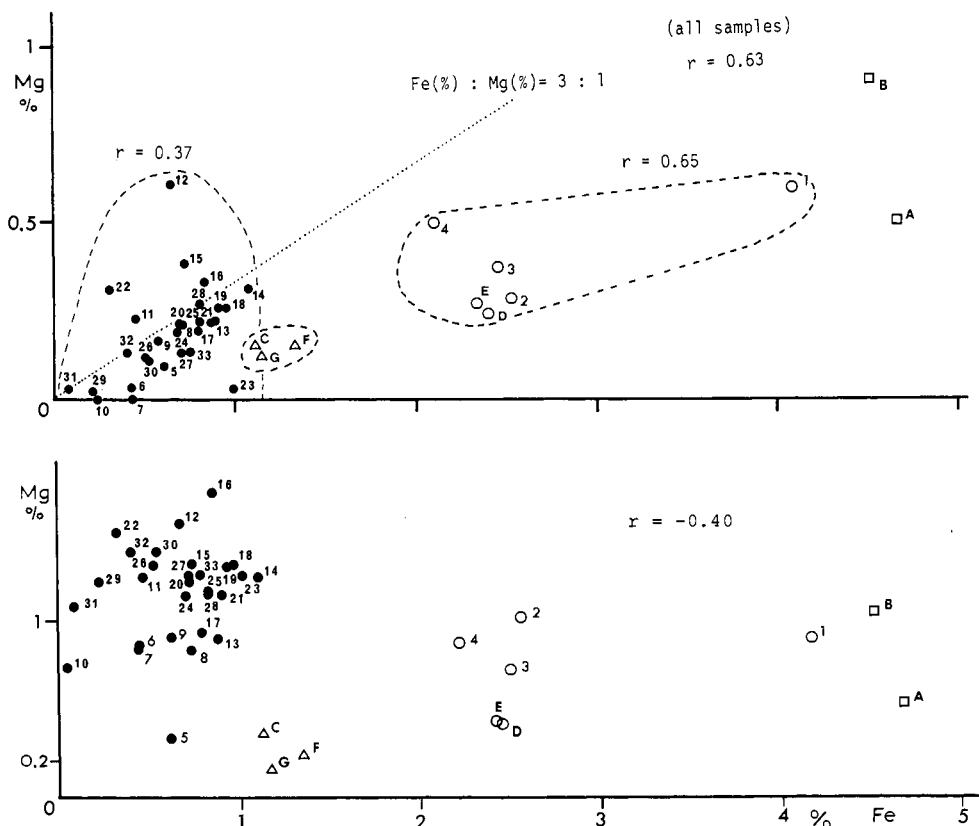


Fig. 2-8. Correlations between Fe and Mg in bulk sediment fraction (lower figure) and in AA-insoluble (noncalcareous) sediment fraction (upper figure). The line, $\text{Fe}(\%) : \text{Mg}(\%) = 3 : 1$, is considered as characteristic relationship of deep-sea sediments in the Pacific. (From Yamamoto and Yuine, 1985.)

(silicate) fraction of the Kin Bay sediments, their association can not be significantly correlated with respect to their relationships in pelagic sediments and cherts (Figs. 2-7 and 2-8).

The Fe–Mg relationship is shown for surface sediments of the East China Sea

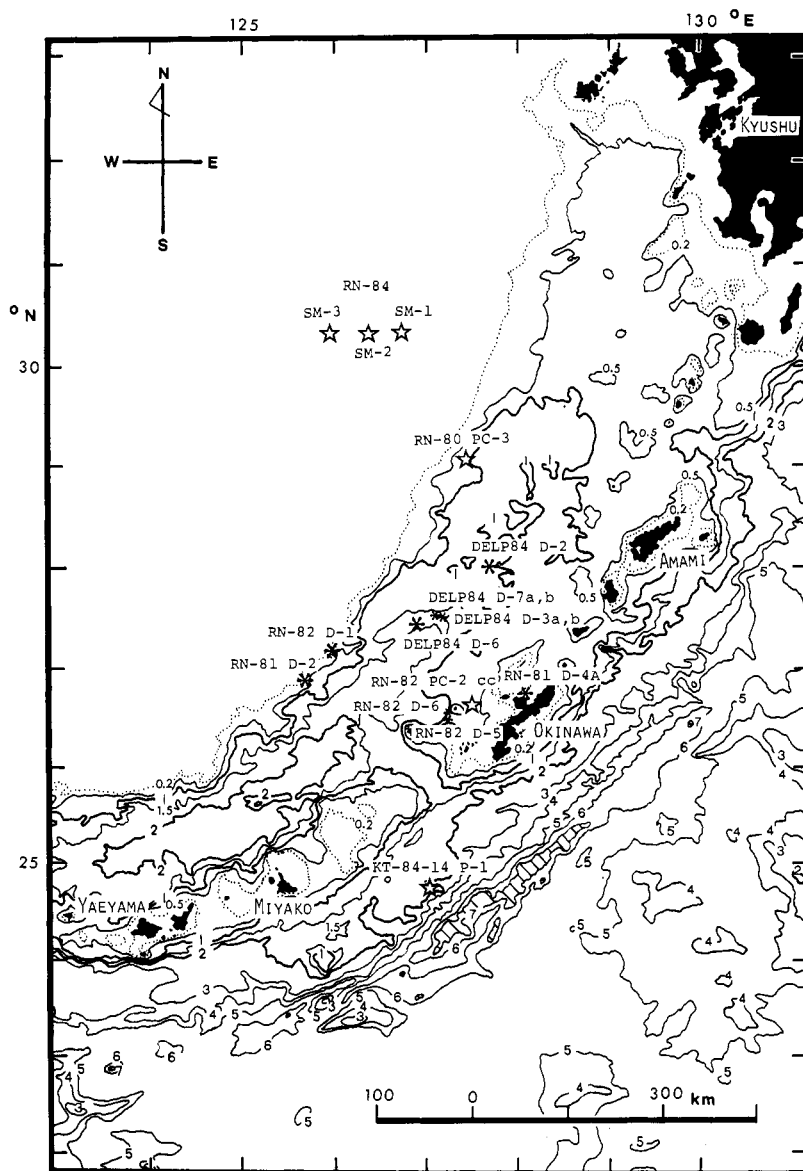


Fig. 2-9. Surface sediments and some core-samples from the East China Sea and adjacent region. Bathymetric contours are in km. Asterisks = dredged stations; stars = piston and Smith-McIntyre coring stations.

region in Figs. 2-9 and 2-10. It does not show any significant correlations between Fe and Mg as a whole (Yamamoto, 1986a). The sediments investigated include various types (Kimura et al., 1986): (1) siliciclastic sands on the continental shelf; (2) grayish muds on the continental slopes including the Okinawa Trough; (3) brown muds from some surface floors of the Okinawa Trough and the Ryukyu Trench slope; and (4) calcareous sands on the shallow seafloors off the Ryukyu Islands. Among them, the brown muds from the Okinawa Trough and the Ryukyu Trench slope resemble the pelagic sediments in terms of the heavy-metals concentration and the Fe – Mg relationship (Yamamoto, 1986a). Although in the brown mud more data points (Fe and Mg contents) are needed to check Fe – Mg correlation, the other types of sediments from the East China Sea region can be considered as of terrigenous-type Fe – Mg relationship, i.e., there is no correlation between Fe and Mg contents.

The relationship between Fe and Mg may be one of the most useful criteria for paleoenvironmental interpretations for both pelagic and terrigenous types of sediments. Walter and Stoffers (1985) recognized Fe-rich smectite as a factor that has high loadings for Fe, Mg and Si contents, as indicated by the factor analysis results based on geochemical data of 594 sediment samples from the East Pacific Rise region. Earlier, Yamamoto (1977) has shown that Fe and Mg form a separate group of principal components from other groups of metallic elements, for both the

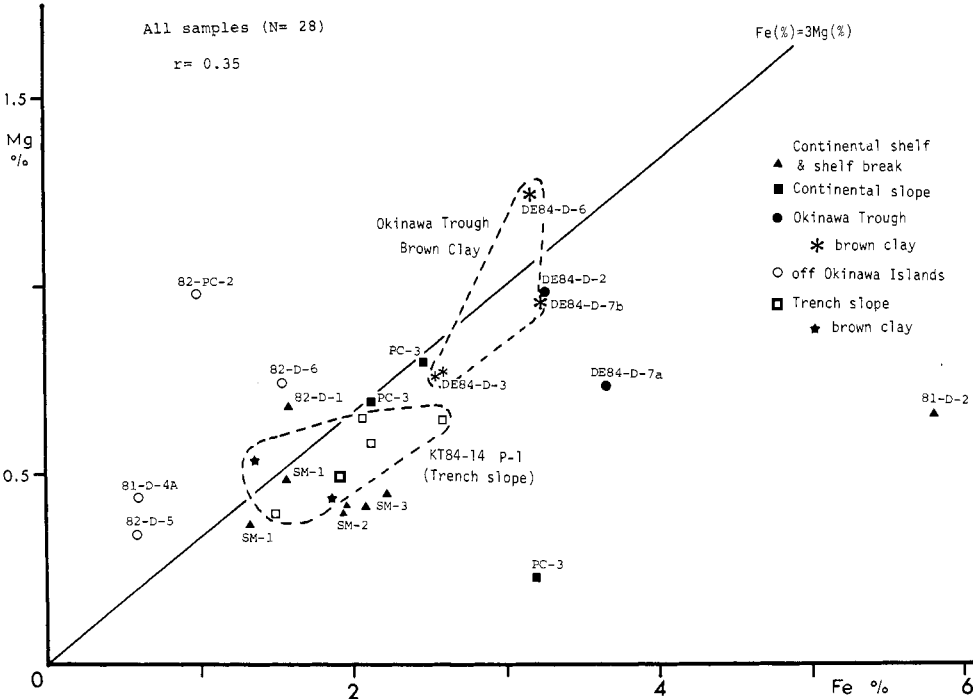


Fig. 2-10. Correlation between Fe and Mg in bulk sediment fraction of the East China Sea samples. (From Yamamoto, 1986a.)

Atlantic and Pacific deep-sea sediments. The high correlation between Fe and Mg can be a significant diagnostic feature for pelagic deep-sea sediments, as it can be used as a discriminatory criterion between pelagic deep-sea and terrigenous shallow-water sediments.

FERROMAGNESIAN CLAY MINERALOGY AND CLAY MINERALIZATION IN THE DEEP SEA

Iron and Mg are abundant elements and rank next to Al in the Earth's crust. They (Fe and Mg) replace Si or Al lattices occasionally in the aluminosilicate minerals

TABLE 2-2

Fe/Mg ratios of ferromagnesian minerals

Mineral groups	Fe/Mg ratio (mole ratio)
<i>Silicate minerals</i>	
Olivine (solid solution of forsterite and fayalite) $(\text{Fe,Mg})_2\text{SiO}_4$	vary
Pyroxene group:	
Common augite $(\text{Ca,Mg,Fe,Al,Ti})(\text{Si,Al})\text{O}_3$	vary
Hypersthene $(\text{Mg,Fe})\text{SiO}_3$	vary
Diopside $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$	vary
Hornblende group:	
Common hornblende $(\text{Ca,Na})_{2-3}(\text{Mg,Fe,Al,Ti})_5(\text{Si,Al})_8\text{O}_{22}(\text{OH})_2$	vary
Actinolite $\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	vary
Mica group:	
Celadonite $\text{K}(\text{Mg,Fe}^{3+})\text{Si}_4\text{O}_{10}(\text{OH})_2$	vary
Glauconite $\text{K}(\text{Fe}_{1.33}^{3+}\text{Mg}_{0.67})(\text{Si}_{3.67}\text{Al}_{0.33})\text{O}_{10}(\text{OH})_2$	ca.2
<i>Clay minerals</i>	
Illite $\text{K}_{\leq 1}[\text{Al}_{\leq 2}(\text{Fe}^{3+},\text{Mg})_{>0}](\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2$	vary
Chlorite (mixture of clinocllore and chamosite) $(\text{Mg,Fe})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$	vary
Smectite group:	
Fe-montmorillonite $\text{Na}_{0.33}(\text{Al,Fe,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$	1 (?)
Fe-saponite $\text{Na}_{0.33}(\text{Fe,Mg})_3(\text{Si}_{3.67}\text{Al}_{0.33})\text{O}_{10}(\text{OH})_2$	
<i>Carbonate minerals</i>	
Ankerite $\text{Ca}_2\text{MgFe}(\text{CO}_3)_4$	1

(Krauskopf, 1967, pp. 183 – 184; Berner, 1971, pp. 165 – 168). The mineral phases in which Fe and Mg are present are listed in Table 2-2. The Fe(%) /Mg(%) ratios are constant in only a few species of the ferromagnesian minerals. The possible mineralogical phases which may cause a good correlation between the Fe and Mg contents of the deep-sea sediments (constant ratio) are considered in the foregoing sections.

In Fig. 2-11, the results of some mineralogical investigations on the sediment samples in which Fe and Mg are correlatable are shown. In the figure, the bulk mineralogy through the X-ray diffraction analysis (XRD) indicates such ferromagnesian minerals as olivine, chlorite, illite, and possibly smectite, the main peak of which may appear at the (2θ) angle lower than 6° . The main peak of olivine is recorded at the 32° angle (2θ) and it represents the major mineral peak for pelagic red clay sample (DSDP Leg 6, Site 45.1, Core 1-0), or higher values than plagioclase for several samples (KH80-1 St. 5, 2 – 4 cm; KH80-1 St. 9, 2 – 4 cm; KH81-3 PC-2, 110 – 112 cm; KH81-3 PC-3, 410 – 412 cm; KH81-3 PC-6, 10 – 15 cm). The olivine peak can be differentiated from the plagioclase peaks (Borg and Smith, 1968; Smith, 1974) as exemplified in the RN81 D-2 and KH81-3 PC-2, 10 – 12 cm samples.

The peak at the 32° angle has been interpreted as one of siderite peaks in the earlier descriptions in the reports of the Deep Sea Drilling Project (Rex, 1968; Rex and Murray, 1970; and also in appendix III of the Initial Reports, Vol. 4, pp. 745 – 753). As the chemical and leaching data on the pelagic red-clay sample (Table 2-3) indicate, however, the major peak in the 32° angle can not be interpreted as that of siderite. The chemical data suggest that the peak at the 32° angle is actually olivine. Although the presence of olivine may not fully account for the correlation between Fe and Mg, its presence in the ferromagnesian clays can be related with the genesis of the clays, particularly from the viewpoint of clay mineralization of basaltic rocks (Yamamoto, 1982).

TABLE 2-3

Chemical analytical results on red clay(DSDP Site 45.1, Core 1-0)

	Total digestion	2% HCl leaching	Ammonium acetate leaching
Soluble fraction* (%)		32	26
Ca(%)	2.0	1.0	< 1.0
Mg(%)	1.13	0.80	0.30
Fe(%)	3.76	1.05	< 0.001
Zn(ppm)	260	280	150
Mn(%)	0.360	0.035	< 0.001
Ni(ppm)	< 100	< 100	< 100
CO ₂ (%)**	5.28		

* Soluble fraction was determined by weighing insoluble residue on GS-25 filter (filtering area 9.6 cm^2 , pore size $1\text{ }\mu\text{m}$, glass fiber).

** Ignition loss between 550° and 950°C .

Concentrations in whole fraction of dry weight sample.

The most probable mineral phase, which may account for the correlation between Fe and Mg, can be interpreted to be ferromagnesian clay minerals among which smectite is the most probable one. Although illite and chlorite, among the ferromagnesian clay minerals, are variable in the $\text{Fe}(\%) / \text{Mg}(\%)$ ratios (Hathaway, 1979), the smectite group includes some mineral species in which the $\text{Fe}(\%) / \text{Mg}(\%)$ ratio is constant. Iron-montmorillonite and Fe-saponite are known as such smectite minerals that can contain Fe and Mg in a constant ratio (Sudo and Ota, 1952; Sudo, 1954; Miller et al., 1966; Bischoff, 1969). Weaver and Pollard (1975) have investigated in detail the mineral chemistry of clay minerals and also examined the Fe–Mg correlations in these clay minerals. According to this study, the constancy of the $\text{Fe}(\%) / \text{Mg}(\%)$ ratio was not strongly recognized in the smectite clay minerals, but the study has left room to wonder whether the $\text{Fe}(\%) / \text{Mg}(\%)$ ratio is constant in some species of the smectite minerals or not, on examining several tables of chemical data presented. Particularly, Weaver and Pollard (1975) have noted that most of the smectite minerals can form by the alteration of volcanic material and also that much of the authigenic montmorillonite in the Pacific has a relatively high Fe content. The smectite minerals can be converted to illite (Roberson and Lahann, 1981; Howard and Roy, 1985), probably by changing the original $\text{Fe}(\%) / \text{Mg}(\%)$ ratio of the mineral. The chlorite minerals may be contained in the clay as mixtures of several detrital chlorite minerals (Griffin et al., 1968; Hathaway, 1979).

The smectite, including Fe-montmorillonite and Fe-saponite, is the most common mineral product derived from weathering of basaltic rocks on land and in the sea (Engel and Engel, 1963; Bertine, 1974; April, 1981; Curtin and Smillie, 1981; Keith and Staples, 1985; Moore et al., 1985; White et al., 1985). Nontronite and beidellite, which belong to the smectite group, though their mineral chemistry does not indicate Fe and Mg in the formulae, are also reported as the submarine weathering products of basalts (Thompson et al., 1985; Walter and Stoffers, 1985). The aqueous exposures and deposits of basaltic rocks were observed frequently in various parts of the ocean floor by some investigators (Engel and Engel, 1963; Hart, 1969; Bertine, 1974; Farrow and Durant, 1985).

During the halmyrolytic weathering processes, groundmass glasses of the basalt were altered to smectite minerals (Keith and Staples, 1985). Engel and Engel (1963) have reported that the portion of olivine in the altered basalt is replaced by smectite, i.e., the alteration of olivine can also produce smectite. The olivine which was occasionally recognized in the red clay and gray clay of deep-sea sediments, as demonstrated in Fig. 2-11, can be considered as a residual product of clay-forming processes affecting basalt. In the weathering products of basaltic rocks, the minerals other than smectite and olivine are produced preferentially as the coarse-grained materials, the distribution of which may be restricted to the precursor basaltic rocks in the deep sea. The smectite and olivine can be spread on the deep-sea floors as fine-grained minerals.

The clay-forming processes in the ocean floor may be accompanied by hydrothermal alterations of basalts (Hart, 1970; Wolery and Sleep, 1976; Kawahata and Furuta, 1985; Thompson et al., 1985). The enrichment of Fe in the smectite minerals to form Fe-montmorillonite, Fe-saponite and nontronite can be accounted for by the hydrothermal supply of Fe (Boström, 1970) and clay neoformation under this

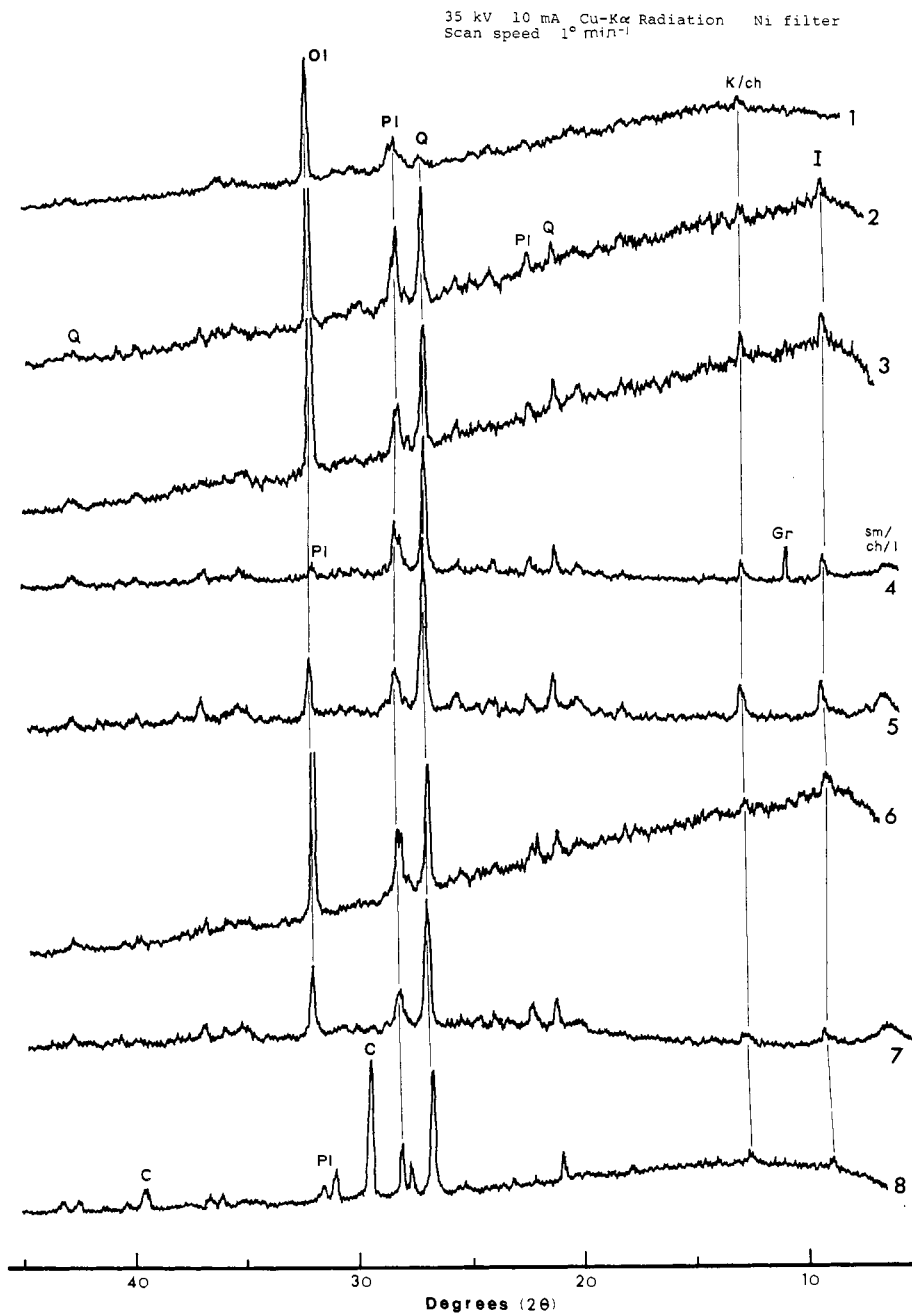


Fig. 2-11. X-ray diffractograms of deep-sea red clay, abyssal brown or gray clay, trench clay, and terrigenous gray sand as reference. Notations of diffraction peaks; *Ol* = olivine; *Pl* = plagioclase; *Q* = quartz; *C* = calcite; *I* = illite; *K/ch* = kaolinite and chlorite; *sm/ch/I* = smectite, chlorite and illite; *Gr* = green rust (Fe-oxides). 1 = DSDP Leg 6, Site 45.1 Core 1-0, red clay; 2 = KH80-1 St. 5 2-4 cm, brown clay; 3 = KH80-1 St. 9 2-4 cm, brown clay; 4 = KH81-3 PC-2 10-12 cm, Mn-micronodule bearing red clay; 5 = KH81-3 PC-2 110-112 cm, gray clay; 6 = KH81-3 PC-3 410-412 cm, gray clay; 7 = KH81-3 PC-6 10-15 cm, gray clay; 8 = RN81 D-2, gray medium sand.

condition. Although the origin of deep-sea clays comprises some ferruginous authigenic minerals of various types (Miller et al., 1966; Bischoff, 1969; Cronan, 1973, 1974; Bertine and Keene, 1975; Dymond et al., 1980; Aoki and Kohyama, 1985), the ferromagnesian smectites (such as Fe-montmorillonite) are the most common and widespread minerals, as judged from the strong correlations between Fe and Mg in the deep-sea sediments and other characteristics of the deep-sea sediments (Bischoff, 1969; Yamamoto, 1982, 1985a; Walter and Stoffers, 1985). Inasmuch as nontronite has restricted distribution at the area of the spreading axis (Thompson et al., 1985), the Fe-rich smectite, which was termed as a very widely distributed clay mineral in the deep-sea floors by Aoki and Kohyama (1985) and Walter and Stoffers (1985), should be denoted as the Fe-montmorillonite in a popular sense.

CONCENTRATION PROCESSES OF HEAVY METALS IN DEEP-SEA SEDIMENTS

In recent years, hydrothermal enrichments of heavy metals in deep-sea sediments, particularly at the spreading ridge crest, have been studied by many investigators (Boström and Fisher, 1969; Boström, 1970; Corliss, 1971; Piper, 1973; Bischoff and Dickson, 1975; Wolery and Sleep, 1976; Edmond et al., 1979; Walter and Stoffers, 1985). Although the precise mechanisms of the enrichment are controversial as to

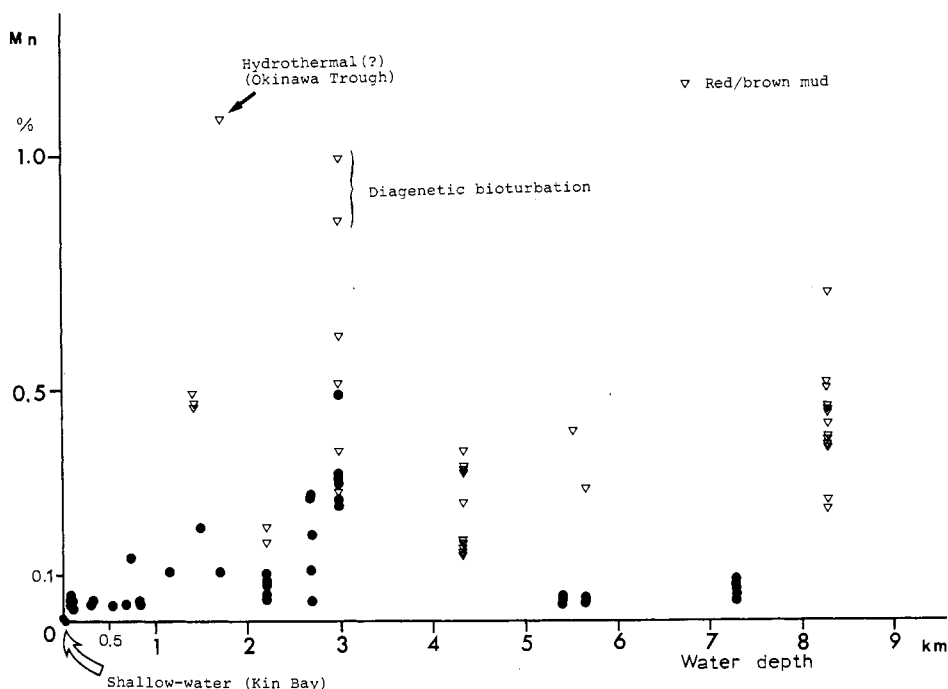


Fig. 2-12. Relationship between water depth and Mn concentration in surface sediments. Mn concentrations are corrected for calcium-carbonate free basis. Reddish sediments and grayish sediments are differentiated by patterns; triangles = red-brown mud; dots = gray mud.

whether the heavy metals are supplied from the volcanic emanation beneath the ocean floor or enriched during settling of particulates in the water column, one of the prominent characteristics that may differentiate the deep-sea sediments from shallow-water sediments is the concentration of heavy metals in deep-sea clays (Goldberg and Arrhenius, 1958; Yamamoto and Ujiié, 1983; Sugisaki, 1984).

Among transitional heavy metals, Mn is a distinctively diagenetic element with an occasional concentration in sediment locally or as a stratigraphic horizon (Yamamoto et al., 1979; Kitano et al., 1980; Sakata et al., 1981; Swinbanks and Shirayama, 1984). In the ocean, Mn is enriched in the deeper basin sediments as a result of scavenging and other processes in the sinking particulates (Tsunogai, 1978; Brewer et al., 1980). The relationship between the water depth and concentration of Mn on a carbonate-free basis is presented in Fig. 2-12. The data were obtained by the present author. According to this figure, the sediments sampled from the seafloors shallower than 1 km are not concentrated by more than about 1000 ppm of Mn on the basis of calcium-carbonate free concentrations. Generally speaking, the surface sediments from deeper ocean floors tend to be concentrated in Mn. There is a tendency that brownish mud is more enriched with Mn than grayish mud (Fig. 2-12). Some anomalous concentrations are recognized in the bioturbated

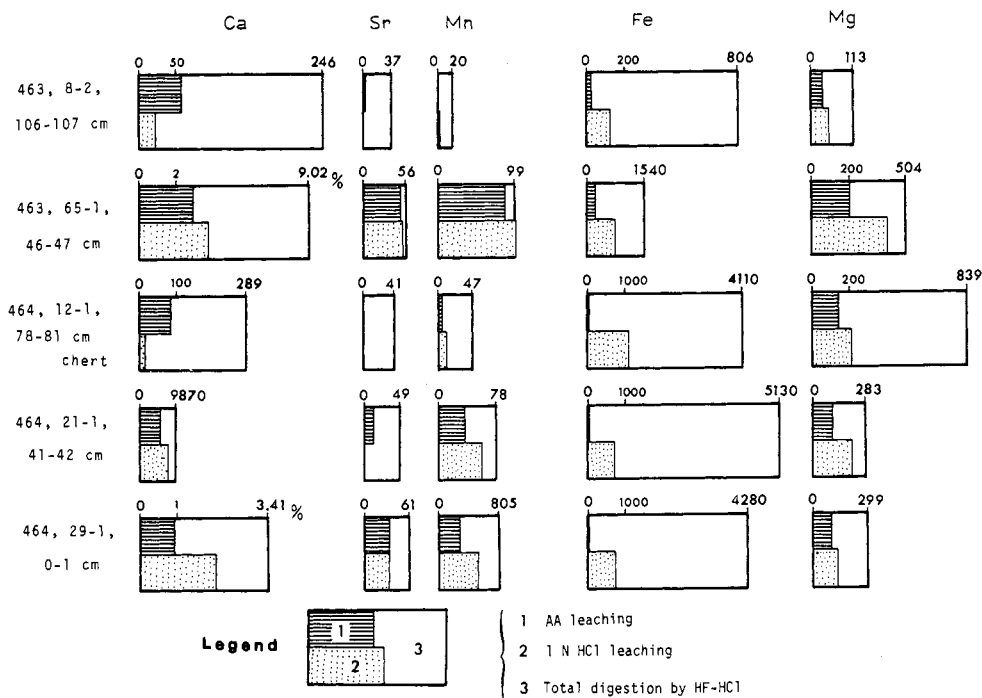


Fig. 2-13. Results of leaching experiments of Mn on DSDP flint samples. Concentrations are shown in ppm, otherwise indicated as %. (From Yamamoto, 1986b.)

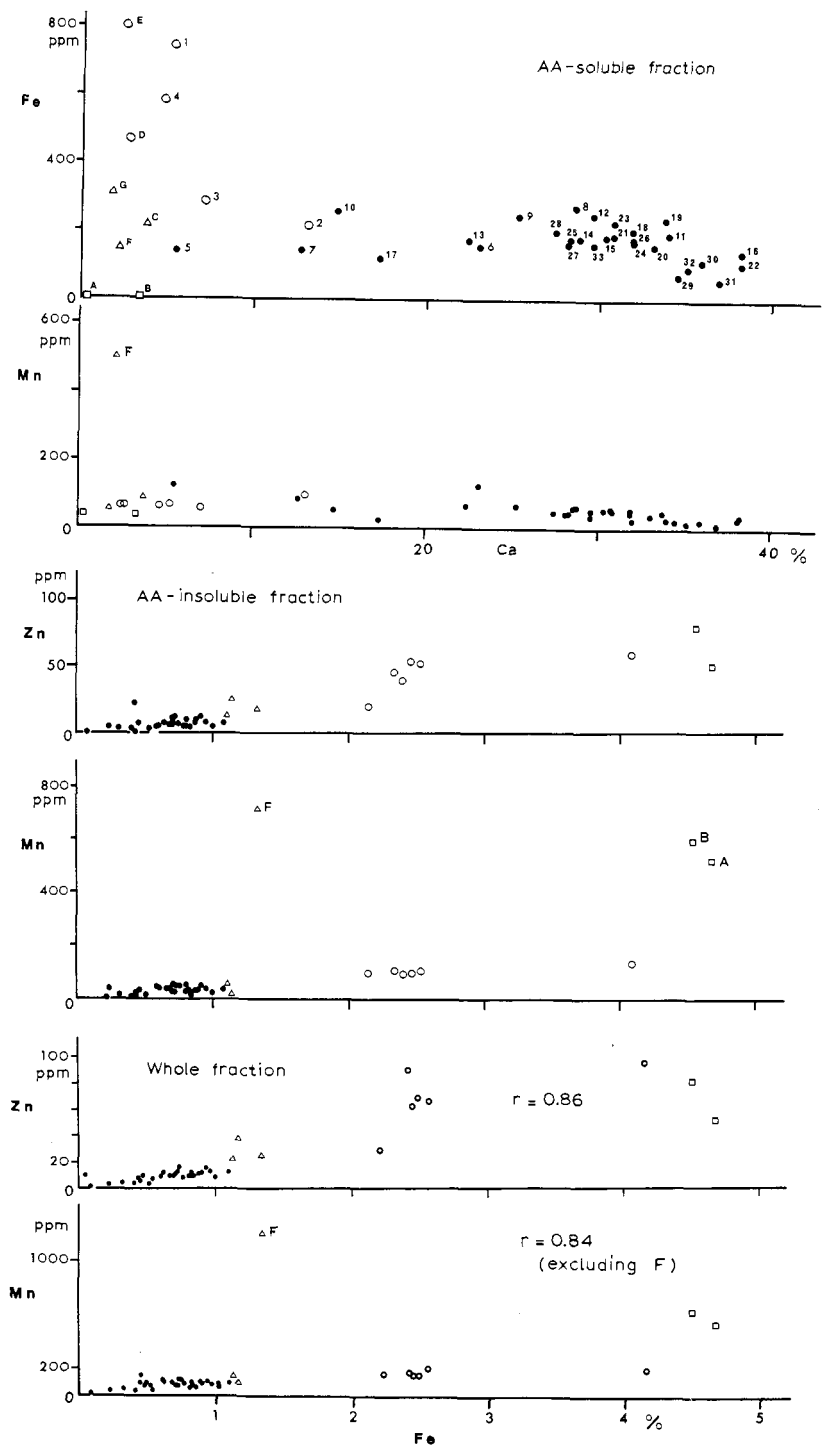
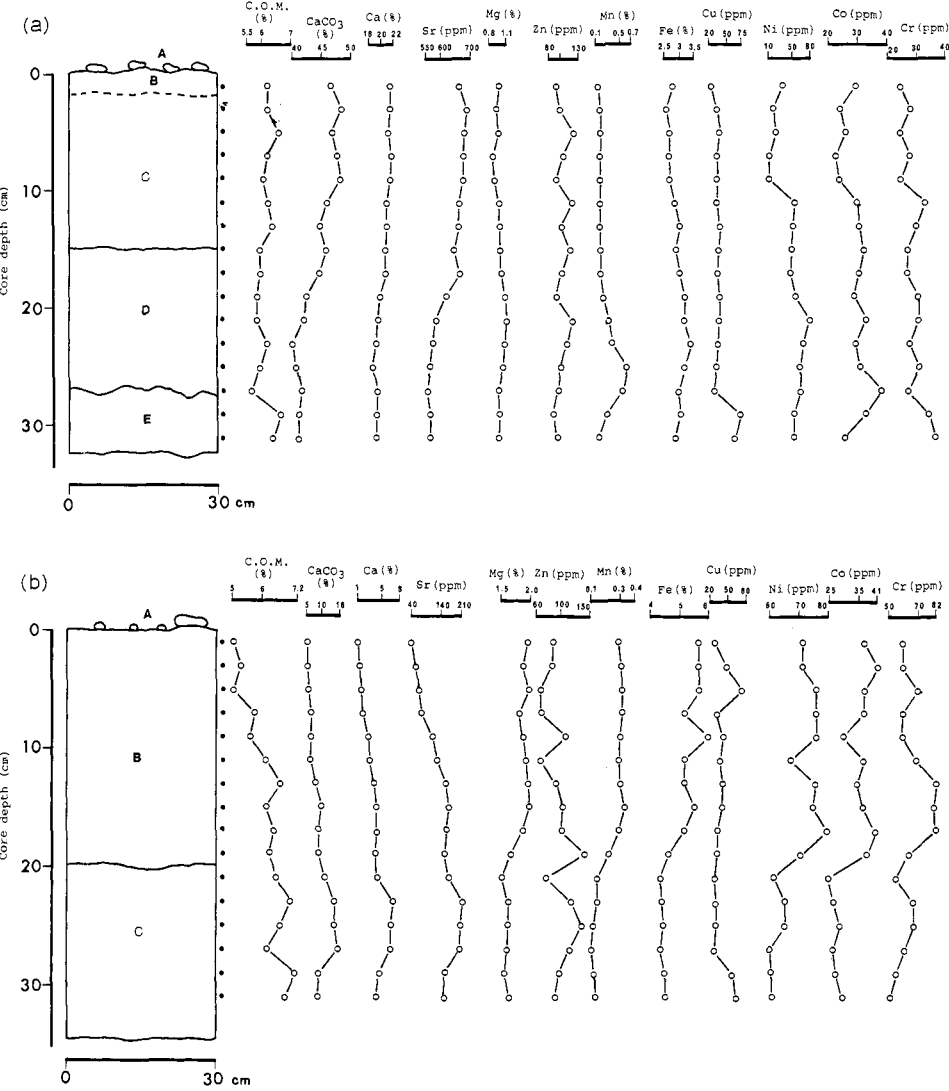


Fig. 2-14. Relationships among metallic elements in surface sediments of the Kin Bay and the Tengan River estuary regions. Sample labels and sites are same as Figs. 2-7 and 2-8. Mn concentrations in reddish soil are significantly higher than those in estuarine and marine sediments. High Mn concentration in river sand is due to dark-colored mud fragments, which are possibly rich in Mn. (From Yamamoto and Yuine, 1985.)

calcareous ooze from the Ogasawara Trench slope (KH80-1 St. 4) and in the possibly hydrothermal reddish clay from the Okinawa Trough (DELP84 D-7b), as shown in Fig. 2-12. The more detailed mechanisms are interpreted by Yamamoto and Oomori (1984) and Yamamoto (1986a).

The enrichments of Mn were observed in carbonates enclosed in the flint nodules (Yamamoto, 1986b). Several leaching experiments of Mn from the carbonate enclosures in flint nodules indicate that Mn is significantly concentrated in the carbonate enclosures (Fig. 2-13). The mechanism of the enrichment is speculative; however, it might be related to the bioturbation of foraminiferal ooze into the flint nodules, as the similar mechanism of Mn enrichment was observed in the burrowed



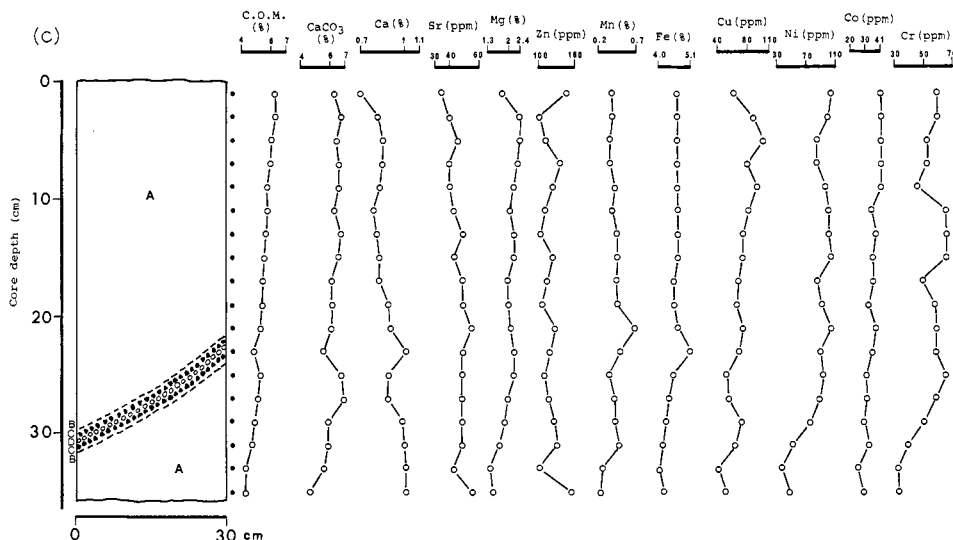


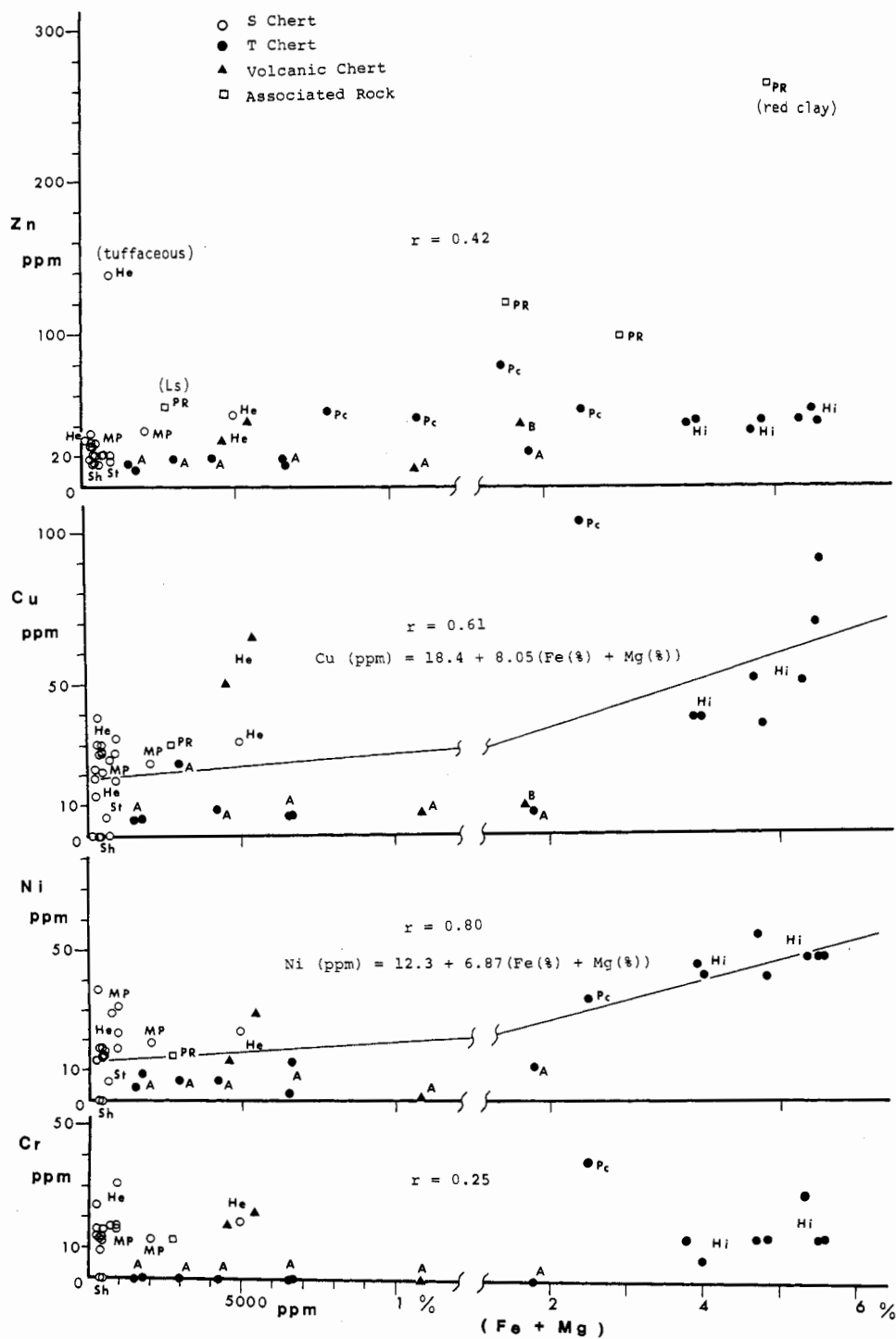
Fig. 2-15. (a) Sediment and chemical stratigraphy at KH80-1 St. 4 (water depth = 2970 m) in the Ogasawara Trench slope. Lithology: *A* = Pumice and scoria gravel; *B* = light gray foraminiferal sand; *C* = light gray nanno-foram sandy mud; *D* = brown nanno-foram mud with abundant burrows; *E* = gray nanno-foram mud with burrows. Contacts: *B* and *C* = gradual; *C* and *D* = sharp; *D* and *E* = gradational. Sampled positions (circles) are shown at right side of lithologic column. *C.O.M.* = combustible organic matter.

(b) Sediment and chemical stratigraphy at KH80-1 St. 5 (water depth 4310 m) in the Ogasawara Trench slope. Lithology: *A* = scoria and pumice gravel; *B* = reddish-brown nanofossil silty clay with dark brown burrows; *C* = pale yellowish-brown nanofossil silty clay with reddish-brown burrows. Contacts: *B* and *C* = gradational.

(c) Sediment and chemical stratigraphy at KH80-1 St. 9 (water depth 8260 m) in the Ogasawara Trench. Lithology: *A* = brown clay with radiolarians, diatoms and abundant siliceous spicules; *B* = volcanic shard layer; *C* = black volcanic sand lamina; *D* = well-preserved radiolarian sand lamina. (From Yamamoto and Oomori, 1984).

calcareous ooze (Swinbanks and Shirayama, 1984). Manganese, however, can be leached out from the sediment enriched in Mn. Yamamoto and Ujiie (1983) and Ujiie et al. (1983) have recognized that the brown mud supplied into the calcareous sand at the coral-reef environment does not show high concentrations of Mn, although the reddish soil in the source area may contain significantly higher concentrations of Mn. As illustrated in Fig. 2-14, Yamamoto and Yuine (1985) have attempted chemical analyses for the bulk compositions of the reddish to brownish soil – sediment samples in addition to the AA leaching. They observed that after the Mn in the reddish soil has been possibly leached out, the latter was deposited as Mn-poor brown mud in the estuary. On the basis of the Mn concentrations in the AA-insoluble fraction, the concentration of Mn is about 400 ppm lower in the estuarine brown mud than in the reddish soil on land area (Fig. 2-14).

Other transitional heavy metals, such as Zn, Cu, Ni, Co and Cr, show enrichments in the sediments according to biogenic and volcanic influences. Some



examples on the stratigraphic behaviors of these elements are presented in Fig. 2-15. Diagenetic enrichments may show some increases of such heavy metals as Mn, Cu, Zn, Ni and Cr in some horizons of the sediment columns. The diagenesis is suspected to be related to the biogenic activities represented as bioturbation and the chemical reactions between pore water and sediment particles. In addition to this, some metallic elements are concentrated in the lamina of the turbiditic volcanic sand, which was recovered from the seafloor of the Ogasawara Trench. The addition of volcanic material, particularly basalt fragments, in the sediment apparently increases the concentrations of heavy metals. Figure 2-16 shows the increase in the concentrations of Zn and Cr due to the addition of fine-grained basaltic fragments in the flinty nodules, particularly in the samples recovered from the Hess Rise (Yamamoto, 1986b).

The concentrations of heavy metals might be higher in the deep-sea clays than in the shallow-water clays on the carbonate-free basis. Table 2-4 demonstrates such an example that the shallow-water sediments are lower in the heavy metal concentrations than the deep-sea sediments. Based on the comparison of the carbonate-silicate mixed sediments from shallow bays, continental shelf, and deep-sea floors, it can be concluded that the heavy metals such as Mn, Zn, Cu and Ni are more highly concentrated in the deep-sea sediments than the shallow-water sediments. Table 2-4 also demonstrates that the deep-sea brown muds are more concentrated in Mn than the grayish mud, although such a tendency is not recognized in the shallow-water sediments. The brown mud in the East China Sea was derived from the Okinawa Trough (Kimura et al., 1986), and it could be considered as of the same origin as the deep-sea red clay because of higher concentrations of Mn and Ni (Yamamoto, 1986a). In the deep-sea, the grayish mud can form in a reducing environment due to the high deposition rates of organic matter, whereas the reddish mud formed in an oxidizing environment with a slower depositional rate of organic matter (Lyle, 1983). At low rates of organic matter deposition, the diffusion of oxygen into the sediment exceeds its consumption (Lyle, 1983) and the diffusion may bring the diagenetic Mn into the oxidizing reddish mud.

The heavy metals in deep-sea sediments are suspected to be derived from either the volcanic emanation beneath the seafloor or the clay mineralization of basaltic rocks in the floor. The heavy metal concentrations in the basaltic rocks are as high as the deep-sea sediments, except for Mn (Nockolds and Allen, 1953, 1954; Goldberg and Arrhenius, 1958; Yeats et al., 1973; Thompson et al., 1976; Yamamoto and Oomori, 1984). The clay-forming processes of basalts can be important sources of heavy metals in deep-sea sediments. In addition to this, the newly formed Fe-montmorillonite is known to adsorb some heavy metals (Traina and Doner, 1985).

Fig. 2-16. Relationships of Zn, Cu, Ni and Cr to concentrations of Fe(%) plus Mg(%) in cherts. Labels beside plots are same as in Fig. 2-4. Anomalous concentrations in Zn and Cr are recognized for 465A, 37-1 sample (labelled as "tuffaceous" and He), and this sample is excluded for calculations of r 's and regression lines. (From Yamamoto, 1986b.)

Statistical summary on metallic elements in biogenic sediments and clay¹

	N	COM(%)	CaCO ₃ (%)	Fet(%)	Mg(%)	Mn(ppm)	Zn(ppm)	Sr(ppm)	Cu(ppm)	Ni(ppm)
I. Shallow-water sediments (Okinawa bays)										
Carbonates	81	4.45 (0.847)	66.1 (11.6)	0.936 (0.364)	1.19 (0.305)	88.1 (30.7)	82.1 (54.1)	978 (272)	4.4 (3.2)	10.4 (3.0)
Gray mud	4	6.13 (0.91)	24.9 (6.19)	2.72 (0.32)	0.752 (0.213)	288 (21.0)	247 (96.0)	600 (172)	6.3 (0.6)	15.9 (1.5)
Brown mud	9	6.68 (2.85)	18.4 (9.24)	3.63 (0.95)	0.836 (0.244)	283 (37.1)	172 (31.0)	178 (120)	7.7 (3.6)	18.2 (11.8)
II. Continental margin sediments (East China Sea)										
Gray sand and mud	22	5.23 (1.79)	21.8 (12.4)	2.13 (1.10)	0.569 (0.198)	419 (194)	32.4 (14.0)	343 (410)	8.4 (4.0)	19.8 (8.8)
Brown mud	6	6.71 (1.04)	26.1 (8.77)	2.46 (0.669)	0.782 (0.265)	3790 (2730)	56.0 (20.5)	344 (134)	13.9 (2.39)	40.6 (9.31)
III. North Pacific deep-sea sediments										
Carbonates	15	5.23 (1.88)	61.0 (18.2)	1.63 (1.12)	0.657 (0.305)	1130 (830)	103 (43.7)	842 (293)	34.1 (2.3)	28.6 (17.7)
Gray mud	25	6.77 (1.60)	3.97 (0.674)	2.69 (0.721)	0.884 (0.321)	492 (141)	48.4 (15.8)	54.4 (18.3)	58.9 (17.6)	54.5 (11.8)
Brown mud	36	5.82 (0.76)	7.52 (2.83)	4.69 (0.55)	1.86 (0.31)	3280 (1240)	112 (34.9)	88.3 (59.9)	58.5 (23.3)	77.4 (16.6)
IV. Atlantic deep-sea sediments										
Carbonates	73	7.83 (2.65)	69.5 (11.6)	0.575 (0.311)	0.172 (0.042)	218 (136)	34.9 (14.6)	633 (253)	20.8 (23.8)	-
Gray mud	10	12.5 (0.84)	13.9 (8.69)	2.45 (0.39)	0.333 (0.049)	274 (183)	155 (140)	445 (216)	65.6 (72.1)	-
V. North Pacific deep-sea cherts										
Bedded cherts	4	1.93 (0.45)	1.25 (1.25)	1.22 (0.69)	0.576 (0.322)	734 (894)	65.6 (22.4)	-	-	-
Chert nodules	23	1.46 (0.40)	3.05 (4.30)	0.165 (0.356)	0.0191 (0.018)	69.5 (165)	30.4 (25.5)	41.7 (11.8)	25.5 (13.5)	34.8 (13.4)
(Total)	308									

¹ Mean (standard deviation) . . . dry weight concentrations.

COM: Combustible organic matter between 100° and 550°C.

Source of data: Yamamoto (1977, 1981, 1984, 1985a, 1986a, b); Yamamoto and Ujiie (1983); Yamamoto and Oomori (1984); Yamamoto and Yuine (1985).

RECOGNITION OF DEEP-SEA SEDIMENTARY ROCKS THROUGH Fe/Mg RATIOS

For geologists, the modern ocean floor and its depositional environments have been suspected to be important keys for reconstruction of the ancient depositional environments through sedimentary sequences. For example, cherts have been considered as the sedimentary rocks which were deposited on the deep-sea floors of the open sea. In the modern ocean floor, siliceous ooze or biogenic opal-CT which could be a source of sedimentary cherts is known to deposit in the open sea including marginal shelf seas (Lancelot, 1973; Keene, 1975; Von Rad et al., 1977). The depositional environments of sedimentary cherts, therefore, can not be regarded only as the pelagic equivalent of deep-sea environments, without indicating the evidence of the pelagic deep-sea environments. The sedimentary cherts should contain the information to show such evidence. The correlation between Fe and Mg may be useful as evidence of deep-sea environments for sedimentary cherts, because the deep-sea ferromagnesian clay minerals may be characteristically present in the cherts of deep-sea origin. In addition, the concentration of heavy metals could be used as the indicator of deep-sea environments for sedimentary cherts.

There are some geochemical studies on cherts from the land area (e.g., Matsumoto and Iijima, 1983; Steinberg et al., 1983). Although Hein et al. (1981) showed that the deep-sea cherts have higher boron (B) content than the shallow-water ones, any other evidence to prove the deep-sea origin of cherts has not been furnished as yet. The possible proof could be made by investigating the Fe(%) / Mg(%) ratios in sedimentary cherts (Yamamoto, 1986b). The Fe(%) / Mg(%) ratio is believed to be very uniform in the deep-sea cherts in comparison to the shallow-water cherts. The ferromagnesian silicate minerals contained in the cherts can become index minerals indicating the pelagic depositional environments in which the ferromagnesian minerals may be supplied from the clay mineralization of basaltic rocks. It can be applied to recognition of the depositional environments for other sedimentary rocks, particularly for reddish shale, assuming that the oceanic basalt is the source of the fine-grained silicate minerals.

The reconstruction of water depths of the depositional environments should be made by geochemical methods other than the Fe(%) / Mg(%) ratio (Halbach and Puteanus, 1984), because this ratio only indicates that basaltic oceanic crust is the source. The other possible estimation on the paleo-depths in the deep sea is whether the paleo-depth was deeper or shallower than the calcite compensation depth (CCD), if the dissolution of calcite during the depositional processes could be recognized in the ancient sedimentary records. No apparent chemical change of carbonates was recognized by the dissolution processes of carbonates in modern sediments (Yamamoto, 1977). According to some geochemical studies on the modern sediments from the Japan Trench area (Mann and Müller, 1980; Matsumoto and Iijima, 1980; Nohara, 1980a, b), no apparent chemical and mineralogical characteristics were recognized in the noncalcareous clays due to the depth changes in the deeper basins of the Japan Trench.

The clay mineralization in the deep sea may involve unique reaction processes on the basaltic oceanic crust. Although terrigenous clays can be transported into the deep sea through several repetitions of transportation and deposition (Gorsline,

1985), the clays in deep sea may be different from the terrigenous ones in terms of genesis and composition. The clay minerals in the deep sea are generally rich in the montmorillonite (smectite), which might be produced by the halmyrolytic alteration of volcanic products (Griffin et al., 1968; Weaver and Pollard, 1975; Aoki and Oinuma, 1978, 1984). The terrigenous clays or clayey sediments are characterized by high concentration of detrital quartz (Rex and Goldberg, 1958; Kolla and Biscaye, 1977) and other detrital minerals. When the detrital minerals are supplied from the continent and transported into the open sea, the finer mineral grains may be deposited near the continent and the coarser grains will be transported offshore, because of hydrodynamic and other reasons (Honjo et al., 1974; Yamamoto, 1979). Pelagic clays, therefore, are not derived from the continent; instead, the pelagic clays are assumed to be formed authigenically on the ocean floor. If one can identify the authigenic pelagic clays, possibly by geochemical methods, in the ancient sedimentary rocks, one may be able to recognize a similar depositional environment on the modern deep-sea floor for an ancient sedimentary record.

SUMMARY AND CONCLUSIONS

The concentrations of heavy metals in clay fraction of deep-sea sediments were compared with those of some shallow-water sediments in the coastal areas of the Okinawa Islands and in the East China Sea. Also, the comparison was made between Fe—Mg correlations of these deep-sea and shallow-water sediments. The comparisons indicate that the deep-sea sediments of the Pacific floor are more enriched with heavy metals including Mn than the shallow-water sediments and the correlations between Fe and Mg are stronger in the deep-sea sediments. The correlation between Fe and Mg might be explained by the high concentrations of ferromagnesian silicate minerals in the deep-sea sediments and this correlation may become the recognition criterion for deep-sea sedimentary rocks which are presently exposed on land area.

The high concentration of Fe-montmorillonite clay in the deep-sea sediment might explain the high correlation between Fe and Mg content in the sediments. The Fe-montmorillonite may contain equal proportions of the Fe and Mg in its mineralogical structure (Bischoff, 1969). The formation of Fe-montmorillonite in the deep-sea clay might be caused by the halmyrolytic alteration of deep-sea basalts. Olivine present in the deep-sea clay is a side product of clay mineralization of basalt (Yamamoto, 1982). Although the relation of the concentrations of Fe-montmorillonite and olivine clays to the correlation between Fe and Mg contents is not clearly understood, the very high concentration of Fe-montmorillonite and olivine in the deep-sea clay and the constant $\text{Fe}(\%) / \text{Mg}(\%)$ ratio are the most important features of deep-sea sediments. When these clay minerals with the constant ratio of $\text{Fe}(\%) / \text{Mg}(\%)$ are changed into another mineralogical phase, the constant ratio of $\text{Fe}(\%) / \text{Mg}(\%)$ could become the indicator of the deep-sea sedimentary environments in the geological records.

The high concentrations of heavy metals are characteristic features of the deep-sea clays, when they are compared with the shallow-water clays. Among the transi-

tional heavy metals, Mn can be enriched in the deeper water sediments due to adsorption onto the sinking particulates, but the primary mechanism in the concentrations of Zn, Cu, Ni, and other heavy metals is caused by the possible volcanic emanation beneath the deep-sea floors as well as the adsorption onto the sinking particulates in the water column. The enrichment of heavy metals such as Ni and Co may be also related to the mineralogical structures of deep-sea clays. The Fe-montmorillonite clay is able to adsorb more heavy metals than other clay minerals (Traina and Doner, 1985), or the genesis of the Fe-montmorillonite is associated with the hydrothermal enrichments of heavy metals in the deep-sea clays. Although the exact mechanism is very speculative, the statistical comparison between the non-calcareous deep-sea and shallow-water clays suggests that the deep-sea ferromagnesian clays are metalliferous.

The presence of the ferromagnesian pelagic clay minerals enriched with heavy metals in the modern deep-sea clays can be a useful recognition criterion of the depositional environments of the deep-sea sedimentary rocks in the geological records. Although the original mineralogical makeup of ancient sedimentary rocks may have changed during the diagenetic processes, the geochemical information preserved in the original minerals or rock could remain unchanged during the diagenetic processes in the sedimentary rocks for such metallic elements as Fe and Mg. Magnesium can be contained in several different phases, such as in the interstitial water, carbonate fraction, and silicate-clay mineral fraction; however, the Mg trapped in the crystalline structures of the silicate-clay minerals may be rather stable and the bulk Mg contents of the rock could remain unchanged during the diagenesis. If one can identify the Fe(%) / Mg(%) ratio in the silicate-clay mineral fractions of the sedimentary rock, the ratio may become the important key to the recognition of deep-sea depositional environments. When one cannot identify the Fe-montmorillonite and other minerals indicative of pelagic environments in the sedimentary rocks because of the diagenetic transformation of the minerals, chemical information, particularly such information as Fe(%) / Mg(%) ratio, may become a better recognition criterion of the depositional environments. This ratio, which is particularly interesting in the sedimentary cherts, can also be used in the shales and other sedimentary rocks for the recognition of deep-sea pelagic depositional environments. The concentration of the transition heavy metals in the pelagic ferromagnesian clays should be carefully examined in both the modern sediments and ancient sedimentary rocks in order to reconstruct the ancient deep-sea depositional environments through the sedimentary records.

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Chapter 3

DIAGENETIC TRANSFORMATIONS OF MINERALS AS EXEMPLIFIED BY ZEOLITES AND SILICA MINERALS – A JAPANESE VIEW

AZUMA IIJIMA

Part I. Zeolitic diagenesis

INTRODUCTION

Over two centuries have passed since zeolite was discovered and named by Cronstedt in 1756. Collection and mineralogical description of beautiful, coarse crystals were the primary studies on zeolites for a long time till early this century, and this still continues. In Japan the discovery of a new zeolite, yugawaralite, by Sakurai and Hayashi in 1952, is remarkable, though the data of its chemical composition was revised by Seki and Haramura (1966). It was a great benchmark event that the concept of zeolite facies was established by Eskola in 1936 as the lowest grade of the metamorphic facies. The concept of zeolite facies was greatly developed by Coombs and co-workers in 1950's based on hydrothermal synthesis as well as field work in Triassic geosyncline deposits of New Zealand (Coombs, 1954; Coombs et al., 1959). Coombs' work focused attention on the genesis of fine-grained zeolites in sedimentary rocks, especially in volcanoclastic rocks. In Japan the study of zeolitic rocks was certainly stimulated by Coombs' work, although Sudo and co-workers discovered earlier microscopic mordenite and clinoptilolite in "Ohya-ishi", a famous building stone of green altered pumice tuff of Miocene age from Ohya, Tochigi, and in a few bentonite deposits (Ota and Sudo, 1949; Sudo, 1950; Sudo et al., 1963). On the other hand, the pioneer researches on zeolites in saline, alkaline lake deposits by Hay (1966) and Sheppard and Gude (1968) in 1960's undoubtedly influenced the study of zeolitic diagenesis in Japan by Iijima who studied the Green River Formation with Hay (Iijima and Hay, 1968) and by the Japan and U.S. Joint Seminars on Natural Zeolites in 1971 and 1974. The demand for zeolite aggregates as a natural resource has increased in Japan since early 1960's and also stimulated the study of zeolitic rocks.

Japan is one of excellent localities in the world to study the occurrence and genesis of natural zeolites, because volcanic glass of varying composition that is the best raw material of zeolites occurs widely in volcanoclastic rocks of younger geologic ages (Fig. 3-1). Zeolites are common in altered vitric tuffs interbedded with thick piles of geosynclinal deposits of Tertiary and Cretaceous age. In the so-called Green Tuff region, in which the relatively thick, subaerial and submarine volcanics and volcanic sediments of Miocene age have been altered to green-colored rocks, fine-grained zeolitized tuffs constitute many minable zeolite deposits which are utilized for paper filler, carrier of fertiliser, soil reformer, concentrators of oxygen and nitrogen gas, purification of sanitary water, etc.

The occurrence of zeolites in Japan was reviewed by Iijima and Utada (1966, 1972), Minato and Utada (1969), and Utada (1971, 1973). Zeolites in marine sediments and sedimentary rocks and zeolitic diagenesis were summarized by Iijima (1978a, b). Iijima reviewed the geology of zeolites and zeolitic rocks (1980, 1986a), and further investigated a petrochemical aspect of the zeolite formation in volcanoclastic rocks (1984). Utada (1980a) reviewed rock alterations in the younger orogenic belts of Japan. Seki (1969, 1973) summarized zeolite facies from metamor-

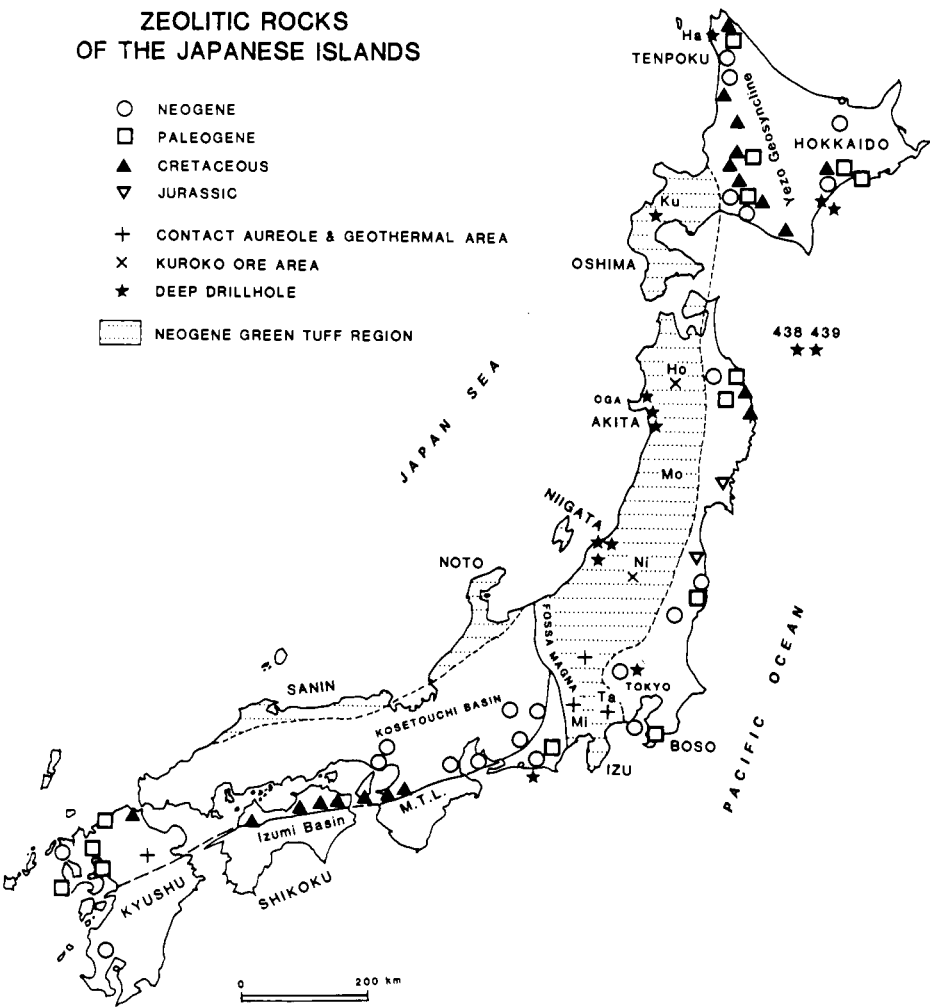


Fig.3-1. Distribution map of zeolitic rocks of the Japanese Islands. Zeolites of different occurrences are abundant in the Neogene Green Tuff region where thick piles of marine and non-marine volcanics were deposited. *Ha* = MITI-Hamayuchi well; *Ku* = MITI-Kuromatsunai well; *Ho* = Hokuroku district; *Mo* = Mogami district; *Ni* = Nishiaizu district; *Ta* = Tanzawa Mountains; *Mi* = Misaka Mountains; *M.T.L.* = Median Tectonic Line.

phic viewpoint, whereas the utilization of zeolites was reviewed by Torii (1978) and Minato and Tamura (1978).

GENETIC TYPES OF ZEOLITE OCCURRENCE

Zeolites, a group of hydrous aluminosilicates, are forming at present or formed in the past on the Earth's surface or near surface, in deep-sea oceanic sediments, and in volcanic and sedimentary rocks at various subsurface depths. Zeolites are frequently found as the principal authigenic constituent of such sediments and sedimentary rocks (Iijima and Utada, 1966; Iijima, 1978a, 1980, 1986a; Hay, 1966, 1978, 1986). Zeolites originate from many kinds of precursor minerals such as volcanic glass, impact glass, non-crystalline and crystalline clays, feldspar, feldspathoid, and even zeolite itself (Table 3-1). Volcanic glass fragments, however, are the most important and suitable starting material for natural zeolites, owing to their high chemical reactivity, their bulk composition similar to zeolites, and their common occurrence in space and time. Consequently, vitric volcanoclastic rocks are superior as both precursor and host rock of zeolites.

The composition of zeolite species and host volcanic rock types are listed in Table 3-2. Water is indispensable to zeolites so that the geologic occurrence of zeolites can best be classified on the basis of the states of interstitial water in zeolitic rocks. A classification scheme is given in Table 3-3. Much work in the field and in laboratories has proved that temperature is a major factor in controlling zeolite formation as shown in Table 3-4, in which natural zeolite species are arranged in the order of formation temperature. Chemistry of pore water plays another important role of zeolite formation: e.g., in saline, alkaline lake deposits, different kinds of zeolites originate in the same single tuff bed at nearly surface condition. As a result of the presence of a geothermal or chemical gradient, zeolites commonly occur in a vertically or laterally zoned arrangement, which is commonly mappable as zeolite zones. Figure 2 demonstrates schematic profiles of such zonation of five of seven genetic types of zeolite formation in volcanoclastic rocks, and Table 3-5 shows common sequences of zeolite units of different genetic types (Iijima, 1984). Only a brief summary of different types is presented here.

TABLE 3-1

Raw material of natural zeolites

Amorphous material	Crystalline material
Volcanic glass	Zeolites
Impact glass	Feldspar
Weathering aluminosilica gel	Feldspathoids
Aluminosilica gel in saline, alkaline lake	Smectite and other clay minerals
Biogenic opal	
Diatoms, radiolaria, sponge spicules	

TABLE 3-2

Composition of natural zeolites and composition of host volcanic rocks. The zeolites are arranged from less siliceous to more siliceous varieties. Data are based on Iijima and Utada (1972, 1981) and Gottardi and Galli (1985)

Species	Si/(Si + Al + Fe)	H ₂ O ¹	Dominant cation	Host rock ²
Partheite	0.50	1.0	Ca	
Amicite	0.50	1.3	Na, K	U
Willhendersonite	0.50	1.7	Ca, K	U
Gismondine	0.50–0.57	2.0–2.2	Ca	U B
Phillipsite	0.52–0.77	1.7–3.3	Ca, Na or K	U B I A
Thomsonite	0.50–0.52	1.2	Ca	U B
Gonnardite	0.52–0.58	1.0–1.2	Na	U B I
Ashcroftine	0.56	2.0	K	U
Mesolite	0.60	1.3	Ca or Na	U B I
Scolecite	0.60	1.5	Ca	U B I
Natrolite	0.60	1.0	Na	U B I
Paranatrolite	0.60	1.0	Na	
Tetranatrolite	0.60	1.0	Na	
Cowlesite	0.60	2.5–3.0	Ca	B
Edingtonite	0.60	2.0	Ba	U B
Garronite	0.63	2.2	Ca	B I
Analcime	0.63–0.74	1.0–1.3	Na	U B I A
Chabazite	0.63–0.80	2.7–4.1	Ca or Na	U B I A
Gmelinite	0.67	2.8	Na	B
Levyne	0.67	3.0	Ca	B
Bikitaite	0.67	1.0	Li	
Laumontite	0.66–0.71	2.0	Ca	U B I A
Wairakite	0.67	1.0	Ca	B I A
Gobbinsite	0.69	2.2	Na	B
Faujasite	0.69–0.71	3.9–4.6	Na or Ca	U B
Merlinoite	0.72	2.7	K or Ba	U
Mazzite	0.72	2.8	K, Mg	B
Stilbite	0.72–0.78	2.8–3.5	Ca or Na	B I A
Offretite	0.72–0.78	3.5	Ca, Mg	B
Harmotome	0.73–0.75	2.4	Ba	U B I
Heulandite	0.73–0.80	2.5–3.1	Ca or Sr	B I A
Erionite	0.74–0.79	3.0–3.5	K, Ca or Na	B I A
Yugawaralite	0.75	2.0	Ca	B I A
Goosecreekite	0.75	2.5	Ca	B
Brewsterite	0.75	2.5	Sr	
Epistilbite	0.75	2.7	Ca	B I A
Paulingite	0.76	4.4	K or Ca	
Barrerite	0.78	3.5	Na	I A
Stellerite	0.78	3.3	Ca	B I
Dachiardite	0.78–0.86	4.5	Ca or Na	B I A
Clinoptilolite	0.80–0.85	3.5–4.0	Na, K or Ca	B I A
Mordenite	0.81–0.85	3.0–3.5	Na or Ca	B I A
Ferrierite	0.83–0.85	3.3	Mg, K or Na	B I A

¹ Number of H₂O is equivalent to 1 aluminum.

² Host rock: U = ultrabasic, B = basic, I = intermediate, and A = acidic.

TABLE 3-3

Classification of geologic occurrence of natural zeolites arranged in order of increasing formation temperature

Deep-sea oceanic sediments
 Weathering in semi-arid tracts (supergene type A)
 Saline, alkaline deposits
 Percolation of meteoric water (supergene type B)
 Burial diagenesis
 Hydrothermal alteration and contact metamorphism
 Primary magmatic

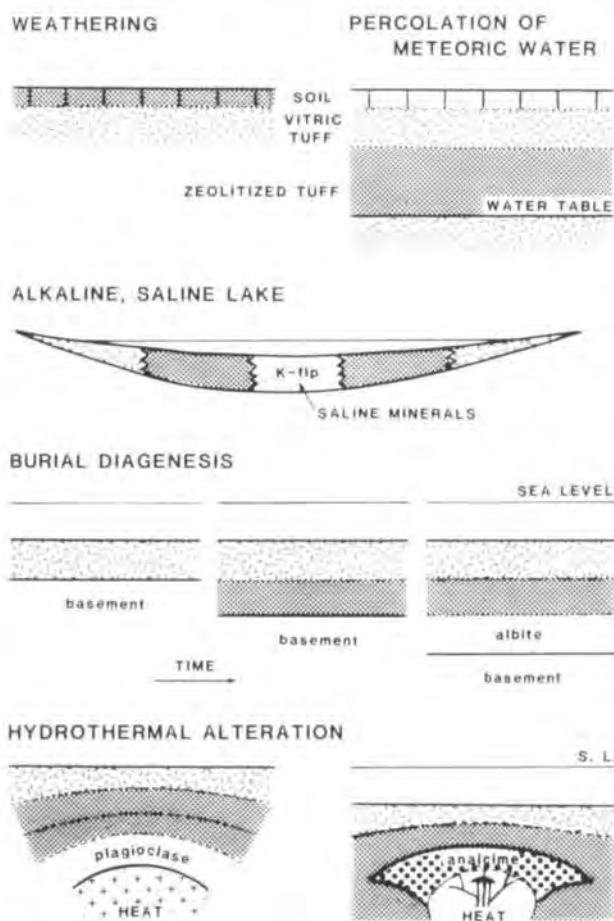
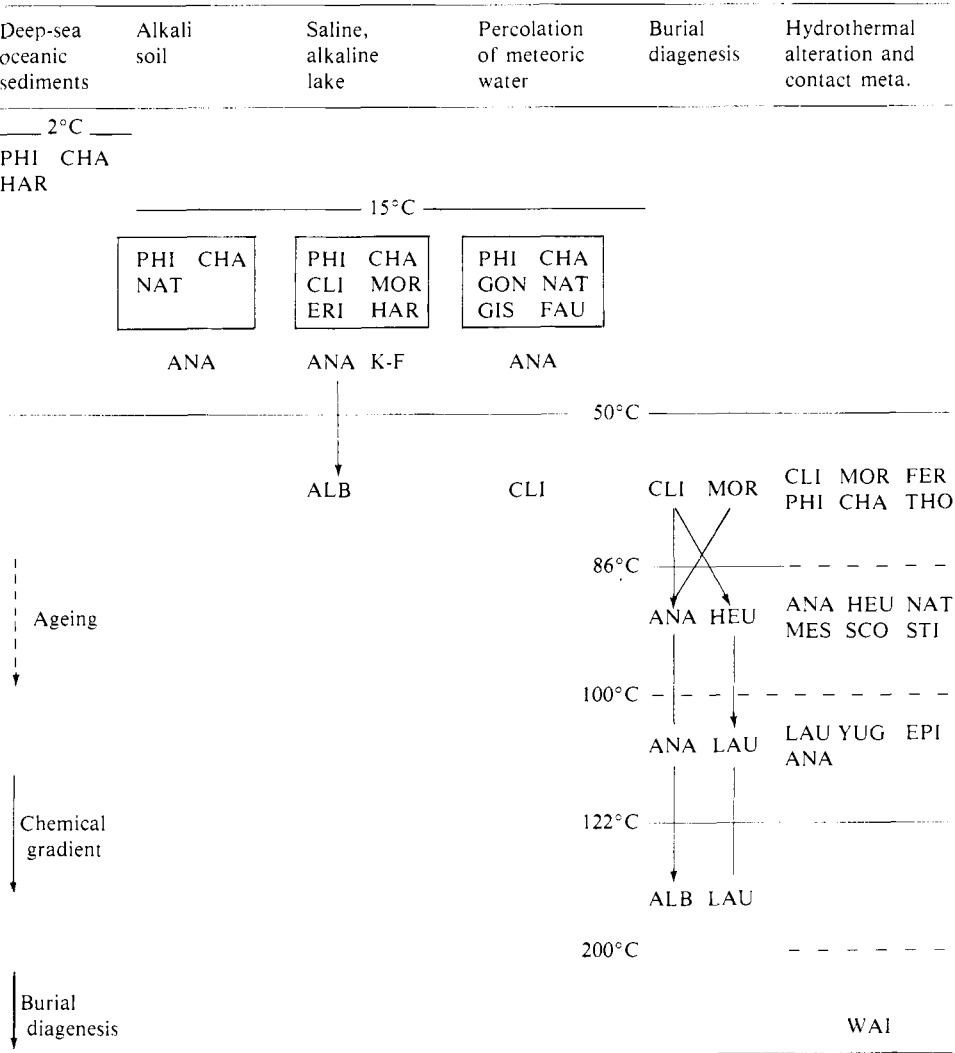


Fig.3-2. Schematic profiles showing alteration zoning of five genetic types of zeolite formation. The gray zones represent zeolite zones. The bottom right profile shows submarine hydrothermal alteration zoning related to the Kuroko polymetallic sulfide ore mineralization; the stippled area shows lenticular analcime zone capping the open, argillaceous zone. *K-flp* = authigenic K-feldspar. (After Iijima, 1984, fig. 1, p. 32. Courtesy of VNU Science Press.).

Deep-sea oceanic sediments

Phillipsite is dominant in deep-sea, oceanic brown clays and altered mafic tuffs of Miocene and younger age in the tract of low sedimentation rate of the Pacific

TABLE 3-4
Types and approximate temperatures of the zeolite formation and zeolite species



PHI = phillipsite, CHA = chabazite, NAT = natrolite, CLI = clinoptilolite, MOR = mordenite, ERI = erionite, GON = gonnardite, GIS = gismondine, FAU = faujasite, ANA = analcime, FER = ferrierite, THO = thomsonite, HEU = heulandite, STI = stilbite, MES = mesolite, SCO = scolecite, LAU = laumontite, YUG = yugawaralite, EPI = epistilbite, WAI = wairakite, HAR = harmotome, K-F = K-feldspar, ALB = albite.

and Indian oceans (Iijima, 1978a; Kastner and Stonecipher, 1978). Phillipsite is very slowly formed by interaction of mafic glass fragments with interstitial water at a restricted sub-bottom depth between about 1–2 and 4 m (Glaccum and Boström, 1976). Clinoptilolite is, on the other hand, abundant in altered silicic tuff, pelagic clay, siliceous and calcareous oozes of pre-Miocene age in the region of rather high sedimentation rate of the Atlantic Ocean and marginal seas. Clinoptilolite is formed by interaction of silicic and intermediate glass, biogenic opal and mafic glass, or clay with interstitial water at a rather greater sub-bottom depth, hence at an increasing temperature at around 50°C (Iijima, 1978a; Iijima et al., 1980).

Weathering (supergenes type A)

Zeolites form in alkali soils of semi-arid tracts by interaction of minerals with alkaline soil water of pH over 9. In the Quaternary red alluvial deposits of the Olduvai Gorge in Tanzania, for example, rhyolitic obsidian, nepheline basalt tuff, and even non-ash clay are altered to red aggregates of phillipsite, chabazite, natrolite and analcime, which may change to a red analcimolite by aging, a probable analogue of the red analcimolites in the Mesozoic redbeds (Hay, 1970, 1978) in the Congo Basin of central Africa and the Uinta Mountains of Utah.

TABLE 3-5

Genetic types of zeolite formation in volcanoclastic rocks

Deep-sea sediments
Mafic glass → phillipsite
Mafic glass and biogenic silica → clinoptilolite
Silicic glass → clinoptilolite
Weathering (supergenes type A)
Trachytic glass → phillipsite, chabazite → analcime
Saline, alkaline lake deposits
Silicic glass → zeolites → K-feldspar
↓
analcime → K-feldspar
(zeolites: phillipsite, chabazite, erionite,
clinoptilolite, mordenite)
Percolation of meteoric water (supergenes type B)
Mafic and ultramafic glass → phillipsite → chabazite →
gonnardite → natrolite → analcime
Silicic glass → clinoptilolite
Burial diagenesis
Silicic glass → clinoptilolite, mordenite → analcime → albite.
↓
heulandite → laumontite
Hydrothermal alteration and contact metamorphism
Mafic glass → zeolites → laumontite → wairakite →
yugawaralite
Silicic glass → clinoptilolite, stilbite, mordenite →
heulandite, analcime → laumontite → wairakite →
yugawaralite

Saline, alkaline lake deposits

Zeolites form in saline, alkaline lake deposits in closed basins in semi-arid regions. Volcanic glass, amorphous clay, and some crystalline clay minerals react with interstitial alkaline brines to form several varieties of zeolites and K-feldspar by low-temperature and low-pressure diagenesis (Hay, 1966; Sheppard, 1973). Such deposits of Quaternary and Tertiary ages were reported from many localities in the west of the United States and East Africa (Surdam and Sheppard, 1978). Excellent examples are the Pleistocene Lake Tecopa Beds and the Miocene Barstow Formation of Southern California (Sheppard and Gude, 1968, 1969). In the alluvial fan and the lake margin deposits accumulated under a freshwater environment, glass fragments in a silicic tuff bed were slightly to completely altered to smectite. In the playa lake deposits, the glass fragments in the same tuff bed reacted with highly alkaline (pH 9–11) brines to form phillipsite, chabazite, erionite, clinoptilolite and mordenite, which are replaced by analcime by aging. The ratio of analcime to other zeolites in the saline, alkaline lake deposits, therefore, can be represented as a function of geologic time (Hay, 1966, 1978). In the lake-center where sodic saline minerals precipitated, all zeolites were dehydrated to K-feldspar and quartz. As a result, the lateral diagenetic zoning – fresh glass or smectite zone, zeolite zone, and K-feldspar zone from lake-margin to lake-center – characterizes the zeolite formation in the saline, alkaline lake deposits. This zonation is based on the chemical environment in contrast to the analcime zone which is time-dependent.

Percolation of meteoric water (supergene type B)

Zeolites occur in the vadose zone in a thick pile of land-laid vitric ash. Percolating meteoric water through the ash column reacts with glass fragments to increase in pH and concentration, until zeolites precipitate in the interstitial pores and voids of dissolved glass shards (Hay, 1963; Hay and Iijima, 1968). As a result, the open system produces vertical zones consisting of surface soil, fresh ash or slightly altered, opal – montmorillonite-cemented tuff, and zeolitic tuff. Boundaries of each zone are roughly parallel to the topography. In the phreatic zone below the groundwater table, unaltered or bentonitic, non-zeolitic tuff appears again. Typical examples are the Plio-Pleistocene Koko Crater Tuff on Oahu Island, Hawaii (Hay and Iijima, 1968) and the Oligocene John Day Formation of Oregon (Hay, 1963). A column of ultramafic sideromelane tuff, about 12–18 m thick, is enough for percolating meteoric water to precipitate silica-poor zeolites by interaction with sideromelane fragments. On the other hand, a column of rhyolitic tuff, about 200 m thick – that is approximately ten times thicker than the ultramafic tuff – is needed for the formation of siliceous clinoptilolite by interaction of silicic glass fragments with percolating meteoric water.

Burial diagenesis

Zeolites form successively in vitric volcanoclastic rocks interbedded with a marine or freshwater, thick sequence as temperature and pressure increase with the increas-

ing burial depth. The zeolites formed during burial diagenesis are, therefore, distributed in a vertically zonal arrangement, contrasted with the horizontal zonation of zeolites in alkaline, saline lake deposits. Details are given in the next section.

Hydrothermal alteration and contact metamorphism

Zeolites occur in hydrothermally altered volcanic and volcanoclastic rocks. Present-day zeolitization is known in many geothermal areas of the world. If hydrothermal activity is extensive and host rocks are porous and permeable, the zeolites are widespread and the zoning depends on temperature and water chemistry. Such regional hydrothermal activities are usually related to volcanoplutonic intrusives; in other words, to contact metamorphism. Such zeolite zoning was reported from the Tertiary strata in the contact aureole of many penecontemporaneous volcanoplutonic masses in the Green Tuff region of Japan (Utada, 1973, 1980b). Calcic zeolites, such as mordenite, stilbite, heulandite, laumontite, yugawaralite and wairakite are characteristic in hydrothermal alteration of a high geothermal gradient (Iijima, 1980).

A specific zeolite zoning characterized by a lenticular analcime zone is produced by the submarine hydrothermal and diagenetic alteration related to the Miocene Kuroko polymetallic (Pb – Zn – Cu) sulfide ore mineralization (Iijima, 1974; Utada et al., 1974).

Primary magmatic

Analcimes that are considered as a primary mineral of late formation occur in some alkali rocks. The distinction between primary and secondary analcimes, however, is not always easy. Earlier reported occurrences of analcime phenocrysts in much older lavas are unreliable, as the analcime may be a low-temperature replacement of leucite (Hay, 1986). Unequivocal igneous analcime has been documented as microphenocrysts in the unaltered glassy groundmass of very late Pleistocene or Holocene lava of minette composition in the Colima volcanic complex of Mexico (Luhr and Garmichael, 1981): the $\delta^{18}\text{O}$ value of the Mexican analcime is +8.8‰, comparable to igneous feldspar (Hay, 1986).

Two types of zonal arrangement overlap each other where different types of zeolite formation occur in succession or coexist in a particular area. It is often difficult to distinguish the two types without regional mapping and careful petrological analysis. The overlap of shallow burial diagenesis and submarine hydrothermal alteration in the Kuroko areas of Japan is an example which is described later.

Aging also influences zeolite formation, as Hay (1966) pointed out first: the ratio of analcime to other zeolites in saline, alkaline lake deposits increases with geologic time. The zeolites to analcime transformation can occur without increasing temperature and pressure. The presence of zeolitic rocks, which are fairly common in the Cenozoic and upper Mesozoic strata, becomes rather uncommon in the lower Mesozoic and Upper Paleozoic, scarce in the Lower Paleozoic, and negligible in the Precambrian. Iijima (1980, 1986a) showed that the number of zeolite species

decreases rapidly with increasing age (Fig. 3-3). This fact may be due to decomposition and substitution of many unstable zeolites by a few stable zeolites like analcime and laumontite, which are eventually replaced by alkali feldspars and other minerals. Such phenomena seem to be interpreted as suggesting either aging or deeper burial and so increasing temperature of older strata.

The investigations of zeolites and zeolitic rocks in Japan are here briefly reviewed with emphasis on zeolitic diagenesis.

BURIAL DIAGENESIS (OR BURIAL METAMORPHISM)

The concept of burial metamorphism was defined by Coombs in 1954 as the metamorphism that progresses in a thick pile of geosynclinal deposits due to increasing temperature and pressure along with the simple increase of burial depth. Coombs considered zeolite facies as the shallowest facies of his burial metamorphism, and he distinguished two zeolite zones in andesitic graywacke in the Triassic geosyncline of New Zealand: clinoptilolite – heulandite zone and laumontite zone. Reviewing zeolites in sedimentary rocks, Iijima and Utada (1966) preferred “burial diagenesis” to “burial metamorphism”, because most zeolitic rocks have an appearance of sedimentary rocks and are associated with unmetamorphosed mudstone and sandstone. Hay (1966) also used burial diagenesis in his review paper. In any case, a vertical zonation of zeolites and related minerals is expected from the definition of burial diagenesis as shown in Fig. 3-2.

In Japan, regional mapping of zeolite zones was first undertaken by Yoshimura (1961) in Miocene pyroclastic rocks in the Fukushima district of southwestern Hokkaido, followed by Nakajima et al. (1962) and Nakajima and Tanaka (1967) in the Cretaceous Izumi Group in the Izumi Mountains of northern Kii Peninsula. These

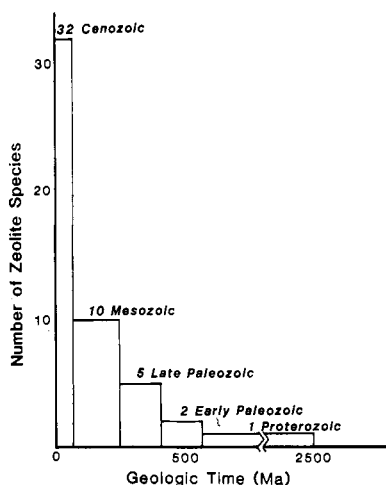


Fig. 3-3. Relationship between number of zeolite species and geologic time. (After Iijima, 1986a, fig. 6, p. 101.)

early researchers set the same zeolite zones as New Zealand. Utada (1965), however, performed regional mapping of zeolite zones in Neogene silicic and andesitic volcanoclastic rocks in the Mogami district of Yamagata. He distinguished five zones: (1) fresh glass zone without zeolites; (2) clinoptilolite – mordenite zone; (3) analcime – heulandite zone; (4) laumontite zone; and (5) albite – quartz – chlorite zone (Fig. 3-4). Later Utada (1973) considered that the laumontite zone is a product of hydrothermal alteration related to the intrusion of a volcanoplutonic complex and that it is superposed upon the zeolite zones formed by burial diagenesis. Miyazaki revised the zeolite zones in the Fukushima district of southwestern Hokkaido, which are very similar to those in the Mogami district (Miyazaki, 1976, in Iijima et al., 1981). In the light of such common occurrence of clinoptilolite and mordenite in shallow burial depth, Iijima and Utada (1966) suggested that the shallowest fresh glass zone and the next shallow clinoptilolite – mordenite zone would be removed by erosion in older folded sections, such as the Triassic geosynclinal deposits of New Zealand. In fact, zeolite of the clinoptilolite – heulandite group in the New Zealand Triassic does not belong to clinoptilolite but to heulandite (Boles and Coombs, 1975).

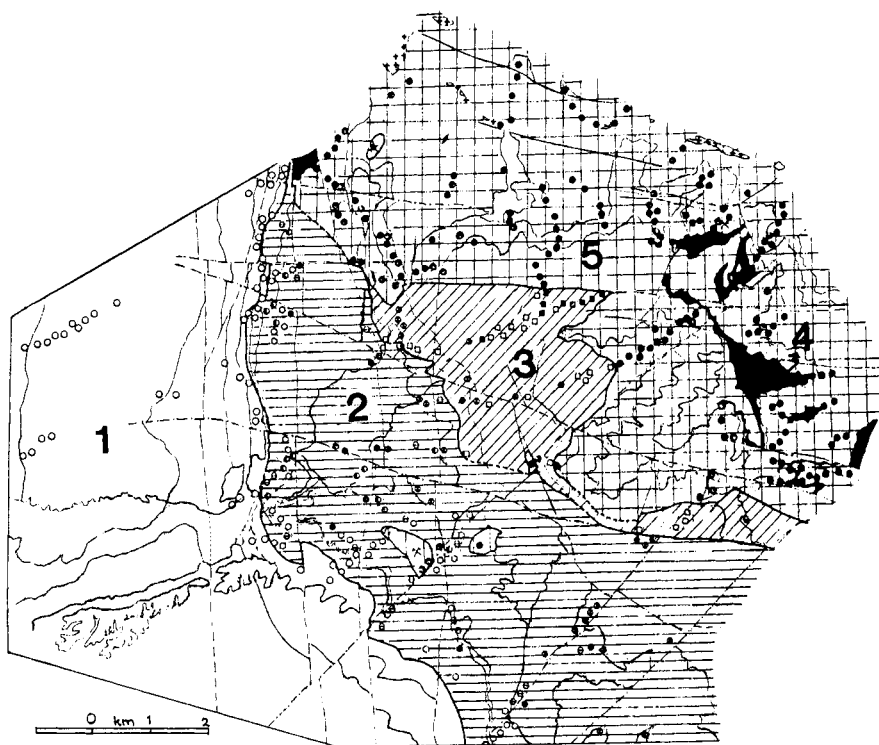
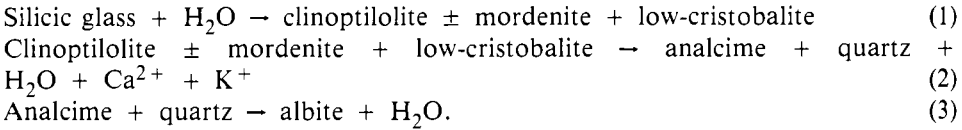


Fig. 3-4. Zonal distribution map of zeolites and related minerals in the Neogene rhyolitic to andesitic volcanic and volcanoclastic rocks of the Mogami district, Yamagata, Northeast Honshu. 1 = fresh glass zone; 2 = clinoptilolite – mordenite zone; 3 = analcime – heulandite zone; 4 = laumontite zone; 5 = albite – quartz – chlorite zone. (After Utada, 1965, fig. 10, p. 195.)

Numerous silicic vitric tuffs transformed to zeolitic rocks during burial diagenesis have been found interbedded with marine mudrocks and sandstones in the Tertiary Uetsu and Setogawa geosynclines as well in the Cretaceous Yezo and Izumi geosynclines. Iijima (1975, 1978a, b) and Iijima and Ohwa (1980) recognized a series of alkali zeolite reactions in silicic vitric tuffs in the geosynclinal deposits:



Based on the reaction series, four diagenetic zones are recognizable: Zone I (fresh glass without zeolite), Zone II (clinoptilolite and mordenite), Zone III (analcime), and Zone IV (albite). Also, transformations of calcic zeolites frequently coincide with the alkali zeolite reactions as follows:

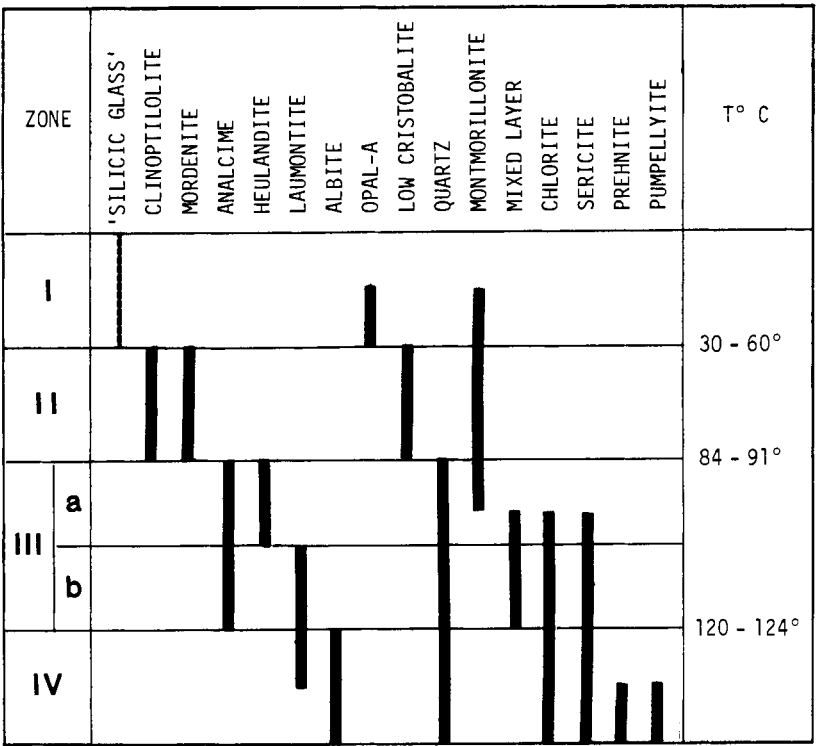


Fig.3-5. Schematic diagram showing vertical zonation of zeolites and related authigenic minerals in silicic vitric volcaniclastic rocks in a thick pile of marine geosynclinal deposits. Temperatures are estimated from static bottomhole temperature measurements in deep drillholes, in which the present-day zeolitic burial diagenesis has been progressing.

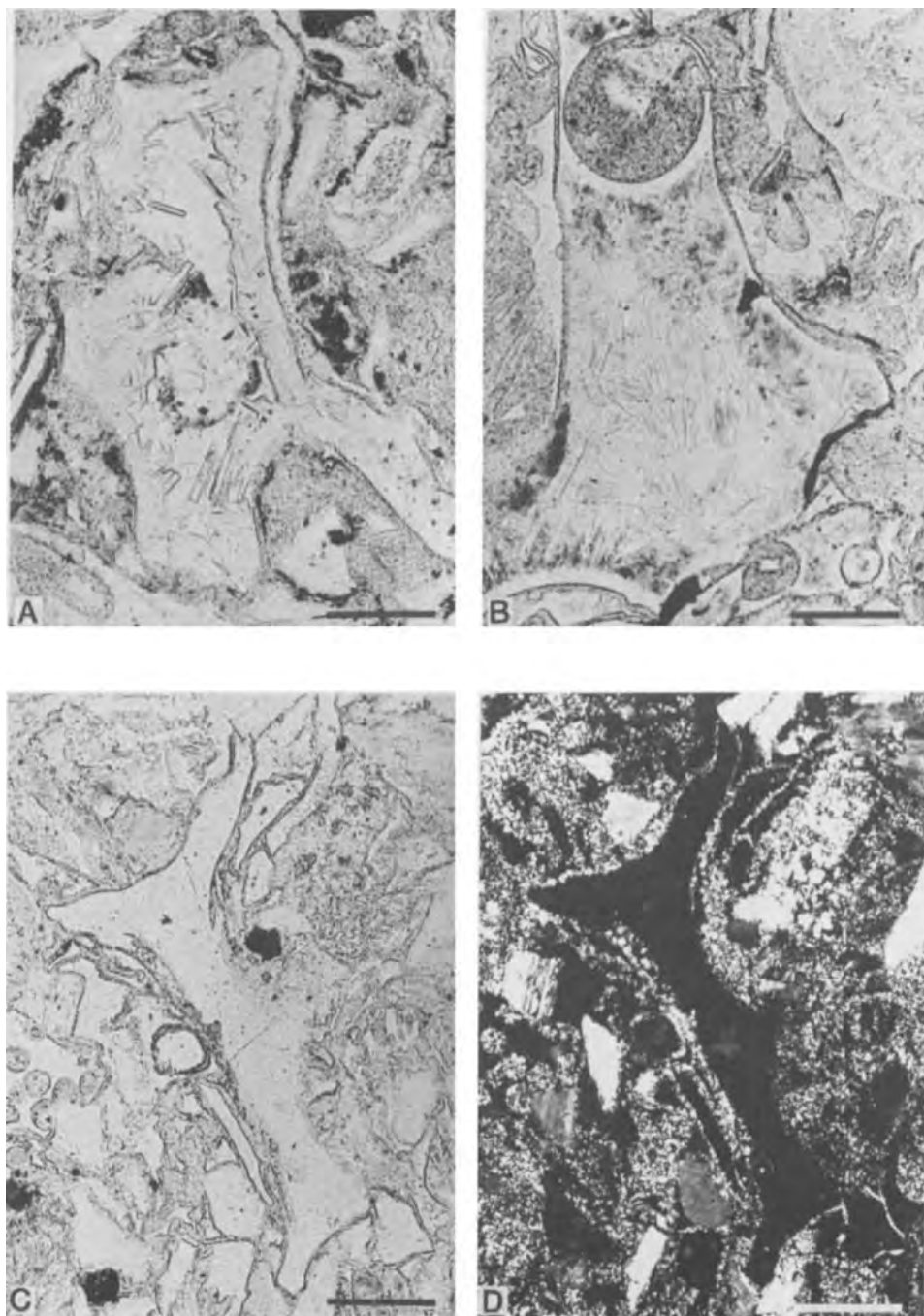
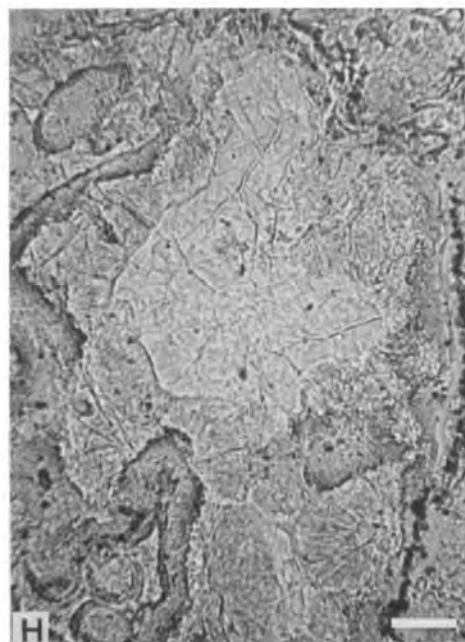
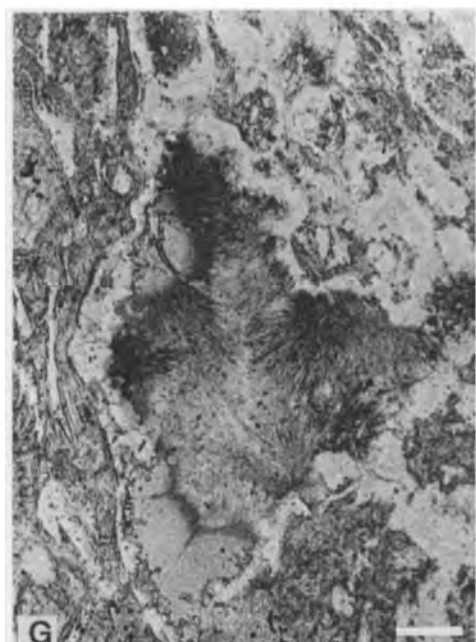
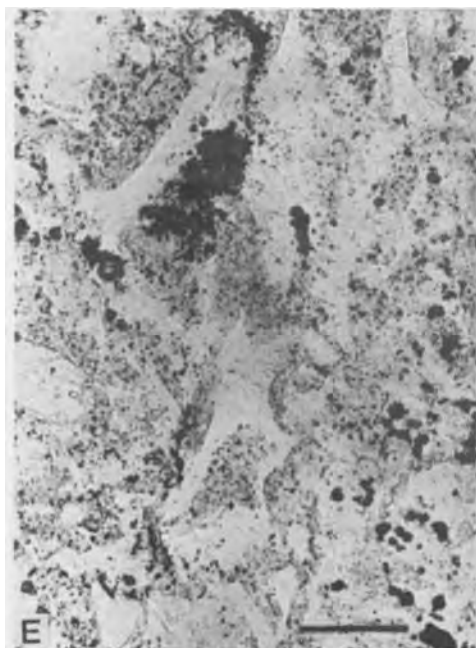
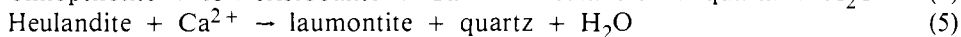
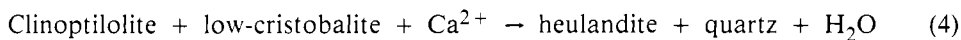


Fig. 3-6. *Caption on p. 161.*





Consequently, Zone III is subdivided into Subzone IIIa (analcime with heulandite) and Subzone IIIb (analcime with laumontite). The occurrence of laumontite frequently extends to Zone IV. Argillitization almost always occurs penecontemporaneously with the zeolitization. The transformation of silicic glass fragments into smectite (and amorphous opal) precedes the zeolitization, so that the smectite exists in Zone I and commonly in Zone II. The smectite alters to chlorite and illite, generally through their mixed-layer minerals, in Zones III and IV; nevertheless, it frequently remains in Zone III of particularly younger strata. The sheet silicates are partly transformed to laumontite. Thus, the diagenetic minerals in silicic vitric tuffs are vertically zoned in a thick pile of geosynclinal deposits (Fig. 3-5).

The above-stated reactions and transformations can be observed, as shown in Fig. 3-6, under a petrographic microscope in thin-sections of rocks near the zone boundaries. The occurrence of calcic zeolites is rather uncommon in altered silicic vitric tuffs of burial diagenesis. Local distribution of laumontite suggests even another origin: as exemplified by the laumontite zone of possible hydrothermal origin in the Mogami district (Fig. 3-3). The laumontite in the Cretaceous deposits on the Sorachi anticline of Ishikari, central Hokkaido (Iijima and Ohwa, 1980), might be a hydrothermal alteration product related to the intrusion of diorite – porphyry encountered in coal exploration drillholes (Figs. 3-7 and 3-8).

The vertical zoning of the zeolites due to burial diagenesis is primarily controlled by geothermal gradient, contrasting with the laterally zonal arrangement of zeolite zones in saline, alkaline lake deposits which is essentially influenced by chemical

Fig.3-6. Photomicrographs of some zeolitized silicic vitric tuffs from Japan. Scale bars are 0.1 mm.

(A) Prismatic clinoptilolite filling the void of dissolved glass shards, which are fringed by an aggregate of montmorillonite and low-cristobalite. (Zone II of burial diagenesis.)

(B) Prismatic heulandite replacing a glass shard which is fringed by an aggregate of quartz and chlorite. Clinoptilolite is the precursor of heulandite. (Zone IIIa of burial diagenesis.)

(C) Mosaic aggregates of nearly isotropic analcime replacing bubble-walled glass shards which were initially replaced by clinoptilolite and mordenite. The analcitized shards are rimmed with an aggregate of quartz and chlorite transformed from low-cristobalite and montmorillonite. (Zone III of burial diagenesis.)

(D) Ditto. In double polarizers.

(E) Porphyroblastic laumontite replacing glass shards that had been initially replaced by clinoptilolite, which was then transformed to heulandite. The clay matrix is partially replaced by laumontite. (Zone IIIb of burial diagenesis.) (After Iijima et al., 1984, fig. 5, p. 602. Courtesy of Butterworths.)

(F) Twinned albite and quartz replacing glass shards that had been initially replaced by clinoptilolite and/or mordenite, which were then transformed to analcime. A small amount of the analcime remains as relics. The matrix comprises aggregates of quartz, chlorite, and illite. In double polarizers. (Zone IV of burial diagenesis.) (After Iijima, 1975, plate 8.)

(G) A radial aggregate of hair-like mordenite filling a cavity in altered pumice tuff. The cavity is rimmed by quartz which frequently includes the mordenite. (Mordenite zone of the Kuroko alteration halo.) (After Iijima, 1974, fig. 2, p. 276. Courtesy of The Society of Mining Geologists of Japan.)

(H) A vesicle in altered pumice tuff is, toward the center, filled by a radial aggregate of mordenite and a mosaic aggregate of analcime. Parts of the mordenite are replaced by the analcime (arrow). The vesicle is fringed by montmorillonite. (Analcime zone of the Kuroko alteration halo.) (Ditto.)

gradient of pore water (Fig. 3-2). Temperatures at which the zeolite zones form can be obtained from the analyses of deep drillholes in which the present-day zeolitic burial diagenesis is progressing. Iijima and Utada (1971) investigated core and cutting samples from three drillholes over 5 km deep, penetrating Quaternary and Tertiary marine sections of the Uetsu geosyncline in the Niigata oilfield region beneath

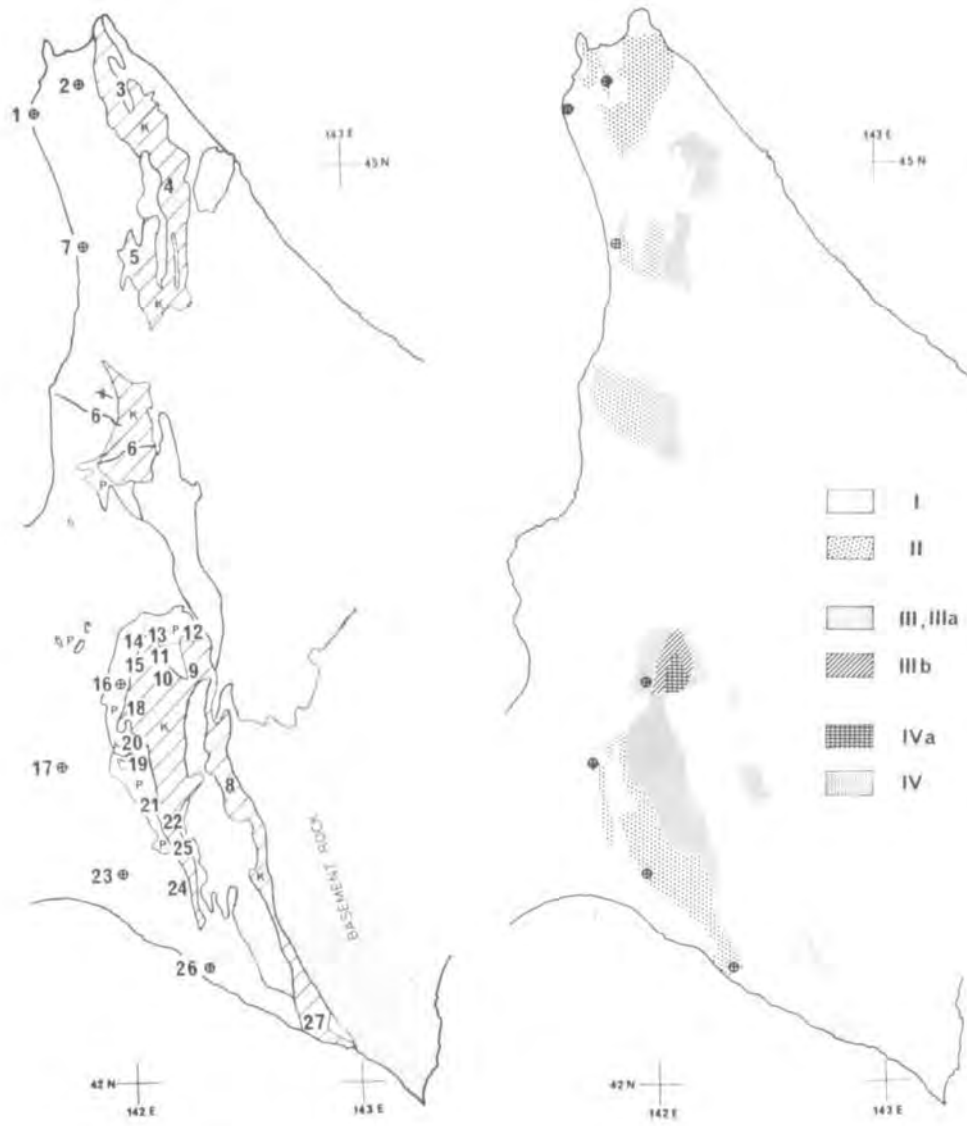


Fig.3-7. Maps showing localities of columns in Fig.3-8 with the distribution of basement rocks and Cretaceous (*K*) and Paleogene (*P*) strata in central Hokkaido (left), and zeolite zones formed by burial diagenesis of silicic vitric tuffs in the Cretaceous and Tertiary strata. For explanation of Zones I–IV, refer to Fig.3-5. (After Iijima and Ohwa, 1980, fig. 1, p. 142. Courtesy of Heyden.)

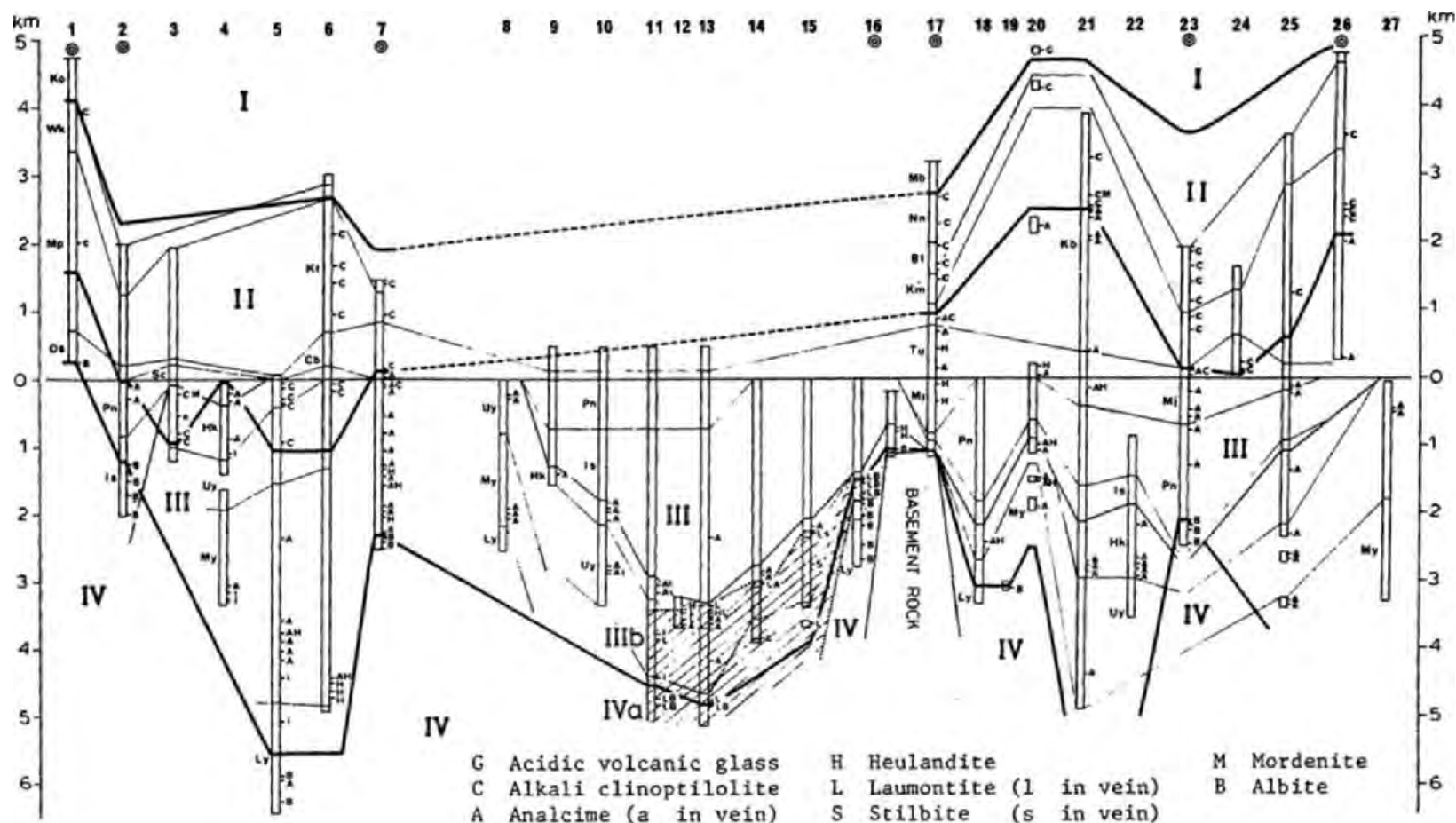


Fig. 3-8. Stratigraphic profile showing zeolite zones formed by burial diagenesis of siliceous vitric tuffs in the Cretaceous and Tertiary strata of central Hokkaido. The local distribution of laumontite in Zone IIb (analcime with laumontite) and Zone IVa (talbite with laumontite) is possibly related to diorite - porphyry intrusion. For explanation of localities, refer to Fig. 3-7. Neogene: Ko = Koetsu, Wk = Wakkanai, Mp = Masuporo, Kt = Kotambetsu, Os = Onishibetsu, Ch = Chikubetsu, Sc = Soya, MB = Moebetsu, Nn = Nina, Bt = Biratori, Km = Karumai, Kb = Kawabata, Tu = Takinoue. Paleogene: Mj = Momijiyama, Pn = Poronai, Is = Ishikari G. Cretaceous: Hk = Hakobuchi G., Uy = Upper Yezo G., My = Middle Yezo G., Ly = Lower Yezo G. (After Iijima and Ohwa, 1980, Fig. 2, p. 143. Courtesy of Heyden.)

Niigata Coastal Plain. The present-day zeolitic burial diagenesis is considered to be progressing in the holes, because Zones I – IV appear successively from the surface to the bottom in the strata which are lying without any appreciable unconformity since Middle Miocene age. Referring to the data in the Akita oilfield region by Huzioka and Yoshikawa (1969), Iijima and Utada realized that the temperatures at the top of each zone coincide at a very limited range in different holes, whereas the burial depths at the top of each zone differ greatly in the holes. They concluded that the series of alkali zeolitic reactions are temperature dependent in the marine sections. The same phenomenon was reported in many other drillholes in Hokkaido, and other localities of northern and central Japan (Iijima, 1975, 1978a, 1978b, 1985; Iijima and Ohwa, 1980; Iijima and Tada, 1981). Figure 3-9 shows the relationship between temperature and burial depth of the zeolite zones in thick marine sequences of ten deep holes in which the present-day burial diagenesis has been progressing. The tops of Zones II, III and IV occur at $41^{\circ} - 55^{\circ}$, $81^{\circ} - 91^{\circ}$, and $120^{\circ} - 124^{\circ}\text{C}$, respectively, which are estimated from static bottomhole temperature (Iijima, 1985). Similar result has been obtained in California Tertiary oilfields (J.R. Boles, pers.

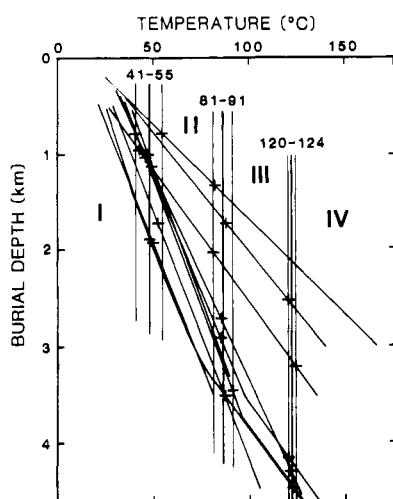


Fig.3-9. Relationship between temperature and burial depth of the zeolite zones in ten deep boreholes in which present-day burial diagenesis has been progressing in Cenozoic marine sequences. Temperatures are estimated from static bottomhole temperature. (After Iijima, 1986a, fig. 2, p. 95.),

commun., 1985). Aoyagi and Kazama (1980) estimated higher temperatures for the zeolite zones following a geophysical correction of measured geothermal gradient, but the correction has been revised toward lower values.

The same zeolite zones are generally recognized in silicic vitric tuffs in the Tertiary sections of the Paleogene coalfields in Hokkaido, Tohoku, and northern Kyushu (Fig. 3-10). Shimoyama and Iijima (1976, 1978) recognized a clear relationship between the degree of coalification of Paleogene coals and the zeolite zones of burial diagenesis (Fig. 3-11): Bituminous coking coals with the vitrinite reflectance in the immersion oil (R_o) of more than 0.75 belong to Zone III, whereas lignites and sub-bituminous coals with R_o of less than 0.75 are contained in Zone II. Shimoyama and Iijima concluded that the R_o values as well as the zeolite zones are not influenced by the degree of folding and, therefore, of tectonic stress, but affected principally

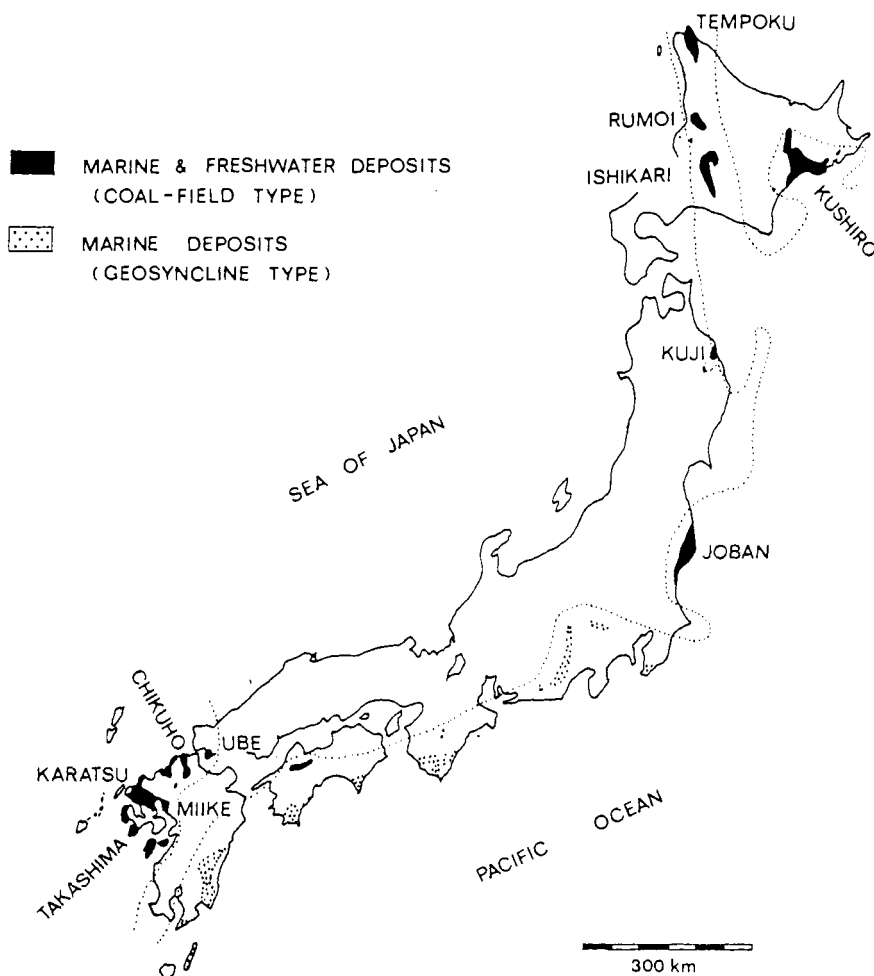


Fig.3-10. Distribution of Paleogene deposits in Japan.

by the geothermal gradient at the maximum burial depth. Estimated temperatures from the zeolite zoning are not inconsistent with those from the degree of coalification. In Paleogene coal-bearing formations in the Fukuoka, Kasuya and Kashii coalfields of northern Kyushu, R_o value is approximately 0.8 at the boundary between Zones II and III (Miki, 1981). In the Miocene section of the western Sannohe district of Aomori, clinoptilolite zone corresponds to $0.35-0.6 R_o$, whereas albitization of plagioclase due to hydrothermal alteration correlates to $1.0-1.8 R_o$ (Suzuki et al., 1979; Hayakawa et al., 1979). Sasaki et al. (1982a), who summarized the relationship between maturity of kerogen represented by R_o and zeolite zones in Tertiary oilfields of Japan, obtained a similar result.

The zeolite zones formed by burial diagenesis of silicic vitric tuffs are not exclusively controlled by temperature but also considerably by pore-water chemistry. Iijima (1975) performed a comparative study on the clinoptilolite – analcime – albite equilibria under various environments, such as saline, alkaline lake deposits, marine geosynclinal sedimentary columns, and active geothermal wells. The transformation of clinoptilolite to analcime occurs at near-surface condition in the saline, alkaline lake deposits (Hay, 1966; Sheppard and Gude, 1968; Surdam and Sheppard, 1978), whereas it occurs at temperatures around $81^{\circ}-91^{\circ}\text{C}$ in the marine sections. The transformation of analcime to albite takes place at $180^{\circ}-190^{\circ}\text{C}$ at a pH_2O less

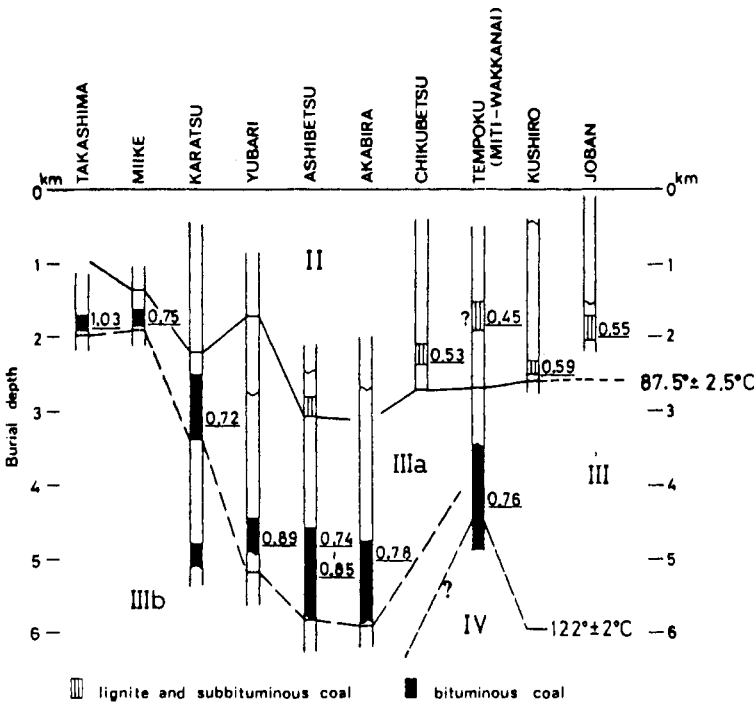


Fig.3-11. Relationship among coal rank represented by vitrinite reflectance R_o , zeolite zones, and burial depth in the Japanese Tertiary coalfields. (After Shimoyama and Iijima, 1978, fig. 5, p. 212.)

than 2 kb in pure water, at $120^{\circ} - 124^{\circ}\text{C}$ at burial depth of 2.5–4.5 km in the marine sections, and at $55^{\circ} - 65^{\circ}\text{C}$ at burial depth of 2 km in the saline, alkaline lake deposits of the Eocene Green River Formation (Iijima and Hay, 1968). In weakly alkaline geothermal wells at Odake of central Kyushu, albitization of calcic plagioclase, that commonly coincides with the analcime to albite transformation during burial diagenesis, occurs at $150^{\circ} - 240^{\circ}\text{C}$ (Hayashi, 1973). Iijima (1975, 1978a) considered that the concentrations of sodium and probably hydrogen ions in pore water would play a role in the lowering of equilibrium temperatures of the zeolitic reactions (Fig. 3-12). In fact, Kusakabe (1982) reported the lowering of reaction temperature with the increase of concentrations of sodium ions in pore water in hydrothermal experiments of the clinoptilolite – mordenite – analcime equilibria. The very limited ranges of reaction temperatures of the alkali zeolite reactions in marine geosynclinal deposits may suggest that the change of pore-water chemistry occurs uniformly and the circulation of pore water is very slow during zeolitic burial diagenesis which takes place prior to extensive folding and faulting.

Rates of the alkali-zeolite reactions during burial diagenesis are considered to be very slow and quite different either from hydrothermal reactions or from saline, alkaline lake deposits (Table 3-6). The reaction rates can be estimated from a thickness of the transitional zone in which zeolites of both shallower and deeper zones coexist, using a burial history diagram. Figure 3-13 shows such a diagram of the Tertiary marine sequence exposed in the Fukushima district of southwestern Hokkaido, northern Japan. The base of the Fukuyama Formation was deposited 21 Ma ago, buried gradually to 3.9 km of maximum depth, about 2 Ma ago, and then folded, uplifted and exposed promptly; this is the usual sequence in the geosynclinal basins of the Japanese Island arcs. The transitional zone in which analcime and albite coexist has a thickness of approximately 100 m. The horizon

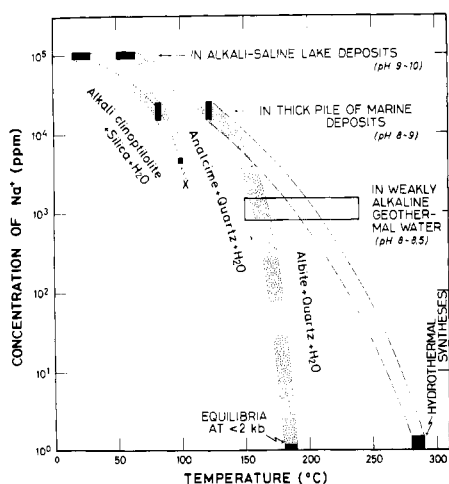


Fig.3-12. Equilibria of the reaction series, alkali clinoptilolite – analcime – albite at a pH_2O less than approximately 2 kb in a silica-saturated environment with respect to temperature and Na concentration of pore water. (After Iijima, 1975, fig. 7, p. 144.)

TABLE 3-6

Zeolitic reactions and their rate in different environments

<i>Volcanic glass + H₂O → zeolites</i>			
Basaltic glass + H ₂ O			
→ PHI + CHA + ANA	200°C	6 days	Laboratory (Iijima, 1980)
Rhyolitic glass + thermal water			
→ MOR + ANA	250°C	40–60 days	Thermal well (Iijima, 1980)
Basaltic glass + hot sea water			
→ CHA	100°C	7 yrs	Surtsey (Jakobsson, 1972)
Nephelinitic glass + soil water			
→ PHI	Surface	1300 yrs	Olduvai Gorge (Hay, 1980)
Rhyolitic glass + saline water			
→ PHI + gel	Surface	600 yrs	Teels Marsh (Surdam and Sheppard, 1978)
Alkalitrachytic glass			Neapolitan
+ meteoric water → PHI + CHA	Near-surface	10 ³ yrs	Yellow Tuff (Sersale, 1978)
Basaltic glass + pore sea water			
→ PHI	5°C	10 ⁶ yrs	Ocean bottom (Czyscinski, 1973; Glaccum and Boström, 1976)
Rhyolitic glass + pore water			
→ CLI + MOR + Low-cristobalite	50°C	10 ⁶ –10 ⁷ yrs	Burial diagenesis (Iijima, 1986a)
<i>Zeolites → analcime + H₂O</i>			
CLI, PHI, CHA, MOR, ERI			
+ saline pore water → ANA + H ₂ O	Near-surface	6 × 10 ⁵ yrs	Tecopa Lake Beds (Sheppard and Gude, 1968, 1974)
PHI, CHA + meteoric water			
→ ANA + H ₂ O	Near-surface	2 × 10 ⁵ yrs	Koko Crater Tuff (Iijima, 1986)
CLI, MOR + pore water			
→ ANA + H ₂ O	86° ± 5°C	?	Burial diagenesis
<i>Zeolites → laumontite + H₂O</i>			
HEU + pore water			
→ LAU + H ₂ O	ca. 100°C	?	Burial diagenesis
<i>Zeolites → alkali feldspar + H₂O</i>			
PHI, CHA, CLI, MOR, ERI			
+ saline pore water			
→ K feldspar + H ₂ O	Near-surface	6 × 10 ⁵ yrs	Tecopa Lake Beds (Sheppard and Gude, 1969, 1974)
ANA + pore water			
→ Albite + H ₂ O	122° ± 2°C	4 × 10 ⁵ yrs	Burial diagenesis (Iijima, 1986)

ANA = analcime, CHA = chabazite, CLI = clinoptilolite, ERI = erionite, HEU = heulandite, LAU = laumontite, MOR = mordenite, PHI = phillipsite

of the top of the transitional zone (= top of Zone IV) was buried to 3.45 km of maximum depth where temperature was 122°C , 2 Ma ago. The horizon of the bottom of the transitional zone, on the other hand, was buried to a depth of 122°C , 2.35 Ma; to the maximum depth of $122^{\circ} + 3.5^{\circ}\text{C}$, 2 Ma (geothermal gradient was estimated to be $3.5^{\circ}\text{C } 100\text{ m}^{-1}$); and uplifted again to the depth of 122°C , 1.95 Ma ago. In other words, it took 0.4 Ma to complete the transformation of analcime to albite during burial diagenesis.

Kano (1978) tried to interpret the formation of zeolites and silica minerals from a kinetic viewpoint (e.g., temperature and time), based on hydrothermal experiments. Sasaki et al. (1982b, c) reviewed the occurrence of vertical zoning of zeolites in deep drillholes in some Japanese oilfields, and tried to interpret it from the geothermal history of host rocks. Their interpretation based on such extensively folded, faulted, and eroded sections seems to be doubtful and erroneous, because the present-day temperatures in such drillholes do not necessarily indicate the formation temperature of zeolite zones during burial diagenesis.

The change of geothermal gradient with geologic age is not uncommon in the Japanese Islands arcs. In the MITI-Kuromatsunai drillhole of southwestern Hokkaido, Iijima et al. (1983) showed that the past diagenetic zeolite zones, which were produced at the maximum depth of burial about 0.5 Ma ago, are modified by recent high heat flow after folding and faulting (Fig. 3-14). Figure 3-15 shows the vertical zonation of authigenic minerals and the zeolite in the drillhole. The temperatures at the tops of Zones II and III are estimated to be 55° and 80°C , respectively, from the static bottom-hole temperature measurements, which are not inconsistent with

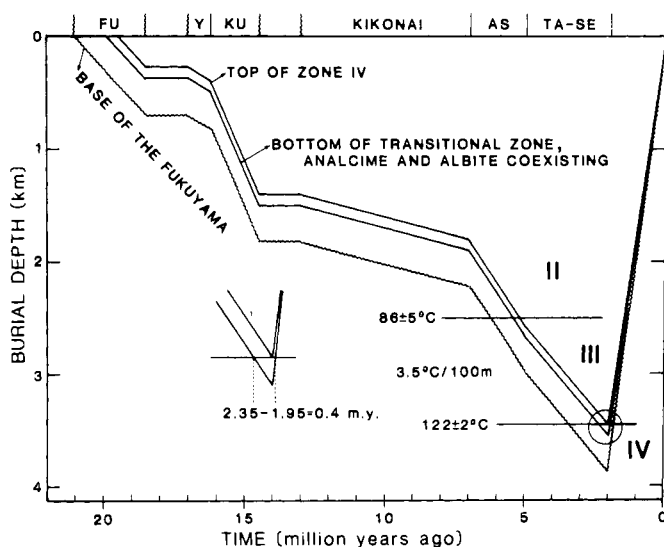


Fig.3-13. Burial history diagram of the Neogene sequence in the Fukushima district, southwestern Hokkaido, showing the rate of reaction of analcime and quartz to albite during burial diagenesis (After Iijima, 1986a, fig. 4, p. 99.)

those of the present-day burial diagenesis. The present geothermal gradient has been determined to be $52^{\circ}\text{C km}^{-1}$. The temperature at the top of Zone IV, however, is 175°C , which is too high in comparison with $120^{\circ} - 124^{\circ}\text{C}$ of the ordinary burial diagenesis. Furthermore, the analcime in the lower part of Zone III, formed by burial diagenesis at the condition of geothermal gradient of $31^{\circ}\text{C km}^{-1}$, has been extensively replaced by smectite, probably due to hydrothermal activity associated with the recent high heat flow.

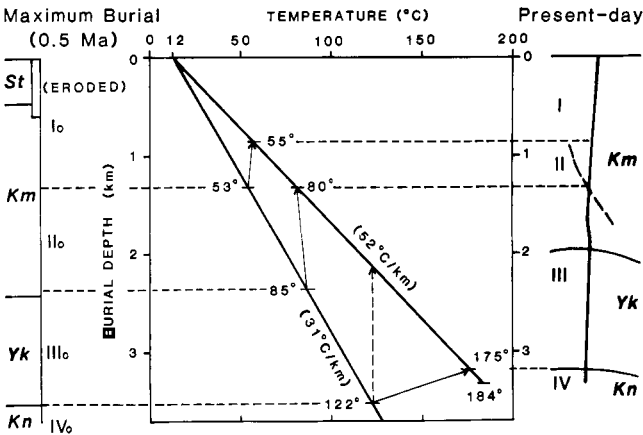


Fig.3-14. Diagram showing the present-day zeolite zonation in the MITI-Kuromatsunai well, which originates from the zeolite zoning formed at a maximum burial depth about 0.5 Ma ago. (After Iijima et al., 1983, fig. 6, p. 599. Courtesy of Butterworths.)

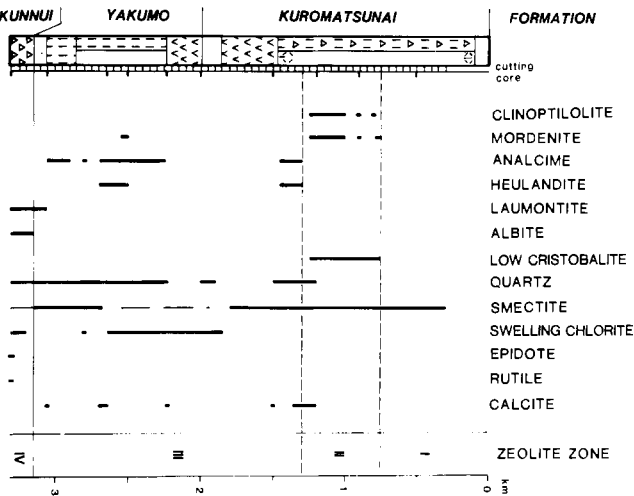


Fig.3-15. Vertical distribution of alteration minerals and zeolite zones in the MITI-Kuromatsunai well in the Kuromatsunai district of southwestern Hokkaido. (After Iijima et al., 1984, fig. 4, p. 599. Courtesy of Butterworths.)

Recently a wildcat well, named the MITI-Omaezakioki well, has been drilled through the offshore Cainozoic sedimentary deposits under the Enshunada Sea off the Tenryu River, Shizuoka, central Honshu. Figure 3-16 shows the stratigraphic sequence, zeolite zones, geothermal gradient, and vitrinite reflectance (R_o) of the well (Iijima, 1986a). Though a middle to lower bathyal para-unconformity is recognized between the Saigo Formation and the Kakegawa Group, Zones I and II are interpreted as resulting in the present-day burial diagenesis, because the I – II boundary does not lie on the para-unconformity but in the middle part of the Saigo Formation and because its temperature is estimated to be 50°C corresponding to that of the present-day burial diagenesis. It is likely that the deep-sea hiatus represents an essentially non-depositional stage, instead of significant erosional stage, considering the above zeolite zones and the straight relationship between R_o and depth, from 0.35 at 600 m to 0.69 at 3110 m. On the contrary, the II – III boundary lies at a depth of 3143 m, where the bathyal siliceous mudstone of the Eocene Setogawa Group (SE) is clino-unconformably covered by the basal sandstone of the Lower Miocene Kurami Formation. Temperature at the boundary is estimated to be 74°C , which is lower than $86^\circ \pm 5^\circ\text{C}$ of the present-day burial diagenesis. Additionally, the R_o -depth line is discontinuous at the clino-unconformity, below which the slope of the

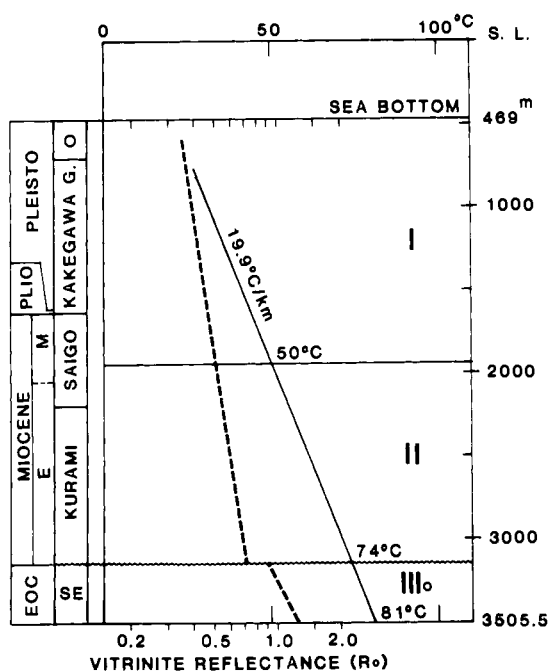


Fig.3-16. Zeolite zones, vitrinite reflectance (R_o), and geothermal gradient in the MITI-Omaezakioki well off the mouth of the Tenryugawa River, the Enshunada Sea. The log R_o – depth line is discontinuous at the unconformity at the base of the Kurami Formation. The temperature of 75°C at the II/III₀ boundary is too low as compared with $81 - 91^\circ\text{C}$ of the present-day burial diagenesis. (After Iijima, 1986b.)

line becomes gentle (0.90 at 3145 m and 1.25 at 3505 m). These facts suggest a great break of the stratigraphic sequence at the clino-unconformity. In the Ohigawa Valley about 45 km north-northeast of the MITI-Omaezakioki well, a > 2 km-thick, sandy turbidite sequence is present at the stratigraphic position time-equivalent with the clino-unconformity.

The burial history diagram of the Cainozoic sequence in the MITI-Omaezakioki well is shown in Fig. 3-17 depicting the development of sedimentary basins. Sedimentation rates are regarded as constant within every stratigraphic unit. The Setogawa Group (SE) in the well was deposited on the sea bottom 41–38 Ma ago, and buried to 2.9–2.5 km at the maximum depth below the sea bottom approximately 20 Ma ago. At that time, the silicic glass fragments of the SE deposits (Zone I₀) had to alter to analcime (Zone III₀) through clinoptilolite and mordenite (Zone II₀), so that the top of the SE must have been heated to at least $86^{\circ} \pm 5^{\circ}\text{C}$. Thus, the former geothermal gradient is estimated to be about $30^{\circ}\text{C km}^{-1}$, 1.5 times of the present gradient of $19.9^{\circ}\text{C km}^{-1}$! During approximately 20–19 Ma ago, the SE and the overlying pre-Kurami deposits underwent a tectonic disturbance associated with solid intrusion of ultramafic rocks, and they were uplifted and eroded rapidly until the top of the SE in the well was exposed on land. The Younger Tertiary basin began to develop 19 Ma ago. The Kurami (KU) and Saigo (S) Formations accumulated on the sea bottom 19–15 Ma ago, which deepened from a coastal environment in Early Miocene time (19 Ma) to middle to lower bathyal deep-sea environment in Middle Miocene (15 Ma). During Middle to Late Miocene and almost whole Pliocene time (15–2.5 Ma), the deep-sea bottom depth kept an “equilibrium state”, that is, neither deposition nor erosion occurred. It is likely that the deep-sea para-unconformity would originate on a specific submarine physiography, probably on an offshore bank. Sedimentation started again 2.5 Ma ago on the lower to middle bathyal bottom, and the Kakegawa (K) and Ogasa (O) groups have been deposited. At present, the silicic glass in vitric volcanoclastic sediments below 1470 m in burial

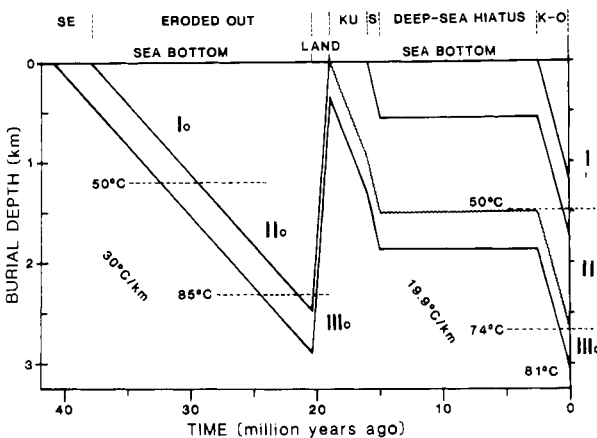


Fig.3-17. Burial history diagram of the Tertiary sequence in the MITI-Omaezakioki well showing twofold zeolite zonations at 20 Ma and present-day burial diagenesis. (After Iijima, 1986b.)

depth, where temperature ranges from 50° to 81°C, alters to clinoptilolite and mordenite (Zone II). The Serogawa Group (SE) below 2674 m in burial depth at 74°C, however, already changed to Zone III₀ during the previous maximum burial approximately 20 Ma ago, so that it remains in Zone III₀ within the condition of Zone II.

In younger orogenic belts like the Japanese Islands arcs, Cainozoic strata are extensively disturbed by tectonic movements. Sometimes Miocene beds have been buried to several kilometers in depth and are undergoing present-day burial diagenesis, sometimes they were folded, faulted, uplifted and eroded rapidly until being exposed. Geothermal gradients as well as thickness and lithology of the strata are frequently variable in both space and time due to a rapid shift of depocenter. Consequently, sedimentary basin analyses are sometimes very difficult by the usual stratigraphic and lithological methods. In such circumstances, the temperature-dependent zeolite zones can serve as a useful tool. Nishimura et al. (1980) and Nishimura (1984) mapped the regional zeolite zones in the Upper Cretaceous Izumi Group of Shikoku and Awaji Islands with an apparent thickness of more than 100 km, and succeeded in reconstructing the elongated sedimentary basin whose depocenter migrated eastwards rapidly along the Median Tectonic Line of southwestern Japan (Fig. 3-18). Nishimura et al. (1980) first calculated the thicknesses of Zones I, II and III assuming that the former geothermal gradient of 25°C km⁻¹ and the top of Zones II, III and IV formed at 50°, 86° and 122°C, respectively. Then, they estimated the original thickness of the Izumi Group at specific localities (see A, B and C in Fig. 3-18). Finally, they reconstructed the Izumi geosynclinal basin. Lithological maps and paleocurrent data indicate steady westward-moving axial turbidity currents. Iijima et al. (1981) performed a similar basin analysis of the Neogene deposits in the Oshima district of southwestern Hokkaido.

Burial diagenesis of mafic vitric tuffs has not been fully understood because of their scarcity.

SUBMARINE HYDROTHERMAL AND DIAGENETIC ALTERATION

Distinctive zeolite zoning is recognized in Neogene volcanoclastic rocks surrounding the Kuroko polymetallic (Pb, Zn, Cu, Ag, Au) sulfide deposits in the Green Tuff region (Fig. 3-2). Kuroko, meaning "black ore" in Japanese, occurs as sedimentary bodies superposed on silicic volcanics and as network veins in the underlying volcanics. The Kuroko deposits in the Hokuroku district of Akita were formed by submarine exhalative activities of Early to Middle Miocene age below around 1500 m deep water column (Uchio, 1983). The deep topographic lows were rapidly filled by silicic volcanoclastic and muddy sediments, which were altered to argillaceous and zeolitic rocks due to sub-bottom hydrothermal activity following the Kuroko mineralization. As a result, the Kuroko deposits are enveloped by an argillaceous alteration halo composed of the inner sericite-chlorite zone and the outer montmorillonite zone. The argillaceous halo is, in turn, surrounded by a distinctive analcime zone and a Na-mordenite zone, both of which are superposed on Zone II (clinoptilolite-mordenite zone) of burial diagenesis.

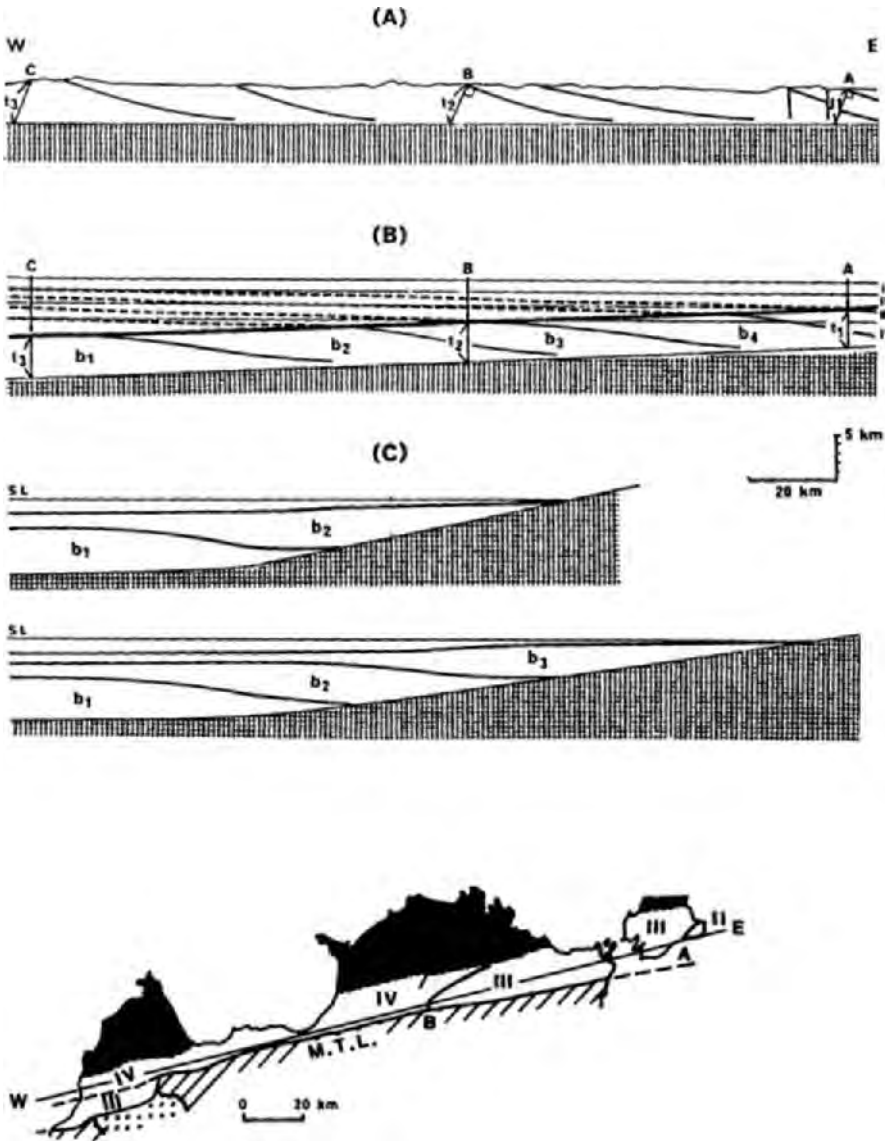
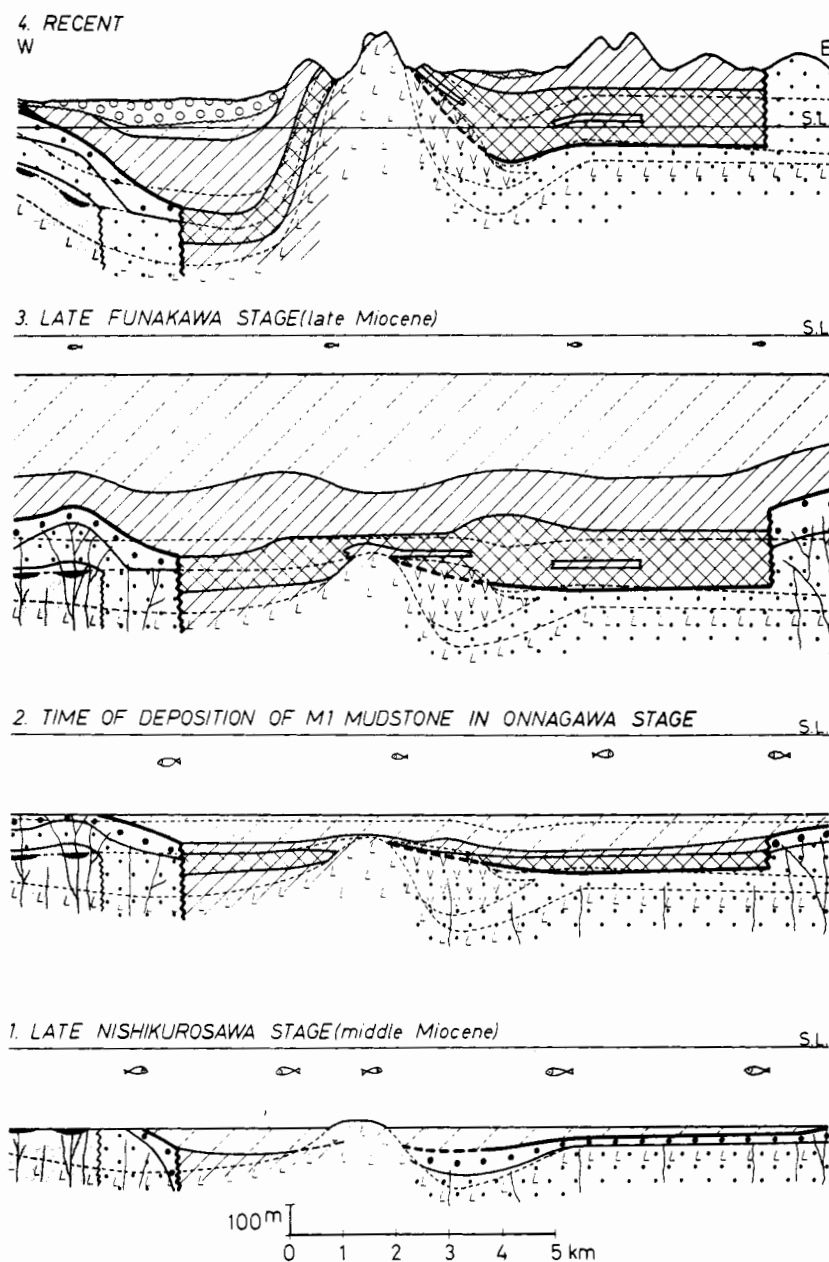


Fig.3-18. Reconstruction of a longitudinal section of the sedimentary basin of the Upper Cretaceous Izumi Group in Shikoku and Awaji Islands, southwestern Japan, on the basis of zeolite zonation due to burial diagenesis. (A) present-day, (B) at the time of maximum burial, and (C) at the time of deposition of b_1 and b_2 , the slope always facing to the west. t_1 , t_2 and t_3 = thickness at localities A, B and C, respectively. I, II, III and IV = zeolite zones. Meshed = basement rocks. M.T.L. = Median Tectonic Line; black = Ryoke granite and metamorphics and the Neogene covering; ruled = Sanbagawa crystalline schist; stippled = Paleogene Kuma Group and Miocene Ishizuchi Group. (Modified after Nishimura et al., 1980, fig. 4, p. 349.)



○○ QUATERNARY GRAVEL, ▽▽ BASIC INTRUSIVE, □-□ ACIDIC VOL-
 CANICS(NISHIKUROSAWA STAGE), ■ KUROKO ORE DEPOSIT, ▽ DUCT
 OF THERMAL WATER, ●● MONTMO.-TRANSIT. ZONE, □ SERICITE-
 CHLORITE ZONE INCLUDING PLAGIOCLASE, □ SERICITE-CHLORITE ZONE
 LACKING PLAGIOCLASE, □ PARTIALLY ALTERED ZONE LACKING ZEOLITE,
 ▨ CLINOPTILOLITE-MORDENITE ZONE, ▩ ANALCIME-CALCITE ZONE

Fig. 3-19. Caption on next page.

Yoshida and Utada (1968) first considered the distinctive analcime zone as a part of the alteration envelope produced by hydrothermal solutions related to the Kuroko mineralization in the Odate area of northern Akita. Iijima (1972, 1974) petrologically and geochemically investigated the argillaceous and zeolitic alteration zones surrounding the Kuroko deposits in the southern part of the Hokuroku district of northern Akita (Fig. 3-19). Iijima recognized distinctive metasomatism caused by extensive migration of soluble chemical elements through penecontem-

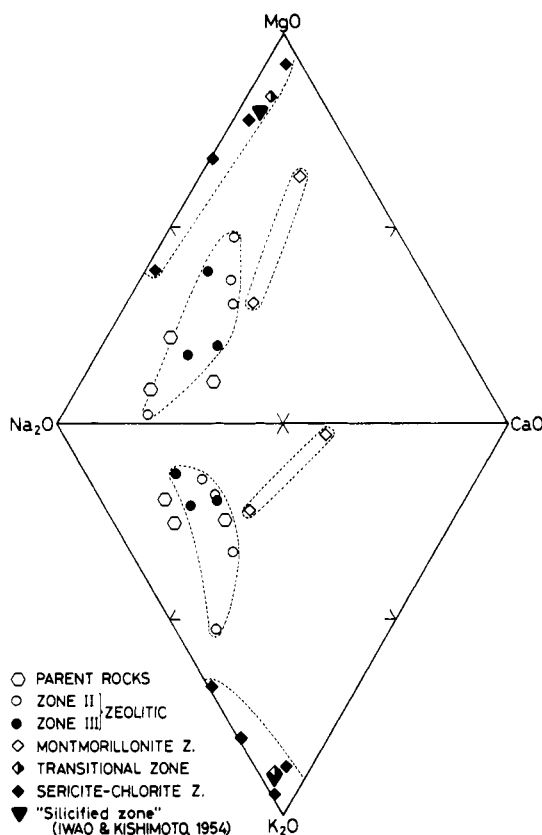


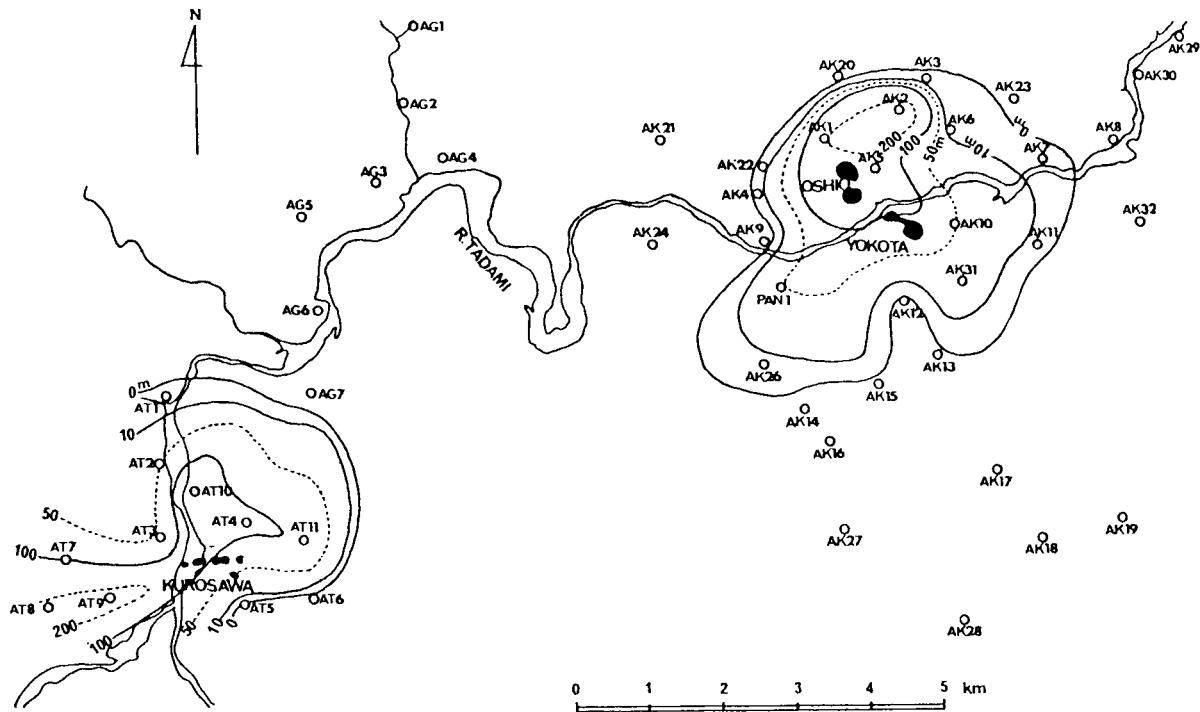
Fig. 3-20. MgO-CaO-Na₂O-K₂O variation (mole percent) diagram of the parent and altered rocks surrounding the Kuroko ore deposits in the southern part of the Hokuroku district, Akita. (After Iijima, 1974, fig. 10, p. 282. Courtesy of The Society of Mining Geologists of Japan.)

Fig. 3-19. Schematic east-west profiles showing development and deformation of the alteration zones surrounding the Kuroko polymetallic sulfide ore deposits in the southern part of the Hokuroku district of Akita from middle Miocene to Recent. 1 = The Kuroko deposits were formed by submarine geothermal activity on the sea-bottom, about 1500 m deep; 2 = pumiceous volcanoclastic sediments filled the basin and underwent the post-Kuroko hydrothermal alteration; 3 = the hydrothermal alteration still continued at depth, whereas clinoptilolite and mordenite of Zone II were formed by burial diagenesis at shallow depth; 4 = the alteration zones were deformed, uplifted, and eroded. (After Iijima, 1974, fig. 14, p. 287. Courtesy of The Society of Mining Geologists of Japan.)

poraneous, porous pumiceous tuff beds during rock – hydrothermal water interactions along the subbottom of the Miocene sea. Figure 3-20 shows the chemical composition of the parent and altered rocks. The Mg and K metasomatism occurred by the reaction of dacitic glass and plagioclase in the pumiceous tuff with hot hydrothermal water of mostly seawater origin to form the inner sericite – chlorite zone, from which much Na and Ca was leached. The Mg and Ca metasomatism occurred by the reaction of dacitic glass with the warm Ca-rich hydrothermal water migrating from the inner zone to form the outer montmorillonite zone, from which much Na and K was leached. The outer montmorillonite and inner sericite – chlorite zones expanded outward; upward and laterally as long as sedimentation of tuffs and hydrothermal activity continued. The hydrothermal activity continued for about 1 – 2 Ma. Simultaneously, in tuffs sufficiently distant from the Kuroko deposits, silicic glass changed to alkali clinoptilolite and mordenite (Zone II) due to burial diagenesis, which might be accelerated by the high heat flow and high Na^+ and K^+ concentrations of hydrothermal water percolating the argillaceous envelope. The clinoptilolite and mordenite reacted with the warm Na – Ca-rich hydrothermal water migrating from the argillaceous envelope to form the distinctive analcime – calcite zone. The analcime – calcite zone, representing the product of the fossil hydrothermal solution flow, occurs as a layered body with a thickness of 100 – 230 m at distance of about 11 km between the Kosaka mining area to the east and the Odate mining area in the west, and intervenes in Zone II to the west and between Zone II and the sericite – chlorite zone to the east.

Utada and co-workers contributed much to the regional mapping of alteration zones related to the Kuroko mineralization. In the Nishiaizu district of Fukushima, Utada and Ishikawa (1973) and Utada et al. (1974) stressed the distinctive analcime zone as an exploration guide of the ore deposits (Fig. 3-21). The analcime zone occurs as a lens between argillaceous zone and clinoptilolite – mordenite zone (Zone II of burial diagenesis), and the ore deposits tend to exist below the central, thickest part of the analcime zone. In the Higashiaizu district of Fukushima, Utada et al. (1978) showed the same alteration zones and concluded that Na-mordenite zone on the outside of the analcime zone is also a hydrothermal alteration product responsible for the Kuroko mineralization on the basis of hydrothermal experiments by Kusakabe (1982) and Kusakabe et al. (1981). Utada et al. (1978) considered that the lateral distribution of submarine hydrothermal alteration zones would be caused by the balance in pressure between deep seawater column and hydrothermal water issue. In addition, the stratigraphic control of impermeable mudstone beds as cap rock is also important (Iijima, 1974). In the central part of the Hokuroku district, the Kuroko hydrothermal alteration envelope is partly masked by later hydrothermal clay alteration zones associated with vein-type ore deposits and intrusive quartz diorite (Utada et al., 1981).

Reviewing hydrothermal alterations related to the igneous activity in Cretaceous and Neogene strata of Japan, Utada (1980b) stated that, instead of sodium zeolite zones, calcium zeolite zones appear at the margin of the Kuroko alteration envelope at Furutobe and Wanibuchi mines: A common sequence is wairakite zone – laumontite zone – heulandite zone – stilbite or Ca – mordenite zone, which is the same in the active Katayama geothermal area of the Onikobe district of Miyagi reported by Seki et al. (1969b). The details are not published, however.



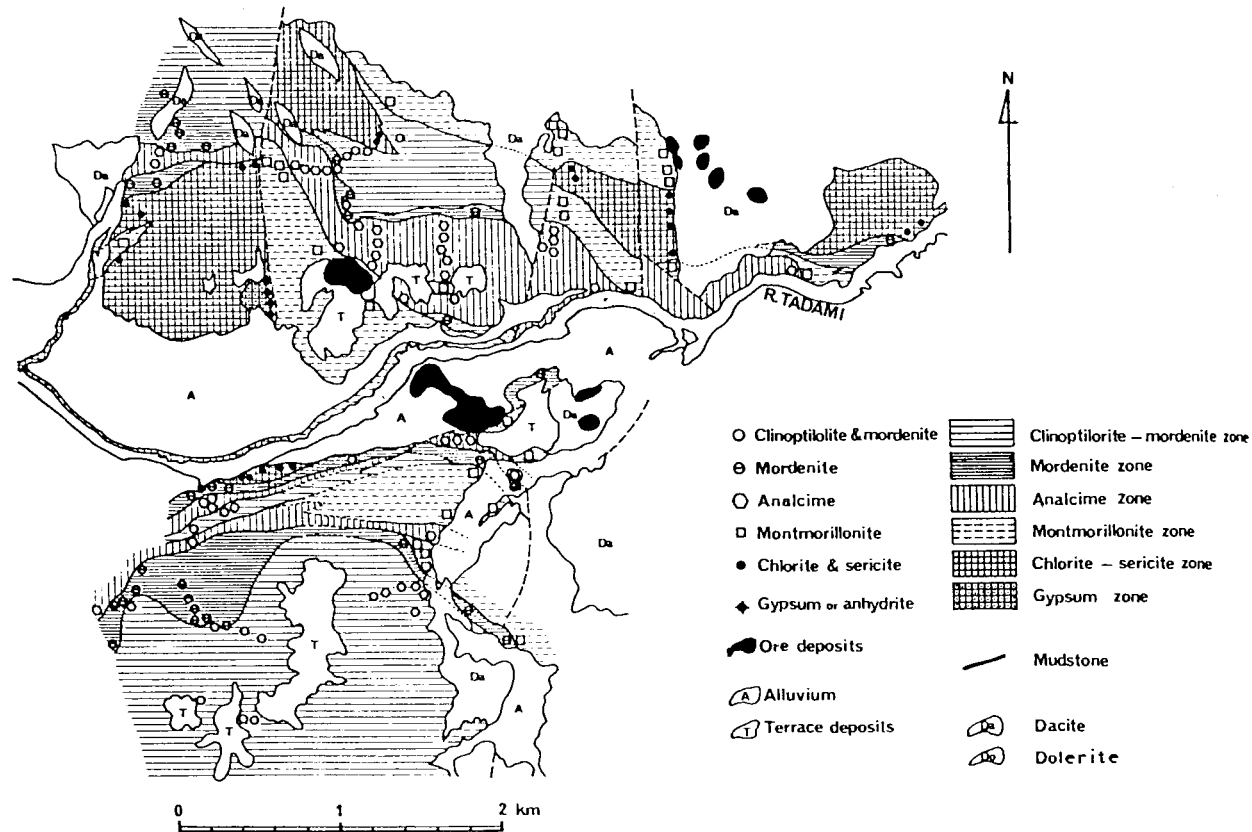


Fig. 3-21. Maps showing alteration zoning around the Kuroko ore deposits of the Oshio and Yokota mines in the Nishiaizu district, Fukushima. The lower map illustrates the isopach of analcime zone which thickens toward the roof of ore deposits. (After Utada et al., 1974, fig. 3, p. 294, and fig. 19, p. 300. Courtesy of The Society of Mining Geologists of Japan.)

CONTACT METAMORPHISM AND BURIAL DIAGENESIS

In the Green Tuff region of northeastern Honshu and Fossa Magna, many granitic bodies of Miocene age intruded thick piles of penecontemporaneous volcanic and volcanoclastic rocks and formed distinctive contact aureoles including zeolite zones. In the Tertiary andesitic volcanic and volcanoclastic rocks of the Tanzawa Mountains of Kanagawa, Seki et al. (1969a) investigated the contact aureole of a quartz diorite mass and distinguished five metamorphic zones based on calcic silicates in andesitic rocks, from inner to outer: (1) amphibolite zone; (2) actinolite – greenschist zone; (3) pumpellyite – prehnite – chlorite zone; (4) laumontite – mixed layer – chlorite zone; and (5) stilbite – (clinoptilolite) – vermiculite zone, the last of which was probably formed by burial diagenesis (Fig. 3-22). Wairakite and yugawaralite occur commonly in the inner part of the laumontite – mixed layer – chlorite zone. Seki studied calcic zeolite series from the standpoint of metamorphic facies (Seki, 1966, 1969, 1973). The formation of calcic zeolites is controlled by temperature, pressure, and silica activity. Utada (1973) investigated contact aureoles of many volcanoplutonic complexes in the Green Tuff region and recognized nearly the same zones as in the Tanzawa Mountains, even in regard to silicic volcanics, except for the occurrence of analcime – (heulandite) zone and clinoptilolite – mordenite or mordenite zone at the margin which are not distinguished from zeolitic zones of burial diagenesis. A contact aureole developed in alternating beds of silicic and mafic volcanoclastic and lava rocks in the western part of the Misaka Mountains, where the relationship of zeolite zoning in between silicic and mafic rocks are clearly observed as shown in Fig. 3-23 (Mizuno, 1974, in Iijima, 1980).

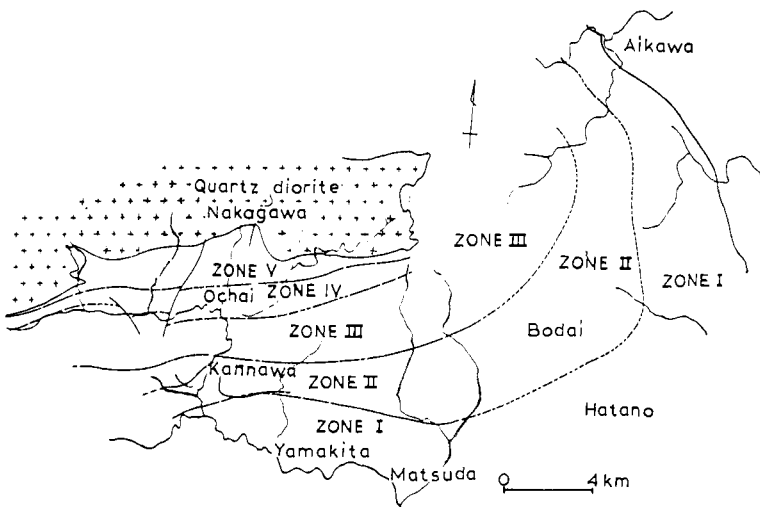


Fig.3-22. Zonal map showing metamorphic grades from the amphibolite facies to the zeolite facies surrounding the quartz diorite mass in the Tanzawa Mountains. (After Seki et al., 1969, fig. 5, p. 12.)

MINERALOGY OF DIAGENETIC ZEOLITES

Clinoptilolite – heulandite

The chemical composition of Japanese clinoptilolites is summarized by Minato and Utada (1971), who classified them into K-, Na-, and Ca-types based on the dominant cations. Minato and Utada (1967, 1971) investigated the thermal stability of the clinoptilolite – heulandite group, and stated that Ca – clinoptilolite can be distinguished from heulandite by its thermal-stability on heating at 400° – 450°C for 4 h, whereas Na- and K-clinoptilolites are stable on heating at 700°C for 4 h. Koyama and Takeuchi (1976) analysed the crystal structure of K-clinoptilolite and concluded that the K-site plays an important role on the thermal stability of clinoptilolite. In Zone II of burial diagenesis of silicic vitric tuffs, the alkali clinoptilolite is dominant in the upper part of the Zone II, whereas Ca-clinoptilolite tends to occur in the lower part of it (Iijima and Utada, 1971; Iijima, 1975, 1978a). The clinoptilolites in Zone II vary in chemical composition even in a thin section. In the Upper Cretaceous Nakanosawa Tuff, Sr-rich alkali clinoptilolites in the shard pseudomorphs are slightly but significantly more siliceous than those filling vesicles; the Si:Al ratio averages 4.86 for 10 samples in the former and 4.74 for 10 samples in the latter (Iijima, 1971; revised analysis in Iijima, 1978a). Sr-rich heulandite of Zone III in altered silicic vitric tuff of the Upper Cretaceous Hakobuchi Group is represented by the silica-rich variety (Iijima, 1978a; Iijima and Ohwa, 1980). It is noteworthy that unusual single idiomorphic crystals with zonal composition ranging from silica-rich Ca – clinoptilolite to silica-rich heulandite were discovered in intergranular openings of porous vitric biocalcarene of the Lower Pliocene Shirahama Limestone at Shimoda, southern Izu, central Honshu (Iijima and Matsumoto, 1984). The complicated clinoptilolite – heulandite crystals coexist with phillipsite and are considered to be of a low-temperature hydrothermal origin.

Mordenite

Nakajima (1973a, b) revised the indexing of X-ray powder data for mordenite and showed that refractive indices of mordenite increase with the Ca-content where b (Å) of synthetic mordenites decreases from 2.49 to 2.43 with the increase of $\text{CaO}/(\text{Na}_2\text{O} + \text{CaO})$ ratio. Seki et al. (1972) stated that the Ca-content of mordenite increases with formation temperature. Mordenite associated with albite in silicic tuff of Zone IV is a Ca-rich variety (Iijima, 1978a).

Analcime

Analcimes in altered silicic tuffs of Zone III, that are transformed from clinoptilolite and mordenite, generally have intermediate Si/Al ratio ranging from 2.4 to 2.8 (Iijima, 1978a). In the Upper Cretaceous Izumi Group in the Izumi Mountains, where dawsonite occurs in veins in mudstone, Nakajima and Koizumi (1966) reported that the Si/Al ratio of analcime decreases with increasing burial depth. Re-examination by Iijima (1975), however, reveals that the composition of analcimes

of Zone III in the Izumi Group of Shikoku and in the Cretaceous and Tertiary deposits of central Hokkaido does not change systematically neither as a function of burial depth nor temperature. The distribution of zeolites in the Izumi Group of the Izumi Mountains is atypical, suggesting a local zeolitization without influence of burial diagenesis. The intermediate Si/Al ratio of analcimes in Zone III seems to be inherited mainly from the precursor clinoptilolite and mordenite (Iijima, 1975, 1978a). The analcime minerals possess sodium as the dominant cations with a small amount of K and Ca throughout Zone III, and there is no tendency to increase the calcium content with increasing burial depth (Iijima, 1975, 1978a; Iijima and Ohwa, 1980). It has not been found that wairakite is transformed from analcime in silicic tuffs during burial diagenesis.

Albite

The composition of albites in Zone IV differs slightly in different precursors. Appreciable amounts of K and Ca are contained in albite transformed from analcime which is transformed from clinoptilolite and mordenite as an alteration product of silicic glass, whereas albite replacing plagioclase has a nearly end-member composition (Iijima, 1978a).

PETROCHEMICAL ASPECTS OF ZEOLITIZATION OF VITRIC TUFF

Iijima (1984) summarized and discussed the behavior of main components, exclusive of water, in zeolitized vitric tuffs of different genetic types of the zeolite formation.

In all types of zeolitization of glassy volcanoclastic rocks, volcanic glass is at first altered to more hydrous zeolites, such as clinoptilolite, mordenite, chabazite, erionite, and phillipsite. The precursor zeolites are replaced by less hydrous zeolites, such as analcime, heulandite and laumontite, due to (1) increasing temperature, (2) increasing pH and salinity of interstitial water, or (3) simply aging associated without increasing temperature, as stated previously. The alkali zeolites are finally substituted by anhydrous alkali feldspars.

The behavior of silica and metallic cations during the zeolite formation is considered from bulk chemical composition of both original and altered tuffs. The main components of natural zeolites, exclusive of H_2O , are SiO_2 , Al_2O_3 , CaO , Na_2O , and K_2O . The mole ratios (1) $\log SiO_2/Al_2O_3$ and (2) $(Na_2O - CaO)/K_2O$ of fresh and altered tuffs are, therefore, calculated and shown in the variation diagrams in which $(Na_2O - CaO)/K_2O$ ratio is plotted on the abscissa and $\log SiO_2/Al_2O_3$ ratio is plotted on the ordinate (Figs. 3-24 – 3-27). Arrays with $Na_2O = CaO$ are on the ordinate; arrays with $Na_2O > CaO$ and $Na_2O < CaO$ are on the + and – sides, respectively, of the diagrams. Arrays with high K_2O tend to concentrate near the ordinate.

Silicic tuff

Siliceous clinoptilolite and mordenite are the initial zeolites formed both by burial diagenesis of silicic vitric tuffs in marine and freshwater sections and by percolation of meteoric water through land-laid silicic vitric tuffs (see Table 3-5). In both types (Figs. 3-24 and 3-27), values of $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the tuffs containing the siliceous zeolites are either higher or lower (0.88–1.17) than those of the original tuffs (0.94–1.06). The excess silica occurs as authigenic low-cristobalite, which was released by the alteration of silicic glass to the zeolites and montmorillonite. The gain and loss of silica during the burial diagenesis and the percolation of meteoric water seem to balance within the zeolitic tuffs.

In saline, alkaline lake deposits of closed basins, on the other hand, the most characteristic feature of the initial zeolitization of silicic vitric tuffs is the formation of such less-siliceous zeolites as phillipsite, chabazite and erionite as well as clinoptilolite and mordenite. The zeolitic tuffs are also characterized by the extremely high content of zeolites and by the scantiness of sheet silicates and silica minerals; the zeolites occur not uncommonly even as a monomineralic aggregate, which is rarely produced by burial diagenesis of silicic tuffs in thick marine and freshwater sections. Values of $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolitic tuffs rich in the less-siliceous zeolites are, of course, much lower (0.80–0.91) than that of the original tuffs (0.97–1.02). Ratios of the tuffs composed almost exclusively of the siliceous zeolites are also rather low (0.94–1.00) (Fig. 3-25). Furthermore, values of $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the analcimolites derived from the precursor zeolitic tuffs in the saline, alkaline lake deposits are generally smaller (0.71–0.90) than those of both the original and precursor zeolitic tuffs. Also, the K-feldspar rocks derived from silicic vitric tuffs have much lower values of $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio than those of the original tuffs. Such significant deficiency of silica in the zeolitic and K-feldspar rocks is interpreted

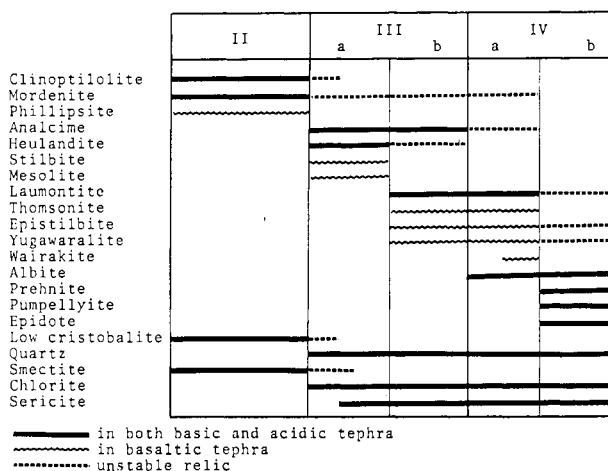


Fig.3-23. Stability ranges of alteration minerals in the Neogene silicic and mafic tephra in contact aureole in the western part of the Misaka Mountains, Yamaguchi. (Slightly modified from Mizuno, 1974.)

as excess silica that was largely dissolved out of the altered tuffs into interstitial, highly alkaline ($\text{pH} = 9.0 - 10.3$) brines, because the brines contain abundant dissolved silica. The dissolved silica is partly precipitated as the Magadi-type chert nodules in mudstone interbedded with the tuffs (Sheppard and Gude, 1973), but the silica budget in the saline, alkaline lake deposits does not seem to be well known.

In thick marine sections, values of $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of analcimic rocks formed by burial diagenesis are almost the same as, or lower ($0.82 - 1.00$) than those of the original tuffs ($0.94 - 1.06$). Ratios tend to be slightly lower than those of the precursor zeolitic tuffs ($0.88 - 1.16$) containing clinoptilolite and mordenite (Fig. 3-24). As compared with those of the analcimolites ($0.71 - 0.90$) in saline, alkaline lake deposits, the values of $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the marine analcimic rocks are large. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of analcime in silicic vitric tuffs is practically controlled by the composition of precursor zeolites (Sheppard and Gude, 1969; Iijima, 1978a) and, possibly, by the salinity of interstitial brines in saline, alkaline lake deposits (Iijima and Hay, 1968). The precursor phillipsite and chabazite, that are characteristic in the saline lake deposits, necessarily decrease the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of analcime, whereas the silicic clinoptilolite and mordenite, that are the precursor of analcime in marine sections, increase the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of analcime. In addition, abundant authigenic quartz plays a far more important role in determining the large values of $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the analcimic tuffs in the deep part of the marine section, though excess silica tends to be dissolved out of the tuffs at an elevated temperature (about $85^\circ - 125^\circ\text{C}$).

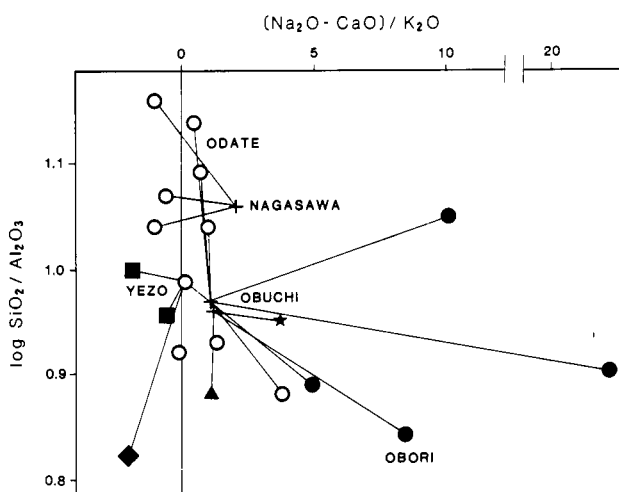


Fig. 3-24. $(\text{Na}_2\text{O} - \text{CaO})/\text{K}_2\text{O}$ versus $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio variation diagram of silicic tuffs altered by burial diagenesis in thick marine and freshwater sections. The tie lines show the same origin of fresh and altered tuffs. Crosses = silicic glass or vitric tuff; circles = clinoptilolite and/or mordenite tuff; dots = analcime tuff; triangles = analcime-heulandite tuff; squares = heulandite tuff; diamonds = laumontite tuff; and stars = albitized tuff. (After Iijima, 1984, fig. 3, p. 40. Courtesy of VNU Science Press.)

In the silicic vitric tuffs which are altered to calcic zeolite, values of $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio tend to decrease with progress of both reaction series:

- (1) clinoptilolite $\rightarrow$ heulandite $\rightarrow$ laumontite $\rightarrow$ prehnite and
- (2) mordenite $\rightarrow$ laumontite $\rightarrow$ prehnite.

The depletion of silica is consistent with the increase of solubility of silica at elevated temperature. The dissolution of silica at elevated temperature agrees with the enrichment of Ca in the altered tuffs composed of calcic zeolites and their derivatives, as considered from the increasing negative values of $(\text{Na}_2\text{O} - \text{CaO})/\text{K}_2\text{O}$ ratio in the progress of the reaction series (Fig. 3-24 and 3-26).

In the submarine hydrothermal alteration halo of the Kuroko-type polymetallic (Pb–Zn–Cu) sulfide ore deposits in northeast Honshu, analcime was formed by the interaction of the two precursors clinoptilolite and mordenite with a weakly alkaline hydrothermal solution, which percolated the chlorite–sericite and the smectite zones surrounding the sulfide ore (Iijima, 1974; Utada et al., 1974). Values of $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the analcemic tuffs are extremely low (0.71) at Nishiaizu, whereas they are rather high (0.94–1.07) at Ohdate. Also, analcemic tuff

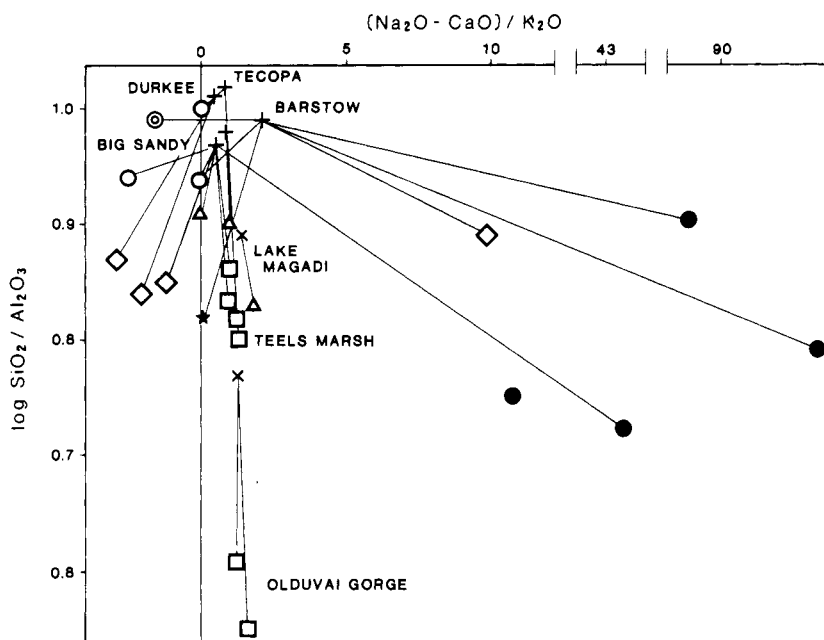


Fig. 3-25. $(\text{Na}_2\text{O} - \text{CaO})/\text{K}_2\text{O}$ versus $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio variation diagram of vitric tuffs in saline, alkaline lake deposits, in which the tie lines show the same origin of fresh and altered tuffs. Crosses = silicic glass or vitric tuff; circles = clinoptilolite-rich tuff; double circles = mordenite-rich tuff; squares = phillipsite-rich tuff; diamonds = chabazite-rich tuff; triangles = erionite-rich tuff; dots = analcimolite; and stars = K-feldspar-rich tuff. (After Iijima, 1984, fig. 2, p. 38. Courtesy of VNU Science Press.)

formed by hydrothermal alteration in the Misaka Mountains has a large $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (1.04). These data reflect extensive migration of silica through the hydrothermal water during the formation of analcime (Fig. 3-26).

In saline, alkaline lake deposits, the range of $(\text{Na}_2\text{O} - \text{CaO})/\text{K}_2\text{O}$ ratio of altered tuffs rich in phillipsite and erionite keeps very close to that of the original vitric tuffs, but the ratio of tuffs rich in chabazite varies from +9.9 to -2.9. There is a general tendency that the values of $(\text{Na}_2\text{O} - \text{CaO})/\text{K}_2\text{O}$ ratio of the original silicic vitric tuffs decrease during the formation of clinoptilolite and mordenite in all types of the zeolite formation including the saline, alkaline lake deposits. This is mainly caused by a relative increase of CaO compared with Na_2O . It is worthy to note that CaO predominates over Na_2O in some tuffs rich in chabazite, clinoptilolite, or mordenite which are formed in such highly alkaline brines in which Ca ions are deficient.

The K-feldspar rocks in the saline, alkaline lake deposits that originate from rhyolitic vitric tuffs, are plotted close to the ordinate of the variation diagram in Fig. 3-25. The K-feldspar replaces the precursor zeolites under a supersaline environment in which K-ions become dominant due to the precipitation of sodic saline minerals, such as trona (Hay, 1966; Sheppard and Gude, 1968; Surdam and Sheppard, 1978).

Values of $(\text{Na}_2\text{O} - \text{CaO})/\text{K}_2\text{O}$ ratio (1) of analcimolites in saline, alkaline lake deposits, and (2) of analcimic rocks and dehydrated albite rocks in thick marine sec-

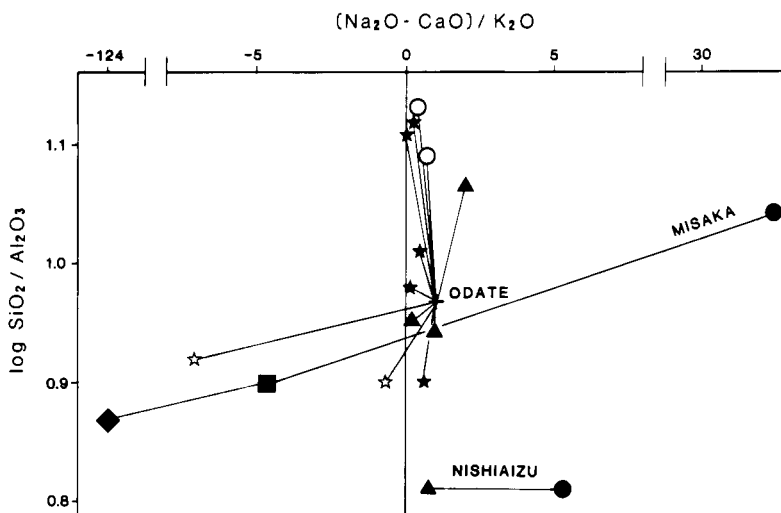


Fig. 3-26. $(\text{Na}_2\text{O} - \text{CaO})/\text{K}_2\text{O}$ versus $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio variation diagram of silicic tuffs altered by hydrothermal activities, in which the tie lines show the same origin of fresh and altered tuffs. Odate and Nishiaizu are the Kuroko polymetallic sulfide ore mineralization areas. Crosses = silicic glass; circles = clinoptilolite and mordenite tuff (by burial diagenesis); dots = analcime-rich tuff; triangles = analcime tuff associated with heulandite, mordenite, or calcite; squares = laumontite tuff; diamonds = laumontite - prehnite - albite - quartz tuff; open stars = montmorillonite tuff; solid stars = sericite - chlorite - quartz tuff associated with authigenic K-feldspar. (After Iijima, 1984, fig. 4, p. 42. Courtesy of VNU Science Press.)

tions are very high, i.e., respectively, 10.8–93.5, with an average of 59.2, and 5.0–32.5 averaging 14.1, as compared with 0.5–2.1 of the original silicic vitric tuffs. The considerable increase in Na_2O content is certainly caused by the addition of Na-ions of interstitial water to the precursor zeolites on analcitzation. The higher enrichment of Na_2O in the lacustrine analcimolites than in the marine analcimic rocks is due to the higher values of $(\text{Na}_2\text{O} - \text{CaO})/\text{K}_2\text{O}$ -ratio of brines in the lake deposits than those of seawater and interstitial waters of marine deposits: the values for brines in Recent sediments of Teels Marsh in Nevada and Lake Magadi in Kenya are, respectively, 61.8 on the average and 121.1 (Hay, 1966; Surdam and Sheppard, 1978), whereas the value of normal seawater is 46.2.

Mafic and ultramafic tuff

Zeolites derived from mafic and ultramafic vitric tuffs are predominantly poor in silica. The composition of host rocks strongly affects the mineralogy of authigenic zeolites formed especially at a near-surface condition. An excellent example is the case of zeolitic palagonite tuffs on Oahu Island, Hawaii, which were formed by the percolation of groundwater in a semi-arid humid climate (Hay and Iijima,

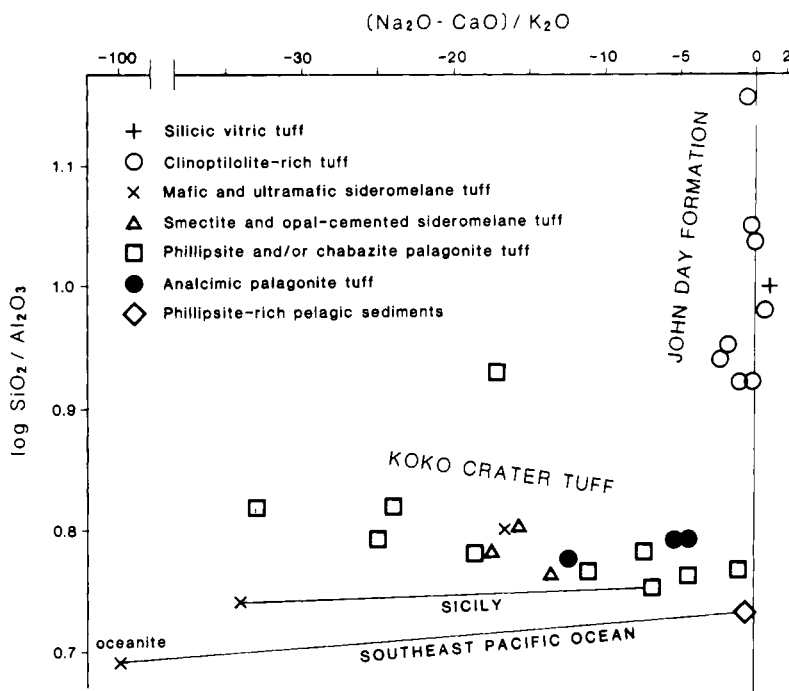


Fig.3-27. $(\text{Na}_2\text{O} - \text{CaO})/\text{K}_2\text{O}$ versus $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio variation diagram of (1) land-laid tuffs of the John Day Formation of Oregon, (2) the Koko Crater Tuff on Oahu Island of Hawaii altered by percolation of meteoric water, (3) submarine palagonite tuff from Sicily, and (4) phillipsite-rich pelagic sediments from the Southeast Pacific Ocean. (After Iijima, 1984, fig. 5, p. 45. Courtesy of VNU Science Press.)

1968). Phillipsite and chabazite predominate in basanite tuffs, whereas less-siliceous gonnardite and natrolite are characteristic of melilite – nephelinite tuffs (Hay and Iijima, 1968; Iijima and Harada, 1968). In the porous palagonite tuffs of the Koko Crater Tuff, values of $(\text{Na}_2\text{O} - \text{CaO})/\text{K}_2\text{O}$ ratio are quite variable (-33 to -1.1), whereas values of $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio are limited ($0.76 - 0.82$ with the exception of one sample having the ratio of 0.93). The original basanite sideromelane tuff is situated at the center of the variation field (Fig. 3-27). In the variation diagram, analcemic palagonite tuffs of the Koko Crater Tuff tend to concentrate on the right-hand side of both unaltered tuff and phillipsite – chabazite-cemented palagonite tuff. This fact suggests relative enrichment of Na_2O in the analcemic tuffs.

In a submarine palagonite tuff of Sicily Island, Italy (Honnorez, 1978), values of $(\text{Na}_2\text{O} - \text{CaO})/\text{K}_2\text{O}$ ratio markedly decrease from -34 of the original basaltic tuff to -6.7 of phillipsite – chabazite-cemented palagonite tuff, whereas values of $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio are almost unchanged. The same relation exists between oceanic tholeiites and phillipsite-rich pelagic sediments from the Southeast Pacific Ocean (Fig. 3-27). Such significant increase in values of $(\text{Na}_2\text{O} - \text{CaO})/\text{K}_2\text{O}$ ratio results from the fixation of Na- and K-ions in interstitial seawater on the zeolitic palagonite tuffs and phillipsite-rich sediments, a few meters below the sediment – water interface. The fixation must have required a few million years as inferred from the very slow sedimentation rate ($< 1 \text{ m Ma}^{-1}$) of pelagic zeolitic clays and from the growth of deep-sea phillipsite at a depth between 1 and 4 m below the sea bottom.

Part II. Silica diagenesis

INTRODUCTION

Much work has been performed on silica diagenesis of fine-grained siliceous rocks and reviewed occasionally (e.g., Dapples, 1967, 1979; Calvert, 1983; Laschet, 1984). The present contribution concentrates on reviewing recent Japanese published information. Fine-grained siliceous rocks on the Japanese Islands exist to varying extents in all Phanerozoic strata except the Cambrian which have not been found in Japan. These rocks occur in marine sections with the exceptions of some continental diatomite of Neogene and Quaternary age. The occurrence and nature of the Japanese siliceous rocks are summarized by Iijima and Utada (1983) as shown in Figs. 3-28 and 3-29.

SILICA PHASES IN FINE-GRAINED SILICEOUS ROCKS

Silica phases found in fine-grained siliceous rocks are listed in Table 3-7. Jones and Segnit (1971) distinguished three metastable silica phases at low temperatures, such as opal-A, opal-CT and opal-C¹, all of which appear in the Japanese Neogene siliceous rocks. Opal-A occurs as unaltered siliceous organic remains of diatoms, radiolarians and sponge spicules, which are transformed to quartz through intermediate opal-CT and opal-C during burial diagenesis. Opal-A is also produced by incipient diagenetic alteration of silicic volcanic glass fragments in vitric tuffs and vitric siliceous deposits (Iijima et al., 1980). Besides the above four silica phases, low-cristobalite and disordered tridymite (opal-T)² appear at low temperatures.

Disordered tridymite that does not involve cristobalite stacking (Iijima proposed here to call it opal-T) occurs most definitely at low temperatures in volcanic and biogenic siliceous rocks. Akizuki and Shimada (1979) described a silica phase from the Hohsaka opal deposit in the Nishiaizu district of Fukushima, which occurs in vugs of hydrothermally altered glassy rhyolite. The opaline silica phase possesses the "opal-CT"-type X-ray powder diffraction pattern, but shows tridymite stacking only by electron diffraction analysis. Akizuki and Shimada proposed, therefore, to call this "opal-CT"-type silica phase "disordered tridymite" (opal-T). Iijima and Tada (1981) described the differences in mode of occurrence of opal-CT and opal-T in the Neogene marine siliceous sections of northern Japan. The opal-T fills interstices and veins of diatomites and opaline cherts and vugs in rhyolites. Opal-T also replaces wood entombed in welded tuff (R. Tada, pers. commun., 1985). Tada and Iijima (1983b) studied the differences in X-ray diffraction and in thermal stability between opal-CT and opal-T. The $d(001)$ spacing of opal-T is around 4.11 Å, which

¹ Opal-A is defined as amorphous opal; opal-CT as disordered cristobalite with tridymite stackings; and opal-C as ordered cristobalite with a small amount of tridymite stackings.

² Opal-T is defined as disordered tridymite.

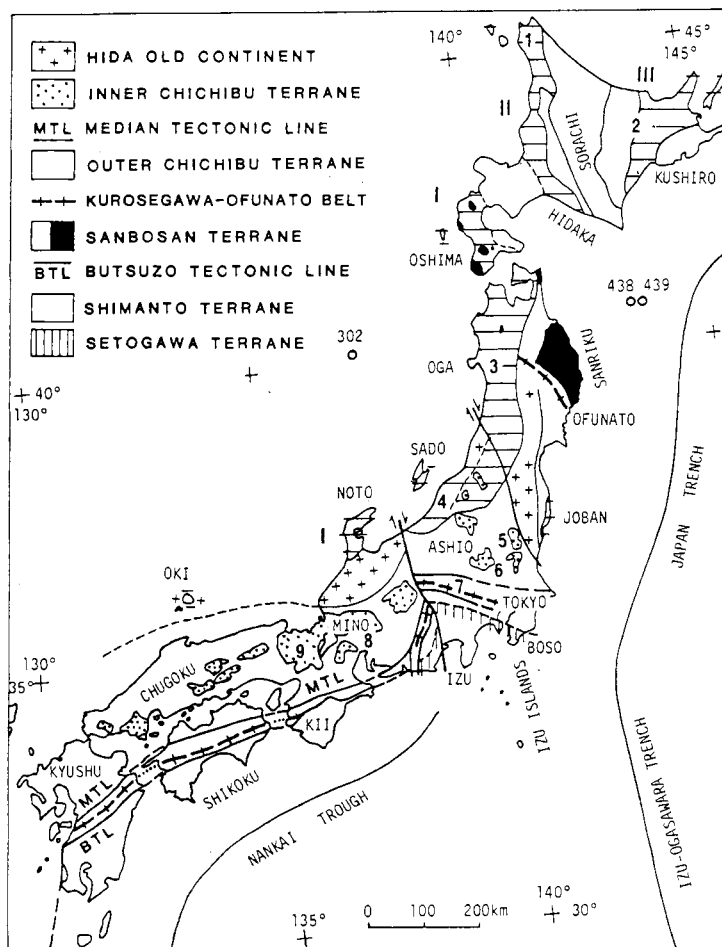


Fig.3-28. Distribution of fine-grained siliceous rocks in the Japanese Islands. Ruled area shows the distribution of Miocene diatomaceous and siliceous rocks in northern and west coasts of Japan: *I* = Japan Sea coast; *II* = central Hokkaido coast; and *III* = east Hokkaido coast. *I* = Tenpoku; 2 = Kitami; 3 = Akita; 4 = Niigata; 5 = Yamizo; 6 = Kuzuh; 7 = Chichibu; 8 = Inuyama; 9 = Tanba; 302, 438, 439 = DSDP sites. (After Iijima and Utada, 1983, fig. 1, p. 48.)

is equivalent to the largest value of $d(101)$ spacing of opal-CT. The opal-CT crystallizes to opal-C with $d(101)$ spacing of $4.06 - 4.08 \text{ \AA}$ by heating at 1000°C for several days, whereas the $d(001)$ peak of opal-T is unchanged even after heating at 1000°C for eleven days. The mixture of opal-T and opal-CT crystallizes unexpectedly to opal-C by heating at 1000°C , however. Tada and Iijima further studied the mixtures of opaline silica phases by X-ray powder diffraction and its implication for silica diagenesis. Such mixtures occur commonly in nature, e.g., opal-CT and opal-T in opaline cherts, and opal-CT and low-cristobalite in vitric opaline porcelanites. The effect of mixing on the strongest $4 \text{ \AA}$ peaks of each phase was observed on X-

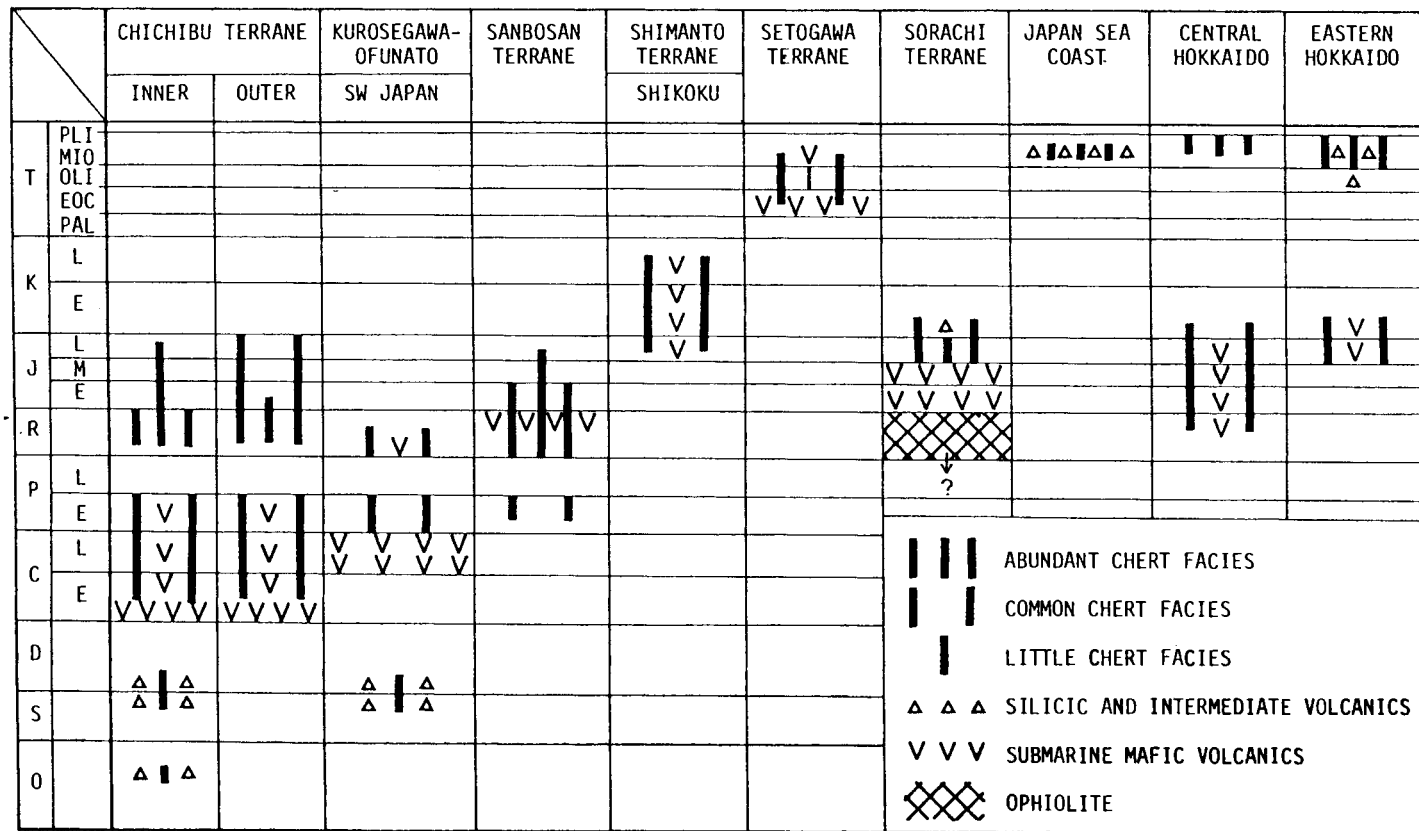


Fig.3-29. Stratigraphic distribution of fine-grained siliceous rocks in the Japanese Islands. For tectonic units refer to Fig.3-28. (After Iijima and Utada, 1983, fig. 2, p. 49.)

ray powder diffractograms of artificial mixtures. In the case of opal-CT and opal-T mixture, the 4 Å peaks are never split but are shouldered, acute, or rounded (Fig. 3-30 and Table 3-8). Tada and Iijima (1983b) concluded that the mixtures of two opaline silica phases with specific ratios can be distinguished by these visual distinctions and peak shape characteristics.

Well-ordered low-cristobalite occurs commonly as an alteration product of silicic volcanic glass fragments in zeolitic vitric tuffs, bentonitic tuffs, and vitric opaline

TABLE 3-7

Silica phases in fine-grained siliceous rocks

Metastable phases	Stable phases
Opaline minerals	Quartz
Amorphous silica (opal-A)	Pseudocubic quartz (melanophlogite)
Low-cristobalite (opal-CT, opal-C)	Length fast-chalcedony
Low-tridymite (opal-T)	Length slow-chalcedony
	Lutecite
Hydrous silicates changing to chert in alkaline, saline lake deposits	
Kenyaite	$\text{NaSi}_{11}\text{O}_{20}(\text{OH})_{20} \cdot 3\text{H}_2\text{O}$
Magadiite	$\text{NaSi}_7\text{O}_{13}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$
Silhydrite	$3\text{SiO}_2 \cdot \text{H}_2\text{O}$
Makatite	$\text{NaSi}_2\text{O}_3(\text{OH})_3 \cdot \text{H}_2\text{O}$

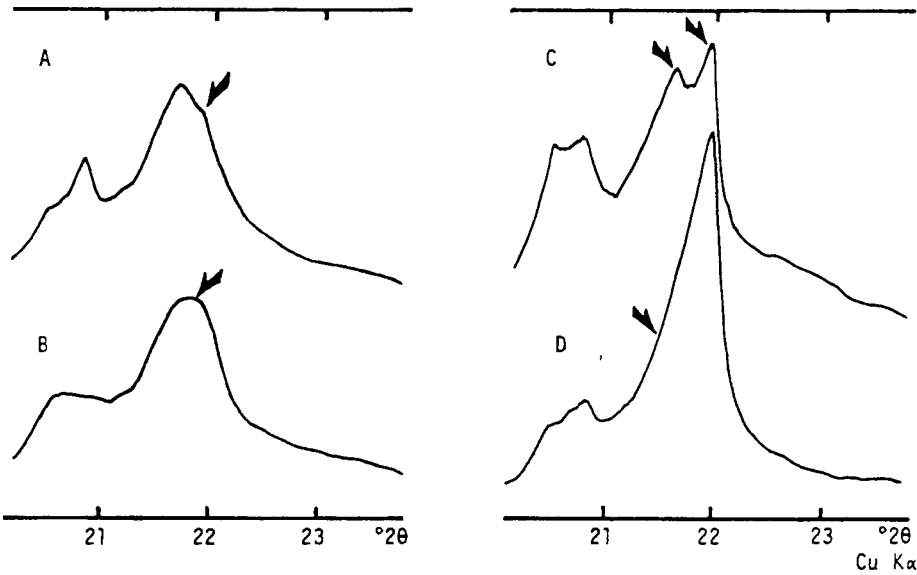


Fig.3-30. Some typical X-ray diffraction powder patterns of 4 Å peak of mixtures of two opaline silica phases. (A) Shouldered peak of 1/2 mixture of tridymite–4.08 Å opal-CT; (B) rounded peak of 1/1 mixture of tridymite–4.06 Å opal-CT; (C) splitted peak of 4/1 mixture of tridymite–cristobalite; (D) tailed peak of 1/2 mixture of 4.06 Å opal-CT – cristobalite. (After Tada and Iijima, 1983, fig. 2, p. 234.)

porcelanites associated with montmorillonite and silicic zeolites, such as clinoptilolite and mordenite (Iijima and Tada, 1981; Tada and Iijima, 1983b). The low-cristobalite has much sharper X-ray reflections than opal-C crystallized from opal-CT in porcelanites, and has no trace of tridymite stacking. The $d(101)$ spacing of low-cristobalite is limited in a narrow range of 4.04–4.06 Å, and does not systematically change with burial depth. It contains more appreciable amounts of Al, Ca, Na and K than opal-CT and opal-T. The transformation of low-cristobalite to quartz tends to occur at a slightly higher temperature, i.e., at greater burial depth than the transformation of opal-CT and opal-C to quartz, but at somewhat lower temperature than the transformation of clinoptilolite to analcime and/or heulandite, which occurs at around 81°–91°C (Iijima et al., 1981; Iijima, 1986a).

In conclusion it can be stated that opaline minerals are strongly affected by the precursor materials as shown in Table 3-9.

BURIAL DIAGENESIS IN SUBSURFACE SECTIONS

Non-calcareous siliceous rocks, such as diatomites, diatomaceous shales, lithified porcelanites, cherts, and siliceous shales are widespread in thick Neogene marine sections of northern Japan, and constitute stratigraphic formations. The Neogene gas- and oilfield regions, such as Akita, Niigata and Tenpoku, are also located in

TABLE 3-8

The visual distinctions in the 4 Å peak shapes of opal-T – opal-CT, opal-CT – cristobalite, and opal-T – cristobalite mixtures

Mixing ratio	T – 4.09 Å CT	T – 4.08 Å CT	T – 4.06 Å CT	4.06 Å CT – Cr	T – Cr
9/1	–	–	–	(tailed)	shouldered
4/1	shouldered	(shouldered) ¹	shouldered	(tailed)	split
2/1	(acute)	(shouldered)	shouldered	(tailed)	tailed
1/1		shouldered	(shouldered) rounded	tailed	tailed
1/2	acute	shouldered	shouldered	(tailed)	(tailed)
1/4	(shouldered) acute	(shouldered)		(tailed)	(tailed)

¹ () means not significant.

TABLE 3-9

Relation of silica phases to precursor material

Silicic glass → opal-A → low-cristobalite → quartz
Biogenic opal (opal-A) → opal-CT → (opal-C) → quartz
Silica-saturated solution → opal-A → opal-T → quartz

northern Japan and in its offshore regions, where these siliceous formations play an important role as source and reservoir rocks (Aoyagi and Iijima, 1983). Much work on silica diagenesis was performed in not only surface but also subsurface sections of the Neogene siliceous rocks (Mitsui, 1975; Mitsui and Taguchi, 1977; Aoyagi, 1979; Aoyagi and Kazama, 1980; Iijima and Tada, 1981; Tada, 1982; Tada and Iijima, 1983a; among others). It was pointed out by Iijima and Tada (1981) that the silica mineral composition and lithologic characters, such as toughness, porosity, and density of fine-grained siliceous rocks in the subsurface sections, differ from those in the surface sections. In the thick subsurface sections of deep drillholes, silica minerals are distributed in a vertical arrangement from a shallower opal-A (biogenic opal) zone to a deeper quartz zone through an intermediate opal-CT zone. The same silica mineral zones were described in the Neogene sections from DSDP/IPOD holes at Sites 438 and 439 off Sanriku (Iijima et al., 1980). Such vertical silica mineral zones are produced by progressive transformations of opal-A siliceous organic remains to quartz through opal-CT during burial diagenesis (Fig. 3-31). Iijima and Tada (1981) concluded that the silica transformations are principally promoted by increasing temperatures with increase of burial depth, and consequently the depth of the top of each zone is a function of geothermal gradient. The temperatures are approximately $22^{\circ} - 50^{\circ}\text{C}$ at the top of opal-CT zone and approximately 72°C at the top of quartz zone, the values being inferred from static bottomhole temperature measurements of some deep drillholes in the Akita and Tenpoku oilfields. Aoyagi (1979) and Aoyagi and Kazama (1980) proposed to use the silica mineral zones as a geothermometer, although its accuracy would be very limited. The silica mineral zones and the zeolite zones are concordant stratigraphically with each other, and the top of the quartz zone exists generally about 70 – 250 m shallower in the subsurface than the top of Zone III (analcime – heulandite zone) in the Neogene marine sections of northern Japan (Iijima and Tada, 1981; Iijima et al., 1981).

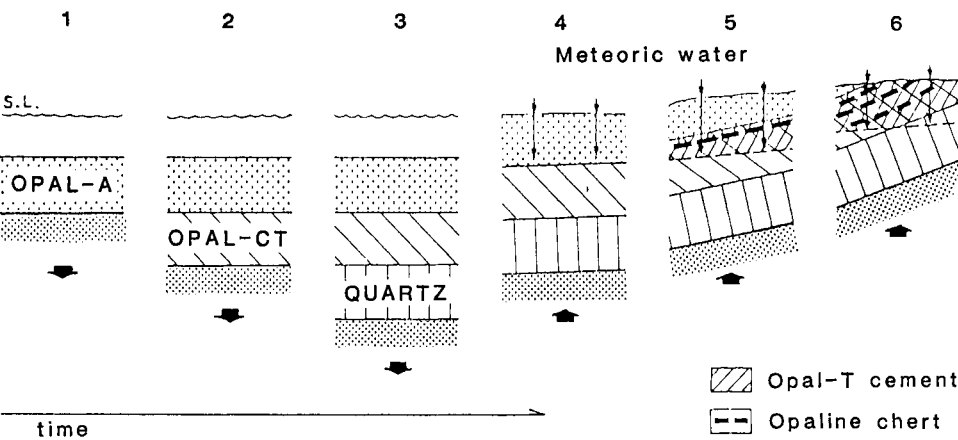


Fig.3-31. Development of zonation of silica phases during burial (stages 1 – 3) and its modification during uplift (stages 4 – 6).

Mitsui and Taguchi (1977) and Iijima and Tada (1981) reported the progressive ordering of opal-CT in the opal-CT zone with burial depth, which is represented by the gradual decrease of $d(101)$ spacing from 4.11 to 4.05 Å, as Murata and co-workers discovered in Miocene siliceous rocks of the Monterey Formation of California (Murata and Nakata, 1974; Murata and Larson, 1975; Murata et al., 1977). The ordering of opal-CT is also affected by the temperature in Neogene siliceous rocks of northern Japan as shown in Fig. 3-32 (Iijima and Tada, 1981).

In summary, the silica diagenesis in Neogene siliceous rocks of northern Japan is strongly affected by temperature compared to other factors such as chemical composition and time. This is probably due to the fact that Neogene siliceous rocks in northern Japan are generally non-calcareous, are relatively homogeneous due to bioturbation, and their burial history is similar to each other (Tada and Iijima, 1983a).

In contrast, chemical composition of siliceous rocks affects silica diagenesis significantly in the Monterey Formation (Isaacs, 1981a). The Monterey Formation examined by Isaacs is generally calcareous, is rich in organic material, and variation in chemical composition within centimeter to meter scale is considerable because of the lack of bioturbation. This small-scale inhomogeneity in composition as well as the presence of calcareous and organic material is the probable cause of early formation of chert in the Monterey Formation.

Iijima and Tada (1981) and Tada and Iijima (1983a) pointed out that the relationship between porosity and burial depth of Neogene siliceous rocks in the subsurface sections can be represented as an exponential curve similar to that of Neogene mudstone down to about 5 km deep (Fig. 3-33). In detail, a small transitional step appears between opal-A zone of diatomites and diatomaceous shales and opal-CT zone of opaline porcelanites due to rapid dissolution of frustules and concurrent

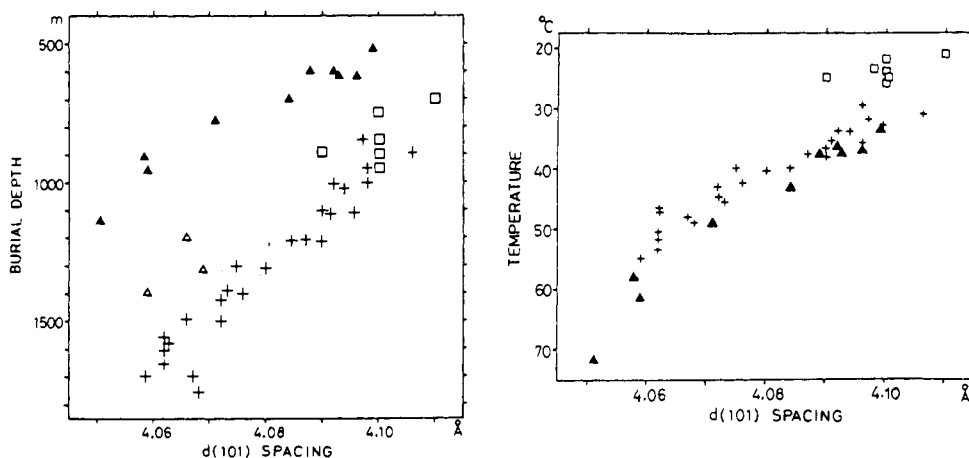


Fig.3-32. Relation of $d(101)$ spacing of opal-CT in opal-CT zone to burial depth and to temperature. Open triangles = Oganaka AK-1 well; solid triangles = Shinonome AK-1 and Tsuchizakioki SK-12 wells; crosses = MITI-Hamayuchi well; squares = DSDP/IPOD sites 438 and 439. (After Iijima and Tada, 1981, figs. 6 and 10, pp. 193 and 195. Courtesy of Int. Assoc. of Sedimentologists.)

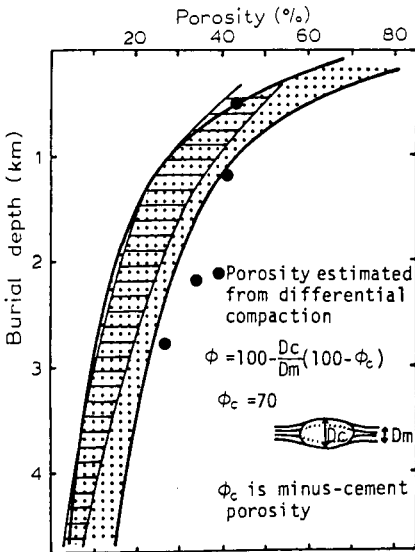


Fig. 3-33. Schematic diagram showing the relationship between porosity and burial depth of the Neogene diatomites and porcelanites (ruled) and mudstones (stippled) collected from drillholes in some oilfields of northern Japan. Solid circles represent carbonate concretions entombed in siliceous rocks in outcrops; their burial depth was obtained from stratigraphic column and their porosity was estimated from differential compaction assuming that original porosity (ϕ_c) was 70%. (Modified from Iijima and Utada, 1983, fig. 6, p. 59.)

compaction. There is, however, no transitional step between opal-CT zone and quartz zone. This fact suggests that the transformation of opal-CT to quartz, generally referred to as chertification, does not contribute to porosity reduction. Isaacs (1982b), on the other hand, reported an abrupt decrease in porosity corresponding to the opal-CT to quartz transformation in the Monterey Shale of California. Tada (1982) and Tada and Iijima (1983a) observed the changes in size and shape of pores in the siliceous rocks with increasing burial depth, both on polished surfaces under the scanning electron microscope (SEM) and in thin-sections mounted by stained epoxy resin under the petrographic microscope (Fig. 3-34). Pores of the diatomites of opal-A zone are composed predominantly of micropores ($2-10\ \mu\text{m}$ in size) with common ultramicropores ($< 2\ \mu\text{m}$ in size) and a small number of macropores ($> 10\ \mu\text{m}$ in size). The micropores occur largely as intergranular pores, whereas the ultramicropores occur as interstices of diatom fragments and pores of frustules. Almost all frustules were dissolved at the boundary between opal-A and opal-CT zones. The opal-CT was spontaneously precipitated as tiny particles of less than $100\ \text{\AA}$ in diameter by the microdissolution-precipitation process and filled the micropores in the neighborhood of dissolved frustules. Thus, ultramicropores prevail instead of micropores in the opaline porcelanites of opal-CT zone. Characteristic opal-CT lepispheres are found only within some macropores, i.e., molds of siliceous organic remains and chambers of radiolarian skeletons, as shown in SEM photographs by Honda (1978). Accor-

ding to Tada and Iijima (1983a), the main factor decreasing the amount of intergranular pores of porcelanites was mechanical compaction in opal-CT zone. It is unknown whether chemical compaction resulting from pressure-solution occurs in opal-CT zone or not. In the quartz zone, micropores again become dominant in quartzose porcelanites and construct a network pore structure in the framework of equigranular quartz particles of about $1\text{ }\mu\text{m}$ in size. Macropores remain as molds of siliceous organic remains and pores of radiolarians and larger diatoms. Micropores gradually decrease with increasing burial depth and macropores are isolated. Quartzose porcelanite in the MITI-Hamayuchi well, however, has still around 20% porosity at a burial depth of about 4.5 km. An approximate 10 km burial depth might be needed for the formation of compact quartzose chert devoid of porosity, extrapolating from the porosity – burial depth diagram (Fig. 3-33).

One of the important conclusions reached by Tada and Iijima (1983a) is that the porosity reduction in Neogene siliceous rocks of northern Japan is principally caused by mechanical and chemical compaction, but not by additional silica cementation. Similar conclusion was reached by Isaacs (1981a, b) for siliceous rocks in the Monterey Formation. It is not certain, however, that this conclusion is directly applicable to Mesozoic and Paleozoic radiolarian cherts. Diatom frustules are almost entirely dissolved during silica transformations in Neogene siliceous rocks (Tada and Iijima, 1983a), whereas there are many radiolarian skeleton remains in the Mesozoic and Paleozoic quartzose cherts (Kakuwa, 1984). Consequently, less com-

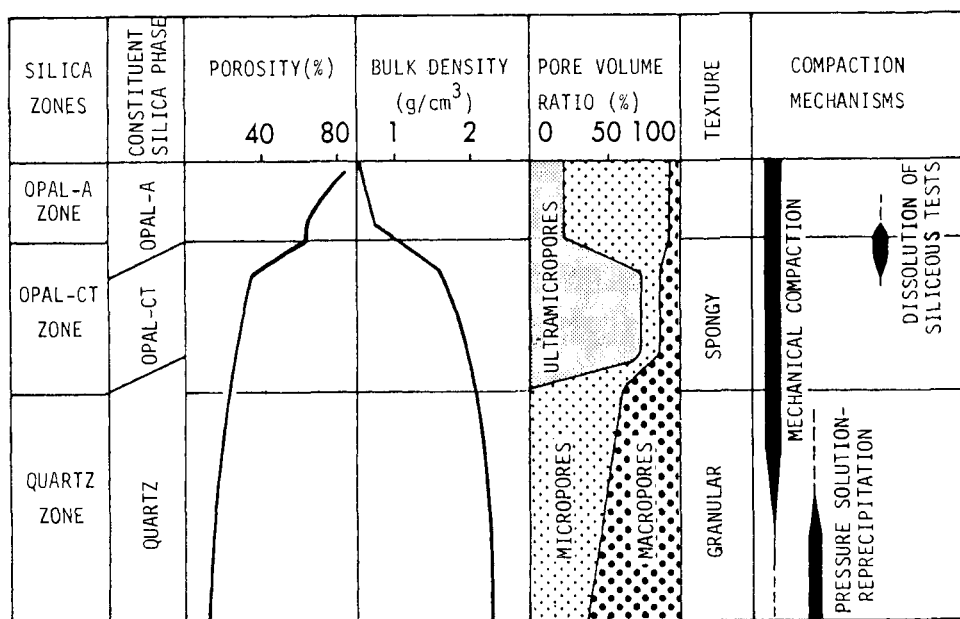


Fig.3-34. Diagenetic changes in silica phases, textures, and mass properties of the Neogene siliceous rocks in northern Japan during burial. (After Tada and Iijima, 1983, fig. 11, p. 925. Courtesy of the SEPM.)

paction occurred during silica phase transformations in radiolarian rocks in contrast to diatomaceous rocks.

Early chert, which was formed by impregnation of additional silica during early stage of burial, is relatively common in calcareous and/or organic-rich parts of the Monterey Formation (Tada, 1984) as well as in deep-sea calcareous siliceous sediments (Heath and Moberly, 1971; Lancelot, 1973; Keene, 1975; Garrison et al., 1975; Kelts, 1976; and others). These early chert nodules show distinct differential compaction suggesting they were formed when host sediments had a porosity of 60–70% (Isaacs, 1980; Tada, 1984). Early chert, however, is rare in the Neogene non-calcareous siliceous rocks of northern Japan.

Bedded cherts of the Tertiary Setogawa and Mineoka terranes and of the Mesozoic and Late Paleozoic Chichibu and Sanbosan geosynclines are not necessarily considered to have been buried as deep as 10 km. The degree of compaction of Lower Jurassic radiolarian bedded chert of the Aoyama Formation, Kuzuh district of Tochigi, can be estimated from the following information: thickness of compacted chert is at least 0.45 of the original thickness as a result of the differential compaction around a silicified wood (Iijima et al., 1986) (Fig. 3-35). Stylolites and microstylolites parallel to or oblique to stratification commonly occur in the bedded cherts as a consequence of pressure-solution (Iijima et al., 1978; Iijima et al., 1981; Yoshimura et al., 1982). Iijima and Tada (1981) proposed that the pressure-solution–reprecipitation process due to either overloading or tectonic pressure plays an important role in the final lithification of porous quartzose porcelanites to compact cherts during burial diagenesis. Microstylolites suggesting pressure-solution are observed in quartzose siliceous mudstone of the Miocene Masuporo Formation at a depth of 3970 m (estimated maximum burial depth of 4200 m) in the MITI-Hamayuchi well of the Tenpoku oilfield region, northern Hokkaido (Iijima and Tada, 1981). In quartzose sandstones, intergranular pressure-solution precedes stylolitization (Heald, 1955). It is also confirmed petrographically (Heald, 1955, 1956; Houseknecht, 1984) and experimentally (Renton et al., 1969) and explained theoretically (Weyl, 1959; Rutter, 1976; Robin, 1978) that intergranular pressure-solution is more intense in finer-grained quartz sand. Intergranular pressure-solution is commonly observed from a depth of around 1000 m in quartz-

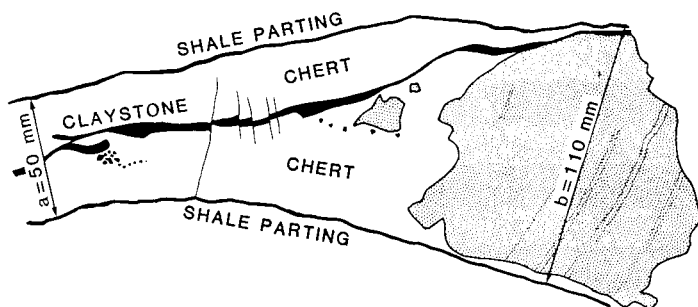


Fig.3-35. Differential compaction of Lower Jurassic radiolarian chert around a silicified wood, *Brachyoxylon* (stippled), in the Aoyama Chert Formation of Kuzuh, Tochigi. The compaction degree a/b is 0.45.

zose sandstones (Tada and Siever, 1985). The following question arises here: in finer-grained quartzose porcelanites, however, at what depth does the pressure-solution – reprecipitation mechanism progresses effectively? Much more experimental study and petrographic observation are needed to solve this problem.

Shibata and Mizutani (1980) measured the isotopic age of Upper Jurassic radiolarian siliceous shale interbedded with black shale of the Hidakanayama district in central Japan. In addition to authigenic quartz, the diagenetic minerals in the siliceous shale are calcite, dolomite, rhodochrosite, chlorite and mica. The averaged Rb – Sr and K – Ar age for whole-rock samples is 128 Ma, which is 17 Ma younger than the age of the early Tithonian (approximately 145 Ma) assigned by radiolarian biostratigraphy. Mizutani and Shibata (1983) interpreted the time difference, 17 Ma, as representing the duration of chemical diagenesis before the Rb – Sr system was closed (Fig. 3-36). The paragenesis of the diagenetic minerals was determined in thin-sections under the petrographic microscope.

LATER DIAGENESIS IN SURFACE SECTIONS OF NEOGENE SILICEOUS ROCK

Opaline cherts occur sparsely as nodules in the diatomites of opal-A zone and commonly as nodules, lenses and layers (often like bedded chert) in the porcelanites of opal-CT zone in the surface sections of the Neogene siliceous rocks in northern Japan. Iijima and Tada (1981) discovered that such opaline cherts consist mainly of low-tridymite (opal-T), which cements opal-A diatom frustules in the diatomites, and which fills intergranular pores of the opal-CT porcelanites. Almost all opaline chert nodules do not show the bending of laminations due to differential compaction, whereas calcitic and dolomitic concretions in the same porcelanites usually

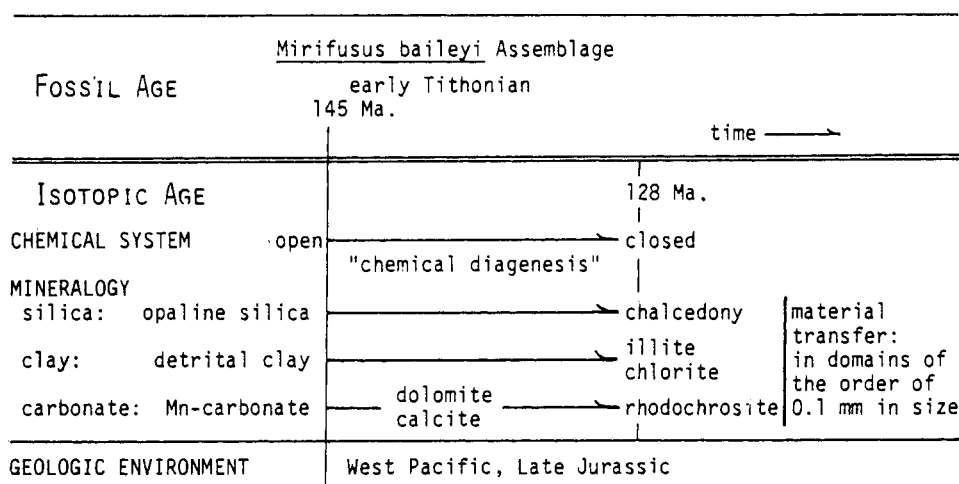


Fig.3-36. Schematic illustration of diagenesis of the siliceous shales of the Upper Jurassic Mazegawa Formation in Gifu, central Japan. (After Shibata and Mizutani, 1983, fig. 7, p. 295.)

show them. Moreover, fossils in the opaline chert nodules are preserved as poorly as those in the host porcelanite, whereas the carbonate concretions yield well-preserved fossils. Considering these observations and the rare occurrence of opaline chert in subsurface sections, Iijima and Tada concluded that the opaline cherts in the surface sections were formed by opal-T cementation, which resulted from precipitation from high-silica groundwater percolating through the overlying siliceous deposits of opal-A zone (Fig. 3-31). This chertification should occur during uplift of the siliceous sections, so that the opaline chert is to be called "late chert" contrasted with "early chert" which formed during burial diagenesis (Iijima and Tada, 1981). Fukusawa (1982) reported the regional occurrence of the late opaline chert, especially in the upper part of the opal-CT zone of the Neogene marine siliceous section of the Tenpoku-Haboro district in northern Hokkaido. In Japan with its wet and rainy climate, meteoric water is percolating Pleistocene and Neogene marine sections as much as 1 km deep, as inferred from the dilution of chlorinity of interstitial water in the surficial part of the section (Iijima, 1975). The porosity of porcelanite in the surface sections is systematically lower than that in the subsurface at the same paleo-burial depth due to the late opal-T cementation.

Tada (1984) found several examples of "late" chert in diatomite of the Monterey Formation in the Santa Maria area, California, although their occurrence is rare. The uncommon occurrence of the late chert may be explained by the dry climate of California and lack of permeable sandstone intercalations (Iijima and Tada, 1981).

Very careful analyses of opaline silica phases are needed for the research on diagenesis of siliceous rocks in surface sections. The identification of opal-T and opal-CT is difficult because they are easily confused with each other, and is very difficult or even impossible for their mixture as described above (see Figs. 3-30 and 3-31). This implies a serious problem, because the progressive decrease of $d(101)$ spacing of opal-CT is disturbed by $d(001)$ spacing of coexisting opal-T (Iijima and Tada, 1981; Tada and Iijima, 1983b). Kano (1978, 1979) studied the diagenesis of siliceous rocks of the Miocene Onnagawa Formation in the Oga Peninsula, Akita. Kano reported three silica mineral zones and a progressive reduction of $d(101)$ spacing of opal-CT in the opal-CT zone. He considered these findings to be due to progressive burial diagenesis. According to Hosoyamada et al. (1981), however, the Onnagawa Formation and the underlying Lower Miocene strata in the peninsula underwent the local low-temperature hydrothermal alteration, which was elucidated by the occurrence of kaolinite at the center of the clay-quartz zone superimposed on Zone II (clinoptilolite-mordenite-cristobalite) of the zeolitic burial diagenesis (Fig. 37). Opal-T nodules and lenses occur commonly in the opal-CT zone and in the basal part of the biogenic opal (opal-A) zone. Kano and Taguchi (1982b) reported the probable existence of reworked opal-CT in the Miocene glauconitic sandstone from the Asami district of Akita. It is probable, however, that the coexisting authigenic "opal-CT" and reworked "opal-CT" would actually be authigenic opal-CT formed during burial diagenesis and authigenic opal-T cement formed during uplift.

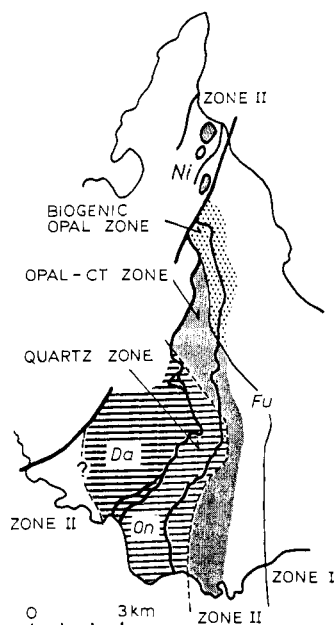


Fig. 3-37. Zonal map of silica phases in the Neogene siliceous rocks and of zeolites in silicic vitric tuffs in the Oga Peninsula of Akita. The zeolite zones I and II were formed essentially during burial diagenesis, whereas the silica zoning was seriously modified by low-temperature hydrothermal alteration. *Da* = Daishima Formation; *Ni* = Nishikurosawa Formation; *On* = Onnagawa Formation; *Fu* = Funakawa Formation.

PRESERVATION OF SILICEOUS ORGANIC REMAINS

The dissolution and preservation of siliceous organic remains in siliceous rocks were studied by some workers. Saito and Imoto (Saito and Imoto, 1972; Imoto and Saito, 1973; Saito, 1977) performed SEM observations of HF-treated surfaces of some Mesozoic and Upper Paleozoic quartzose bedded cherts in the Kuzuh and other districts of central Japan, and they demonstrated that sponge spicules and radiolarian skeletons were the principal original components of the chert beds. Some laminated chert (spiculite) almost exclusively comprise spicules, which are transformed into quartz. Saito and Imoto performed a hydrothermal experiment to make a spiculite from an aggregate of spicules, and obtained the texture similar to the etched spiculite. Based on the observations and experiment, Saito and Imoto (1978) considered the lithification of spiculite to occur as follows: the porosity of accumulations of spicules decreases mechanically at the compaction stage, whereas during burial stage, lithification of chert is progressing by quartz cementation, the silica being derived from spicules by the dissolution-precipitation process. Inoue (1973) also studied the diagenetic change of siliceous sponge spicules by comparing spicules in Miocene marine siliceous rocks with those in Recent marine sediments. From X-ray diffraction analyses and microscopic observations, Inoue (1973) concluded that the crystallization of opaline spicules to quartz through low-cristobalite may not be due to the dissolution-precipitation process but mainly to the solid-solid process. Inoue stated that spicules converted to a quartz mosaic retain their inner structures of axial tubes as well as their outline.

Kakuwa (1984) studied the preservation of radiolarian skeletons in the Jurassic and Triassic radiolarian bedded cherts of Inuyama and Neo in Central Japan. Observing HF-treated chert surfaces by SEM, Kakuwa classified the preservation of spheroidal and ellipsoidal lattice skeletons into four degrees, from well-preserved

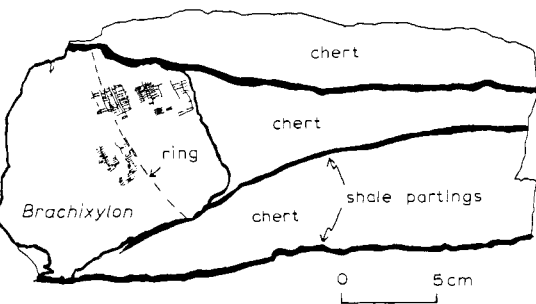


Fig.3-38. Scanning electron micrographs showing the degree of preservation of radiolarian skeletons in quartzose bedded cherts. Degree of preservation of individual skeletons is on the left side. Degree of preservation of collective skeletons in chert is on the right side. (After Kakuwa, 1984, plates 2 – 7, pp. 56 – 61.)

TABLE 3-10

Degree of preservation of collective radiolarian remains in a chert bed, based on degree of preservation of individual remains in the Mesozoic quartzose bedded cherts (after Kakuwa, 1984)

Degree of preservation of collective remains	Range of p^1 values
A	400 – 325
B	324 – 250
C	249 – 175
D	174 – 100

$$p = 4 \times a\% + 3 \times b\% + 2 \times c\% + 1 \times d\%.$$

a , b , c and d are degrees of preservation of individual remains observed by SEM on etched surface, as follows:

Outline of shells	Ornamentational
a clear	well-preserved
b fair	fairly preserved
c poor	extensively destroyed
d vague	completely destroyed

The percentage is calculated from the degree of preservation of 50 individual remains.

skeletons with excellent ornamentation to ghost skeletons whose ornamentation is completely destroyed and whose outline is vaguely recognized (Fig. 3-38). Larger skeletons are, of course, better preserved than smaller ones in the same chert, but most skeletons of 0.05–0.15 mm in size, that are common in the chert beds, tend to have the same degree of preservation. Based on these observations, Kakuwa devised the degree of preservation for collective skeletons in a chert bed, as shown in Table 3-10. In a red-green chert section of Inuyama, red hematitic chert beds generally show higher degree of preservation than green chert beds as pointed by Thurston (1972); this is true even within the same chert bed. Kakuwa concluded that the skeletons in the red hematitic cherts were probably dissolved and recrystallized concurrently with the transformation of hematite and illite in the red chert to chlorite in the green chert. The grain size of quartz cementing the skeletons tends to increase as the degree of preservation becomes lower (Fig. 3-39). The content of clay in the chert beds does not seem to correlate with the degree of preservation.

EXPERIMENTAL SILICA DIAGENESIS

Mizutani (1966, 1967) investigated silica diagenesis from the kinetic aspect based on the transformation of silica under hydrothermal conditions, and showed that the transformation of amorphous silica to quartz through cristobalite is a function of reacting temperature and time (Fig. 3-40). Based on the above result, Mizutani (1970, 1971) proposed that the silica mineral phases of siliceous deposits is controlled by geothermal history which the deposits experienced during diagenesis. In older sediments which have not been deeply buried siliceous organic remains should remain opal-A, whereas in younger sediments which have been buried to a greater depth they should be transformed to quartz. Mizutani (1977, 1978) further studied progressive ordering of cristobalitic silica (opal-CT) under hydrothermal conditions and concluded that it is also a function of temperature and time (Fig. 3-41). Kano and Taguchi (1982a) also studied the ordering of opal-CT under hydrothermal con-

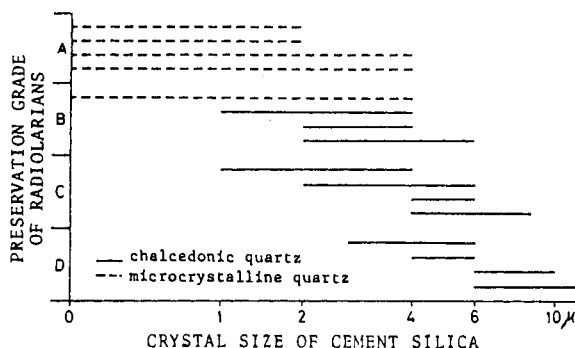


Fig.3-39. Relationship between the type and crystal size of silica cement and the degree of preservation of radiolarian skeletons (0.05–0.15 mm in size) in Mesozoic bedded cherts of Neo Inuyama, Gifu. (After Iijima et al., 1978, fig. 10, p. 383.)

ditions, and found that the rate of the reduction of $d(101)$ spacing of opal-CT from 4.11 to 4.05 Å is strongly affected by reaction temperatures. Mitsushio and Matsuo (1978) performed a hydrothermal experiment on the transformation of silica gel to quartz at temperatures of 100°–400°C at pressures up to 600 atm for up to

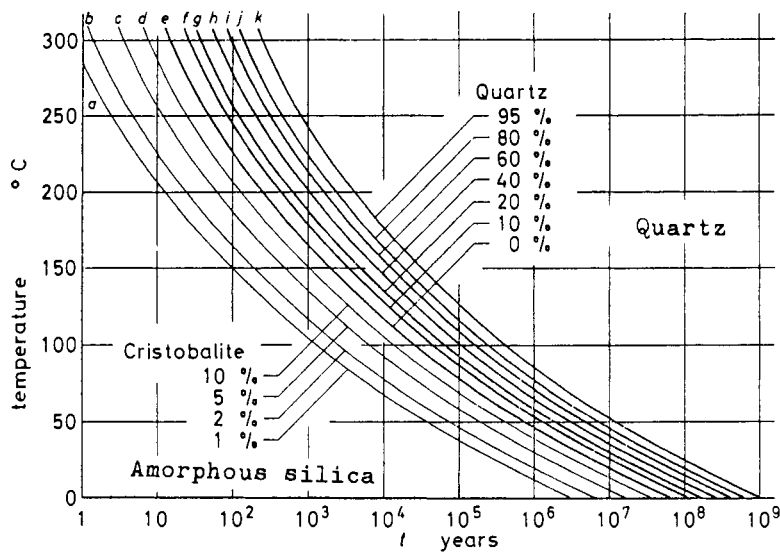


Fig.3-40. Temperature dependency of the rate of transformation of silica phases from amorphous silica (opal-A) to quartz through cristobalite (opal-CT) in nature. (After Mizutani, 1967, fig. 3, p. 104.)

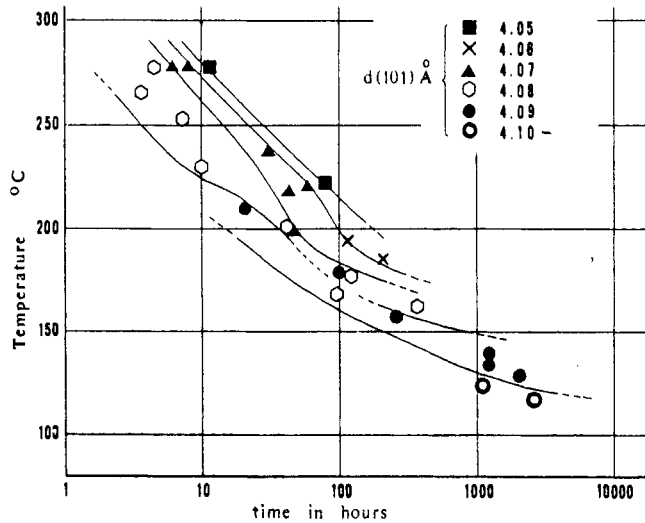


Fig.3-41. Temperature dependency of changes of $d(101)$ spacing of opal-CT in hydrothermal products. (After Mizutani, 1977, fig. 3, p. 133. Courtesy of Springer.)

168 h, and recognized a tendency for quartz to crystallize more easily at lower pressures at a specific temperature.

The interpretation of experimental results, however, is not necessarily straightforward. It is possible that the reaction mechanism is different during laboratory experiments and in natural environments. Not only reaction rate, but also rate-limiting steps and reaction mechanisms are strongly affected by the water–rock ratio (Rimstidt and Barnes, 1980). Consequently, it is important to know the surface area and porosity of both starting materials and experimental products and to estimate the rate-limiting steps in relation to the water–rock ratio. Only a limited effort, however, has been made in this direction (Kastner and Gieskes, 1983). Solution chemistry also affects the transformation of silica (Kastner et al., 1977; Kastner and Gieskes, 1983). Careful consideration should be made before applying experimental results to the processes occurring in nature.

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Chapter 4

AUTHIGENIC GREEN PARTICLES FROM MARINE ENVIRONMENTS

G.S. ODIN and A.C. MORTON

INTRODUCTION

Particles containing green authigenic clay minerals are common in the sedimentary record. As with many aspects of the earth sciences, modern examples provide the key to their geological significance. This chapter, therefore, reviews the available information on the nature and distribution of green particles in Recent marine sediments, discusses the so-called “*verdissement*” process by which they form, and comments upon their geological significance.

Bailey (1856) was the first author to give a precise description of green particles when he discovered grains composed of green silicates in a form resembling internal moulds of foraminifera in both ancient and Recent deposits from the Gulf of Mexico and eastern North America. These particles were named “glauconite”, a term which has now been superseded by “*glaucony*” for reasons discussed below (p. 233).

The subsequent study of green particles has taken place in two distinct phases. The first marks the period of systematic collection and documentation, when the most significant contributions were made by the scientists on board such famous research vessels as *Challenger* (1873–76), *Gazelle* (1874–76), *Blake* (1877–78), *Albatross* (1887–88), *Valvidia* (1898–99) and *Princess Alice* (1888–1900), which made pioneering studies of marine sediments. Geologists involved with these expeditions soon realized that glaucony is a valuable marine indicator and that it occurs most commonly in relatively shallow water (< 500 m depth). A series of detailed papers followed, those by Murray and Renard (1891) and Collet (1908) being particularly noteworthy.

Investigations became particularly active again at about 1960, and still continue today. The geographical distribution of glaucony has been reassessed, and mineralogical studies have given us more precise information on its nature and formation. A second type of particle, here termed “*verdine*” (section on p. 222), has been discovered (Giresse, 1965; Porrenga, 1965), but an understanding of its nature and origin only became known following detailed mineralogical analysis (Odin, 1985a). Although verdure and glaucony have quite distinct mineralogy and chemistry, their morphology and physical properties are similar, perhaps explaining why verdure remained poorly documented for so long. Mineralogical studies have also shown that some green particles are composed of chlorite. In most cases, this mineral can be regarded as an inherited component, resulting from the continental alteration of biotite. Burollet et al. (1979), however, examined black particles from offshore Tunisia under the scanning electron microscope, concluding that they were composed of authigenic chlorite resulting from a marine verdissement process. This inter-

pretation has to be viewed with some doubt, for subsequent XRD analyses have suggested that authigenic clay minerals are not responsible for the dark coloration of the carbonate debris.

Because of the lack of Recent analogues, the green authigenic clay berthierine (“chamosite”), which forms the principal component of ancient oolitic ironstones, is excluded from this discussion. Comparisons, however, are made between berthierine and verdine, because it has been considered recently that the two are similar.

The study of green particles from the marine environment has played an important role in the understanding of mechanisms of clay genesis. Until recently, green authigenic minerals were considered to be formed by the modification of pre-existing clay minerals (the layer lattice theory). As discussed in this chapter, this mechanism can no longer be accepted, because the minerals are now known to develop by a different process, involving new crystal growth. There has been a parallel development in the understanding of the genesis of other clay minerals, with many examples of clay genesis now known to have occurred through complete recrystallization rather than progressive modification by cation exchange.

PHYSICAL PROPERTIES

Morphology

Glaucony and verdine exist in a wide variety of forms. This diversity was first recognized by Cayeux (1897), who noted that authigenic green clays occur as infillings of microfauna, replacements of sponge spicules, partial alterations of calcareous invertebrate tests, grains without apparent organic structure, coatings of detrital minerals, diffuse pigments, replacements of opaline globules and coatings and fillings of cracks in phosphate. Millot (1964) noted that they also occur as replacements of mud pellets, coprolites and biotite flakes. Rarely, glaucony shows

TABLE 4-1
Morphological variety and origins of glaucony

Cayeux (1897); Millot (1964) Glaucony	Triplehorn (1966, 1967) Glauconite pellets
Infillings of microfossils	Ovoidal or spheroidal
Pseudomorphism of sponge spicules	Tabular or discoidal
Replacement of carbonate shells	Lobate
Common green grains	Capsule shaped
Coating and fissure filling in phosphate	Vermicular
Diffuse pigment	Composite
Replacement of opal globules	Fossil casts and internal moulds
Coating and replacement of minerals	
Replacement of mud grains or faecal pellets	
Transformation of biotite flakes	

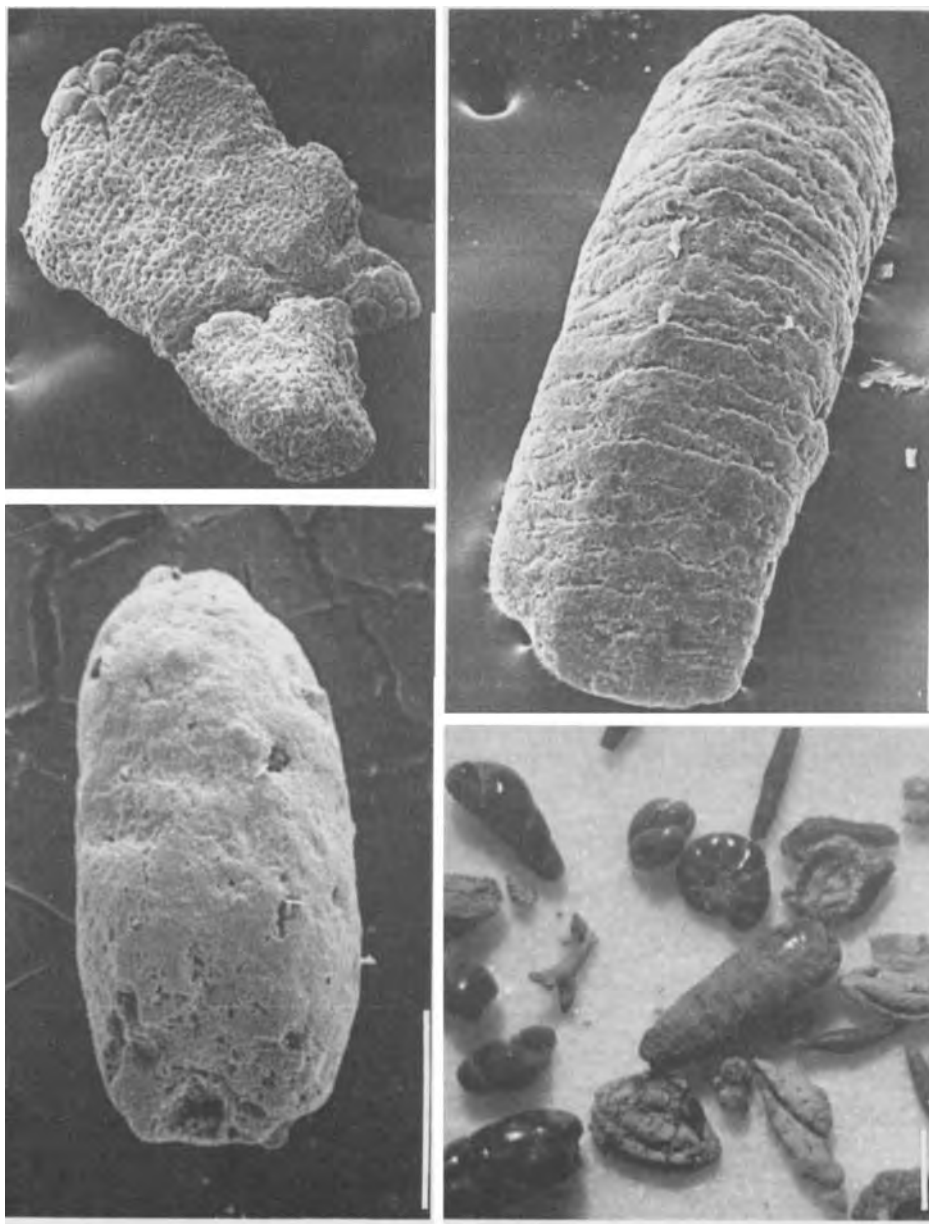


Fig. 4-1. Examples of the four substrates of verdissement, illustrated by glauconitic grains. Scale bars = 100 μm . Top left: glauconitized echinodermal debris, offshore northwestern Spain. Top right: glauconitized mica flake expanded into accordion-like grain, offshore northwestern Spain. Bottom left: little-evolved glauconitic coprolite, offshore Congo. Bottom right: glauconitized internal moulds, Albian, Paris Basin. (All pictures from Odin, 1975a.)

a crude oolitic habit (Harrison et al., 1979; Morton et al., 1984). Triplehorn (1966) listed eight morphological classes: spheroidal or ovoidal pellets, tabular or discoidal pellets, mammillated pellets, lobate pellets, composite pellets, vermicular pellets, capsule-shaped pellets, and fossil casts. This list was later modified by Triplehorn (1967) in response to remarks by Konta (1967), as shown in Table 4-1.

From a genetic viewpoint, however, any classification should be based on the nature of the material which has undergone verdissement, here termed the *substrate*, following Odin and Matter (1981), who proposed four main groupings on this basis (Fig. 4-1).

Internal moulds

Internal moulds are predominantly hosted by calcareous microfossil tests, such as foraminifera, ostracods and small molluscs. Such grains may dominate an assemblage, but more commonly occur in subordinate amounts (Murray and Renard, 1891, pp. 378–391; Collet, 1908; Caspari, 1910; Wermund, 1961; Ehlmann et al., 1963; Bjerkli and Östmo-Saeter, 1973). Internal moulds of siliceous microfossil tests, such as radiolaria, are also known (Morton et al., 1984). Internal moulds characterize the distal, relatively deep-water parts of the continental shelf, at depths in excess of 100–150 m, and becomes less important landwards.

Faecal pellets

These are dominantly composed of argillaceous material, with minor amounts of organic matter. Faecal pellets form the predominant substrate for glauconitization in many ancient and modern sediments (Takahashi and Yagi, 1929; Moore, 1939; Bell and Goodell, 1967; Porrenga, 1967a; Tooms et al., 1970; Giresse and Odin, 1973). Most pellets are ellipsoidal, with the long axis varying between about 150 and 500 μm . According to Pryor (1975), most of the grains are true faecal pellets produced in large quantities by filter-feeding organisms, and are, therefore, essentially characteristic of the inner part of the continental shelf, although they may occur at greater depth locally (Moore, 1939).

Biogenic carbonate or silicate debris

They form either by disarticulation after the disintegration of organic tissue or by biological or mechanical fragmentation, and is frequently found glauconitized (Dangeard, 1928; Cayeux, 1932; Houbolt, 1957; Lamboy, 1974; Odin and Lamboy, 1975). Glauconitized disarticulated echinoderm debris is particularly common in Recent sediments. This substrate occurs in water depths comparable to those of faecal pellets, but tends to occupy areas of more active bottom-water currents.

Mineral grains and rock fragments

Irrespective of their iron, silica and aluminium contents, a wide range of minerals is susceptible to glauconitization (Cayeux, 1916; Wermund, 1961; Ojakangas and Keller, 1964; Odin, 1972; Hein et al., 1974). Similarly, any rock fragment may become glauconitized, irrespective of its clay content. Glauconitized quartz, feldspar, mica, calcite, dolomite, phosphate, chert, volcanic glass, and volcanic and plutonic rock fragments have all been observed. Biotite appears to be particularly

susceptible to both glauconitization (e.g., offshore California) and verdinization (e.g., offshore French Guiana). Dominantly detrital substrates, particularly those composed of quartz and feldspar, usually indicate the close proximity of a river mouth or actively eroding coastline.

A rough appraisal of the nature of the observed substrates indicates, therefore, that no particular substrate is dominant, nor, a fortiori, is required as a starting material for glauconitization or other verdissement process. Nevertheless, carbonate appears to be an especially favourable substrate (Cayeux, 1916, 1932; Millot, 1964, p. 239; Lamboy, 1976).

In any particular sample, green particles may have developed from a number of different substrates, some of which may have undergone earlier verdissement. Therefore, even a purified sample of green particles is likely to be a mixture of initial substrates and authigenic minerals. From observations of Recent sea-bed samples, however, it is possible to show the existence of a complete evolutionary series, from unaltered initial substrates, through grains showing partial verdissement of a recognizable substrate, to wholly green grains, in which the texture of the initial substrate is no longer obvious. In ancient deposits, this evolved stage is more common than it is at the present-day sea floor. The recognition of the initial substrate is frequently facilitated by observing the microstructure in thin-section, because the internal texture remains recognizable during much of the verdissement process. This is because the authigenic minerals either mould the initial substrate or intimately replace it. Consequently, a laminated structure is typical of glauconitized mica (Odin, 1972), a zebra-like structure (Fig. 4-2) is typical of glauconitized bivalves

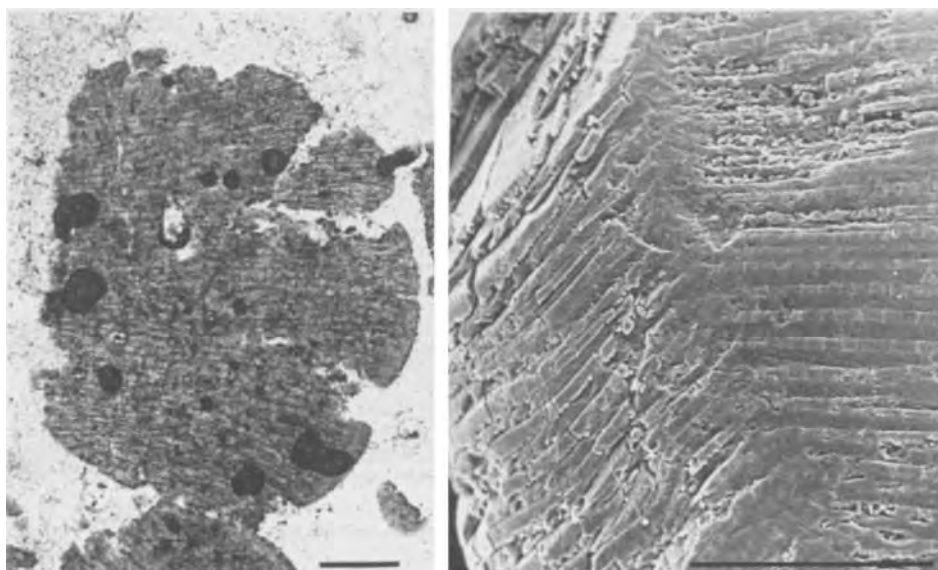


Fig. 4-2. Zebra-like structure in glauconitized mollusc shell debris, as shown in thin-section (left) and SEM (right); Lutetian, Paris Basin. Scale bar = 200 μm . The texture is similar to that displayed by modern bivalves, but the Lutetian particles are now devoid of carbonate, contain 7% K_2O and are 44.5 Ma old (Odin and Dodson, 1982, p. 685). (Pictures from Odin, 1975a.)

(Odin, 1969), and glauconitized echinoderm fragments have a reticulate structure (Odin and Lamboy, 1975).

The verdissement process is not wholly confined to granular substrates. Locally, the green authigenic phase develops as a coating over entire horizons, such as calcareous hardgrounds (Gosselet, 1901; Aubry and Odin, 1973; Juignet, 1974). The development of glauconitic minerals in the mass of a sediment has also been reported, but here it is difficult to determine the exact nature of the verdissement because it is impossible to distinguish authigenic from detrital components. The various possible substrates of verdissement are shown in Table 4-2.

Optical properties

Information on the optical properties of glauconitic minerals may be found in Bendor and Kastner (1965), Cimbalkova (1970), and Velde and Odin (1975). Refractive indices range from 1.59 to 1.63. In general, however, the grain size of the individual crystallites is smaller than the thickness of a petrological thin-section, making visual identification of grain mineralogy almost impossible.

More valuable information can be gained by studies of broken grains under the scanning electron microscope (SEM). At high magnifications, glauconitic minerals show different crystal habits, relating to the degree of evolution (Fig. 4-3). Less evolved grains are characterized by tiny, ill-defined globules less than 0.5 μm in diameter, which, with continued evolution, become attached to each other forming vermicular structures 2 – 3 μm long. More evolved grains are composed of contorted blades, arranged either in a boxwork fashion or as minute lepispheres 3 – 4 μm in diameter (Odin, 1972; Odin and Lamboy, 1975). Highly evolved grains consist of well-developed lamellae between 5 and 10 μm long (Odin, 1974). The lamellae are always slightly sinuous and show subparallel alignment. This structure is best developed at grain centres and is less well defined in the external parts of the grain, particularly on the external surface.

The SEM work also reveals the intimate relationships between the substrate and

TABLES 4-2

Substrates known to host the verdissement process

General substrate	Examples
Grains: 1 Organic debris	Carbonate or silica: echinoderm debris, mollusc debris, sponge spicules . . .
2 Infillings of fossil tests	Foraminifera, ostracoda, bryozoa
3 Faecal pellets	Coprolites of mud-eating organisms
4 Mineral debris	Biotite, muscovite, feldspar, quartz, phosphate, volcanic glass, chert
Coating	Rock boulders, macrofaunal tests, flint Hardgrounds (carbonate, phosphate, silica)
Diffuse	Green clay

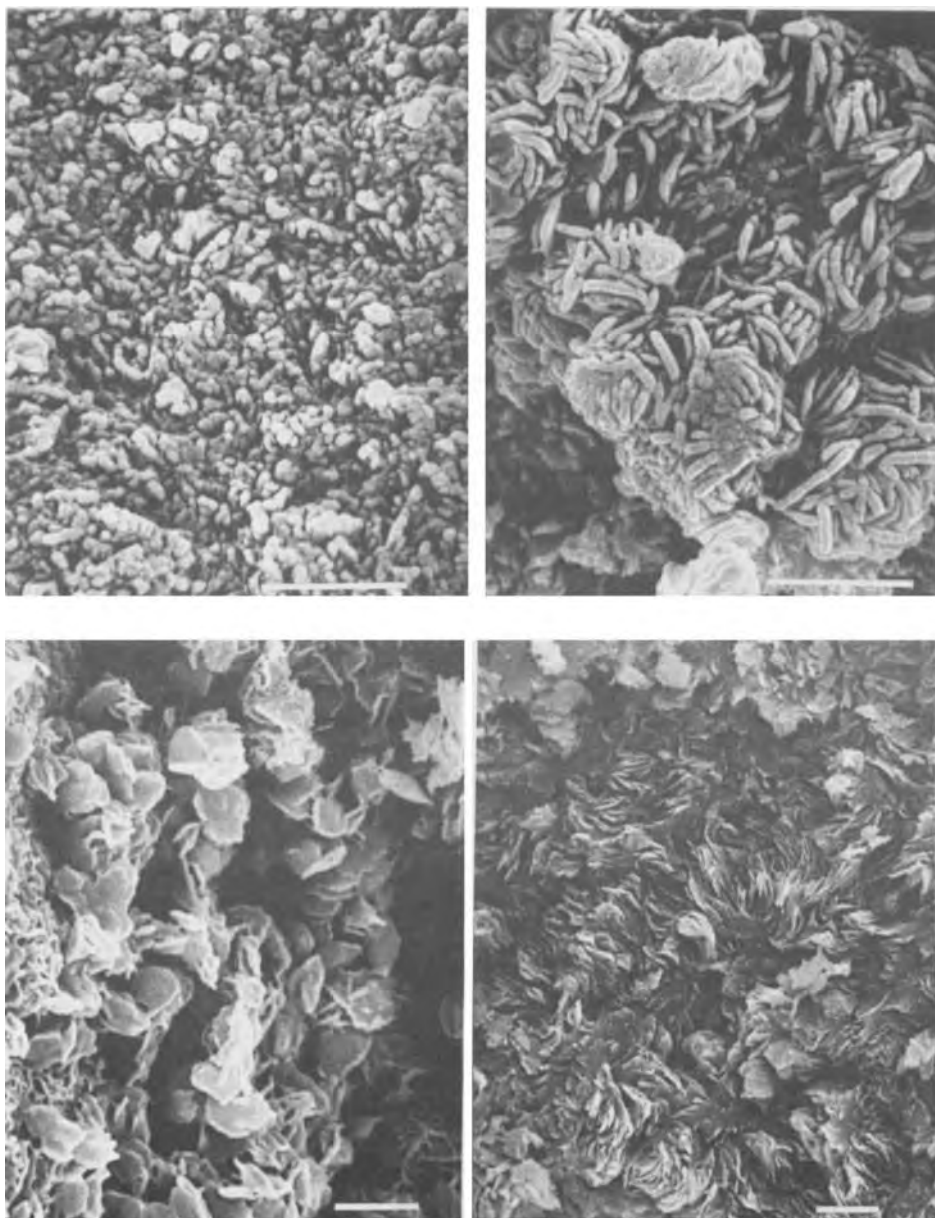


Fig. 4-3. Nanostructure of the glauconitic minerals as observed with the SEM. Scale bars = 5 μm . The globular (top left), caterpillar-like (top right) and bladed (bottom left) habits are from Recent slightly evolved to evolved grains. The well-developed lamellae (bottom right) were observed in a Cenomanian highly-evolved particle. (Pictures from Odin, 1975a.)

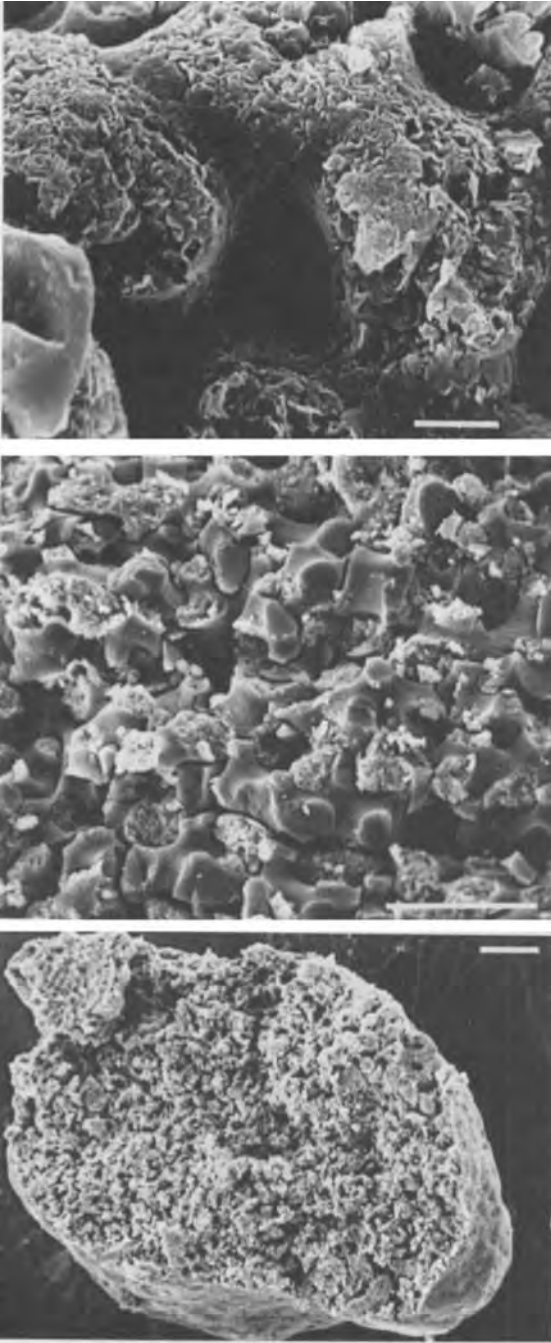


Fig. 4-4. Glauconitized echinoderm debris seen under the SEM. Recent sediments, offshore northwestern Spain. Scale bar is 5 μm in top view, and 50 μm in those below. Pictures show authigenic minerals (top) and echinoderm carbonate structure (middle). Authigenic glauconitic minerals develop first in the pores of the skeleton. (Pictures from Odin, 1975a.)

the authigenic mineral, throwing light on the physical processes involved in the growth of the authigenic minerals. Studies of carbonate debris undergoing verdissement are particularly revealing. The replacement of a shell fragment is shown in Fig. 4-2. Although this grain is wholly green, and no trace remains of the initial aragonitic substrate, it can be seen clearly that each aragonite crystal has been replaced by an individual crystal of a glauconitic mineral, thus retaining the original texture of the grain. Figure 4-4 shows glauconitic verdissement of echinoderm debris. Initially, authigenic clays develop in the pore spaces, leaving the carbonate skeleton intact. With continued verdissement, carbonate dissolves, allowing further growth of glauconitic minerals. Finally, all trace of the original internal texture disappears, and cracks develop at the grain surface through the differential growth of crystals at the grain centre compared with the margin. The development of verdine takes a similar path, although surface cracks are only rarely observed.

It should be emphasized that the various nanostructures observed under the SEM are not confined to the glauconitic minerals. Many other minerals, particularly other clays, occur as globules, vermicules, minute rosettes, and lamellae. The only structure that appears to be specific to glauconitic minerals is the large lamellae found in highly evolved grains.

Specific gravity

Specific gravities of glauconitic grains range from 2.2 to 3.1 (Lloyd and Fuller, 1965; Shutov et al., 1970; Cimbalkova, 1970). Specific gravity usually increases as evolution progresses, so that, in general, the greener the grain, the higher its specific gravity. Nevertheless, glauconitic grains generally float in bromoform. Those which have suffered oxidation, however, sink in bromoform, making this a useful technique for the separation of altered grains from an assemblage.

Although evolved glaucony is denser than quartz, the shape and porosity of glauconitic grains causes them to be hydraulically equivalent to larger quartz grains. Because of this, a glauconitic sand showing a bimodal grain size distribution does not necessarily imply that the green grains are in situ (Odin, 1975a, p. 33).

Paramagnetic behavior

For practical purposes, the paramagnetic behavior of green grains is their most interesting physical property. Magnetic separation permits rapid concentration of green grains even if they are very rare in a sediment. Furthermore, their magnetic behavior also permits the subdivision of assemblages of green grains into groups with higher and lower magnetic susceptibilities. This is particularly valuable as the paramagnetic properties of the green grains are directly related to their evolutionary state. With advancing evolution, they become increasingly paramagnetic, and at the same time the range of paramagnetism declines (Fig. 4-5). Evolved glaucony and verdine have similar paramagnetic properties to minerals such as chlorite, biotite, pyroxene, garnet, olivine, and amphibole. Consequently, careful magnetic separation is required to achieve a pure sample of authigenic green minerals.

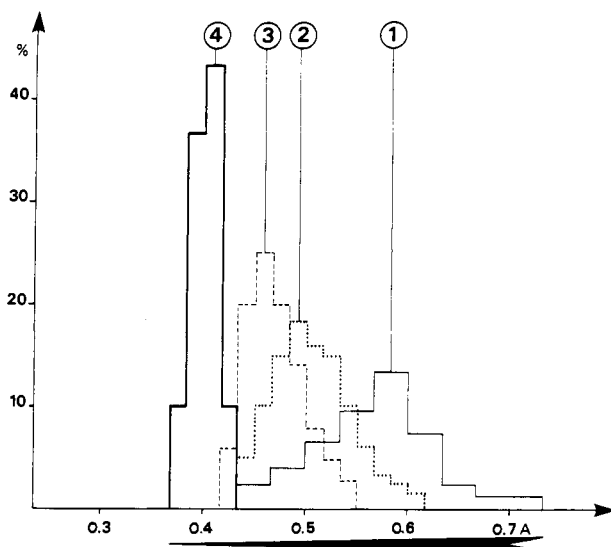


Fig. 4-5. Magnetic behavior of green grains of nascent (1), slightly evolved (2), evolved (3), and highly evolved (4), glaucony. The x axis is the intensity of the electric current in amperes (A). Paramagnetism, along with many other properties such as K content, refractive index, density, and stage of evolution, increases from left to right. The y axis denotes the proportion of attractable grains for each intensity in percent of the total attractable fraction. The lateral inclination of the magnetic separator was fixed at 16° for all of these measurements.

MINERALOGY AND CHEMISTRY

Verdine

Terminology

Some of the green grains found in Recent marine sediments are characterized by a main peak at about $7 \text{ \AA}$ on X-ray diffractograms. This clay was first described by Giresse (1965) under the name "glauconie à berthierine". Shortly after, it was also reported by Porrenga (1965), who regarded it as a $7 \text{ \AA}$ chamosite (Porrenga, 1967a,b). It was subsequently agreed, however, that the term "chamosite" should be restricted to true $14 \text{ \AA}$ chlorites (Brindley et al., 1968, following Millot, 1964, p. 246). Consequently, the mineral was referred to as berthierine, because this mineral is a true $7 \text{ \AA}$ sheet layer silicate. However, there are fundamental mineralogical and chemical differences between the originally described berthierine from ironstones and the green mineral found in verdine. It, therefore, appears that the mineral is neither chamosite nor berthierine, and does not correspond to any presently described species. Until a formal name is proposed, it has been informally named *phyllite V* (Odin, 1985a; see note added in proof).

Because the grains which contain phyllite V also contain vestiges of the initial substrate and represent a very specific facies, a term is also required for the grains themselves. The term "verdine" (from the modified Latin root "viridis", meaning

green) is, therefore, proposed. Verdine, therefore, is a green component of a sediment, usually in granular form, consisting, at least in part, of the authigenic mineral phyllite V, the properties of which are described in detail below.

X-ray diffraction

Phyllite V shows rather broad peaks on XRD traces. In most cases, the main peak has a spacing of approximately $7.2 \text{ \AA}$, which disappears on heating at 490°C for 4 h, apparently excluding the presence of true chlorite-type layers. Recognition of phyllite V by XRD is often further complicated owing to the nature of the initial substrate, which commonly has spacings similar to those of the authigenic mineral. This is found with both kaolinitic substrates, such as the coprolites from offshore west Africa (Gabon, Congo, Ivory Coast), and chloritic substrates, such as the altered biotites from offshore French Guiana. The problem is best tackled by subdividing assemblages of green particles as described above, and analyzing each fraction by XRD. Figures 4-6 and 4-7 show the results of this process, and demonstrate

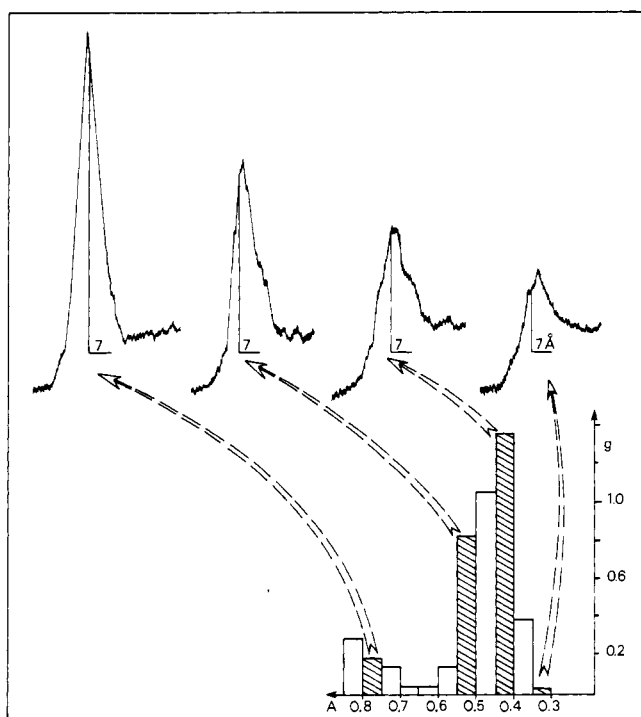


Fig. 4-6. Configuration of the $7 \text{ \AA}$ peak on XRD traces from different fractions of a sample of green grains from the Gulf of Guinea. The grains originated as faecal pellets and lie in a kaolinitic mud matrix. The fractions were prepared by magnetically fractionating all grains attractable at 0.9 A ; their distribution by weight is shown in the histogram. Four of the fractions (shown by cross-hatching) were then X-rayed. The grains attractable at 0.35 A are dark green, and the peak obtained is due to phyllite V, whereas those attractable at 0.8 A are grey, with the peak largely due to kaolinite. (Modified from Odin, 1975a, p. 115.)

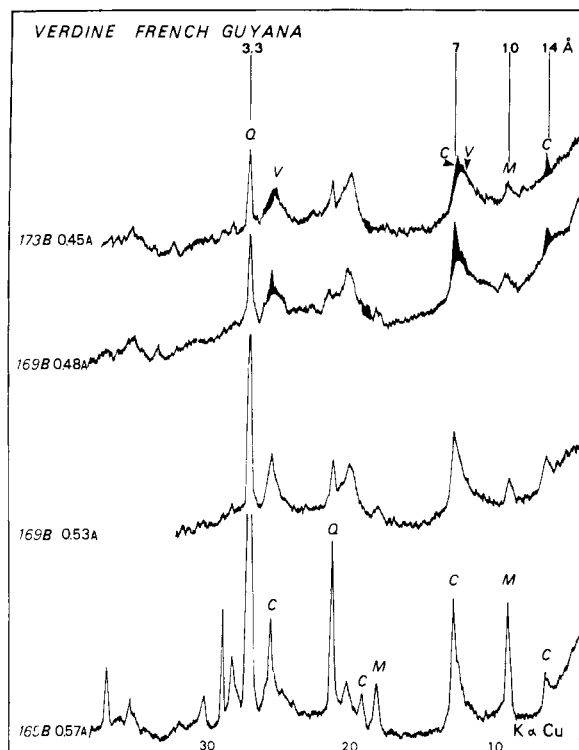


Fig. 4-7. Evolution of chloritized mica flakes to verdine, as shown by XRD. *C* = chlorite, *M* = biotite, *Q* = quartz, and *V* = phyllite V. Evolution is demonstrated by two samples from offshore French Guiana, one (169) at 30 m depth, and the other (173) at 50 m. Evolution advances from the lowermost to the uppermost trace, corresponding to a decrease in the current (A) required to attract the particles. The probable contribution of inherited chlorite is shown in black in the upper two traces. These traces demonstrate that phyllite V can only be identified after detailed fractionation of the grains and subsequent comparison of their XRD behavior.

that with increasing verdissement, the originally sharp peaks of the initial kaolinitic or chloritic substrate are gradually replaced by a broad peak at about the same 7 Å position.

Porrenga (1965) was the first to recognize the importance of phyllite V in Recent marine sediments, in a study of green particles found adjacent to the Orinoco and Niger deltas. He compared their authigenic component with a 7 Å mineral from an ancient ironstone (Fig. 4-8), and regarded both as 7 Å chamosite. This latter mineral must now be regarded as berthierine because it lacks the 14 Å peak of true chamosite. Porrenga noted that “while the chamosites from the ancient rocks are well-ordered, giving X-ray diffraction patterns with sharp peaks, the Recent chamosites yield a few broad reflections only”, implying that the Recent minerals are less well ordered because they are at an earlier evolutionary stage.

This interpretation must be regarded with some doubt in the light of more recent work. Similar grains have now been found off northern South America (Rénié,

1983; Chagnaud, 1984), Senegal (Pinson, 1980), Ivory Coast (Martin, 1973), Gabon and Congo (Giresse and Odin, 1973) and New Caledonia (Odin and Froget, unpublished). In all cases, the 7 Å peak shown by these grains is broad (Fig. 4-9), in contrast to the sharp, "well-ordered" peak shown by ancient ironstones (Fig. 4-8). In at least two cases (French Guiana and Senegal), the grains are relict, estimated to have formed some 10,000–18,000 years ago, but even here, there is no tendency for the peaks to become sharper. It should be recognized, however, that none of these occurrences are from burial depths greater than a few meters, and it is possible that in later burial diagenesis, the poorly ordered 7 Å mineral could undergo some mineralogical modification (see note added in proof).

Many verdine grains from off French Guiana show a well-developed peak at about 14 Å (Pujos et al., 1984; Pujos and Odin, 1986) which is best interpreted as a peak of the original substrate, consisting of partially chloritized biotite. On this basis, the very small 14 Å peaks frequently shown by verdine from other areas have

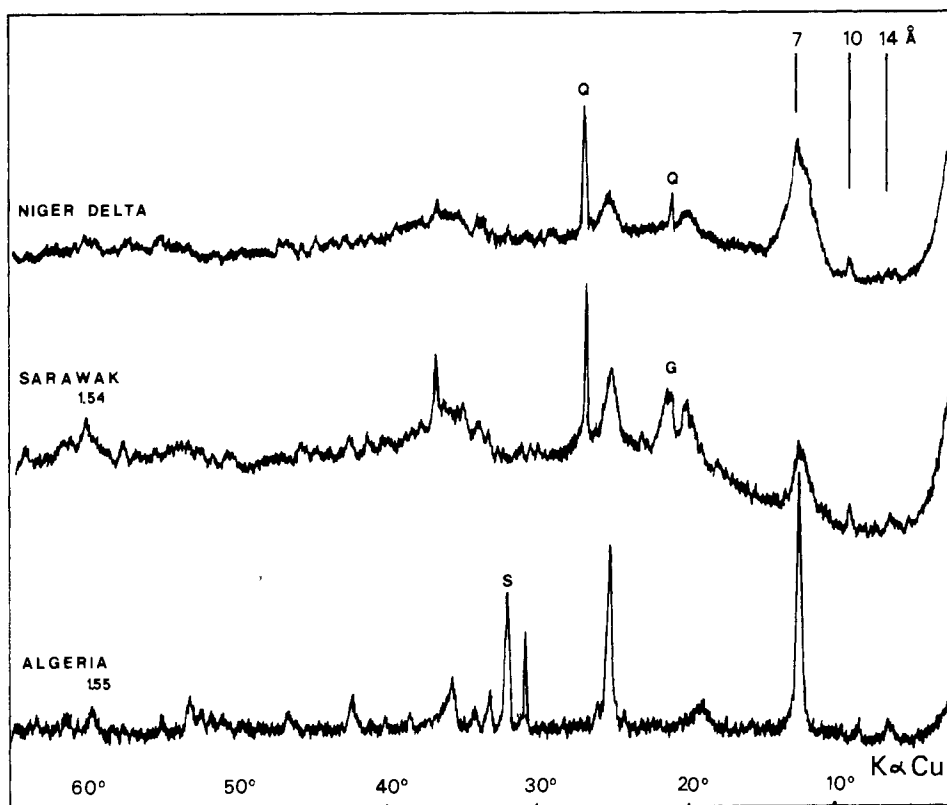


Fig. 4-8. Comparison of the XRD patterns of two Recent verdines (Niger Delta and Sarawak) with that of probable berthierine from Palaeozoic sediments of Algeria (Porrenga, 1967a). There is great difference in configuration of the peaks of the Recent samples compared with those from the Palaeozoic. Impurities are goethite (G), quartz (Q), and siderite (S).

also been interpreted as the remnant of the initial substrate. However, this need not necessarily be the case. S. W. Bailey (pers. commun., 1985) has observed this 14 Å reflection in an examination of film patterns of phyllite V, and regards the mineral as a chlorite of the 1b structural type (the lowest-temperature form), with the weakness of the (001) peaks resulting from the abundance of interlayer iron. He suggests that phyllite V could be regarded as “ferrian chamosite”, a mineral which has not been previously described in nature. Until further research into the mineralogy and chemistry of the mineral, however, the term phyllite V is retained, with the terms chamosite and berthierine rejected for the time being (see note added in proof).

Chemistry

To obtain better definition of the mineralogy of phyllite V, nine samples have been analyzed by classical wet chemical methods. This was undertaken in two different laboratories for comparative purposes, and the reference material “glauconite GL-O” (De la Roche et al., 1976) was used as a standard for all elements. Each sample consisted of carefully purified grains weighing 3 g in total, with XRD and optical analysis employed to estimate the purity of the separates and to ascertain the nature of the substrate. The samples were obtained from three different areas: offshore French Guiana, Senegal, and Gabon. The substrate of the

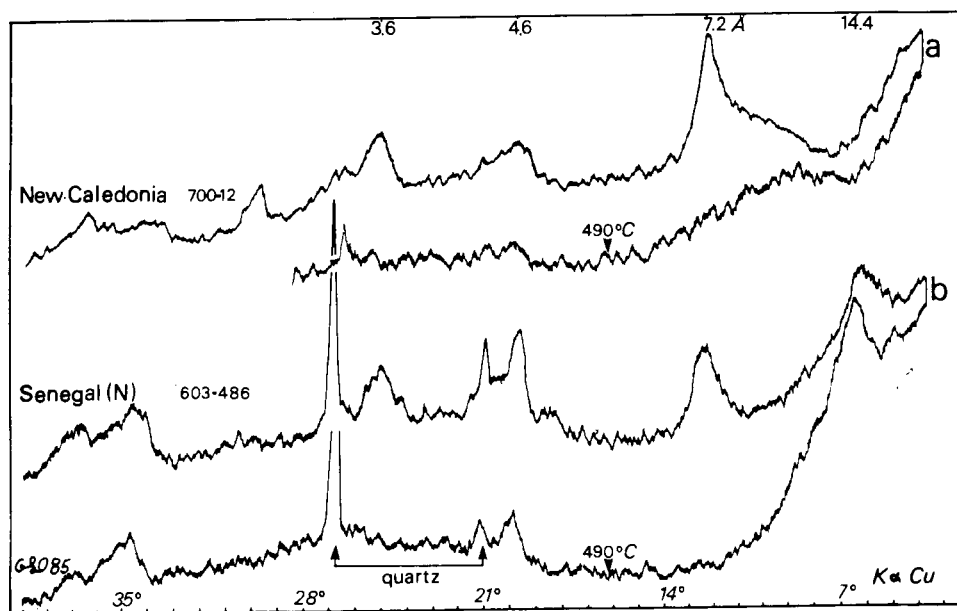


Fig. 4-9. Representative XRD patterns of verdine from offshore New Caledonia and Senegal before and after heating to 490°C for 4 h. The peak at 7 Å is never sharp. In some samples (e.g., that from Senegal), there is a broad peak at about 14.5 Å, which is not due to smectite because it remains after heating. All grains selected for analysis were as pure as possible, being very dark green and highly magnetic. (Modified from Odin, 1985a.)

grains from French Guiana are mainly chloritized mica flakes (Fig. 4-7), with a small proportion of quartz containing magnetic inclusions. No oxidation was observed here. Off Senegal, the substrates are mostly infillings of microfaunal tests, and the grains appear to be free of all impurities except carbonate. Because of the possibility of alteration to the green clays, no attempt was made to remove the carbonate component by acid treatment. Again, no oxidation was observed. Off Gabon, the substrate is mainly coprolitic, originally consisting of kaolinite with subsidiary illite, smectite and quartz. Some oxidation was noted, with many grains crusted with red iron oxyhydroxide (goethite), even after bromoform separation.

The two laboratories obtained comparable results from the reference material GL-O; therefore, the results obtained (Table 4-3) are considered reliable. Because of the presence of extraneous carbonate in samples from Senegal, results from this locality have been corrected by assuming that the green mineral contains no CaO. Similarly, the results obtained from the oxidized grains from Gabon have been corrected assuming their original Fe_2O_3 content was 20%. The results fall within a comparatively limited range, and it is clear that the authigenic phase is homogeneous, a remarkable result considering the diversity of the original substrates and the wide geographical spread. The data in Table 4-3 are, therefore, representative of the major element chemistry of authigenic phyllite V. The chemical analyses given by Porrenga (1967a) for so-called "chamosite" grains from off Nigeria compare well with these phyllite V analyses, with Fe and Mg values particularly close. The Si contents are anomalously high, possibly indicating a lack of purity in the Niger Delta sample. The analysis of the sample from Sarawak (Porrenga, 1967a), however, shows a high FeO content, incompatible with the results given here. Therefore, the accuracy of this analysis must be in question, particularly considering the impurity of the sample and the small amount of data available.

When these results are compared with the most recent synthesis published on ber-

TABLE 4-3

Chemical data for verdine grains. The data reported by Porrenga are from impure material, as the silica content is incompatible with a chlorite- or serpentine-like mineral

	From Odin (1985a)			From Porrenga (1967a)	
	Gabon (2 samples)	French Guiana (6 samples)	Senegal (2 samples)	Niger (1 sample dried)	Sarawak (1 sample dried)
SiO_2	36	36.7 – 39.1	34.8	52	49
Al_2O_3	12	10.8 – 12.3	9.3	8	9
Fe_2O_3	(20)	17.9 – 19.5	21.7	20	4
FeO	4.9	4.9 – 6.5	6.6	—	16.94
MgO	6.2	8.3 – 11.0	13.2	8.4	10
CaO	1.3	0.3 – 0.7	(0)	0.5	0.4
K_2O	1.2	1.1 – 1.4	0.5	0.5	0.5
Na_2O	0.2	0.2	0.2	0.3	0.3
H_2O^-	3.8	1.9 – 3.8	2.8	11.4	9.3
H_2O^+	10.5	9.2 – 12.2	10.8	—	—

thierines (Brindley, 1982), it is clear that phyllite V is considerably richer in Fe^{3+} (Table 4-4). Phyllite V is also much richer in silica, showing that there is less substitution of silica in the tetrahedral sites in phyllite V compared with berthierine. Structural formulae comparing berthierine and phyllite V are summarized in Table 4-5. Comparing these formulae, it is clear that tetrahedral substitution in phyllite V is very much lower than in berthierine from ancient ironstones. The octahedral sites in the berthierine structure are largely occupied by divalent cations (i.e., berthierine is essentially a trioctahedral structure), whereas the octahedral sites in phyllite V contain equal proportions of Fe^{3+} (with little Al) and Mg (with little Fe^{2+}). Consequently, berthierine has a trioctahedral structure, whereas phyllite V is equally trioctahedral and dioctahedral.

The chemistry of phyllite V is also compared to that of the true berthierines analyzed by Brindley (1982) in the triangular diagram shown in Fig. 4-10. This shows that phyllite V has a far more limited compositional range, and occupies a quite distinct field. The clear and systematic difference in the chemical composition of berthierine and phyllite V is of considerable importance sedimentologically. The difference in overall chemistry and in the oxidation state of the iron indicates markedly different genetic conditions, both in elemental composition and in Eh – pH. Misidentification of the facies, therefore, would cause an erroneous interpretation of the paleoenvironment.

Interim summary

The authigenic phase present in verdine grains is remarkably homogeneous despite its wide geographical distribution, across both the Atlantic and Pacific oceans. The XRD shows it to have a phyllitic structure with a well-defined but broad peak at 7 Å. Because crystallinity is invariably poor and the iron content very high, it is probable that this peak is the (002) reflection of a chlorite. The latter has such poor (001) reflections that they are virtually undetectable on routine patterns, but appear on long duration patterns. Alternatively, the small peaks at about 14 Å or

TABLE 4-4

Comparison of chemical data for berthierine and phyllite V. Berthierine data from the 14 analyses quoted by Brindley (1982). Some highly deviating values were discarded as probably due to impurities, but all data were considered in the calculation of the mean. There is lack of overlap in all five major ions considered

	Phyllite V		Berthierine	
	domain	mean	domain	mean
SiO_2	33 – 39	36.9	19 – 27	23.3
Al_2O_3	9 – 12	10.0	18 – 28	22.1
Fe_2O_3	17 – 20	19.3	0 – 5.5	3.2
FeO	5 – 7	5.8	30 – 37	34.8
MgO	8 – 14	10.3	1 – 8	3.5
H_2O	11 – 15.5		10 – 12	

TABLE 4-5

Comparative structural data for berthierine and phyllite V. Berthierine no. 11 of Brindley (1982) was chosen because its composition approximates the mean berthierine composition. Data for berthierine assumes a 7 Å structure, but data in parentheses refer to ionic content of a 14 Å structure. Total bivalent and trivalent octahedral ions were calculated assuming a 7 Å structure. The formula of the phyllite V from French Guiana was calculated by G. W. Brindley (pers. commun., 1983), assuming a 7 Å structure. Data in parentheses show the result if a 14 Å structure is assumed. The characteristics of the phyllite V from Senegal were calculated by S. W. Bailey (pers. commun., 1984) assuming a 14 Å structure

	Octahedral ions		Mg	Fe ²⁺	□*	Tetrahedral ions		Octahedral charge
	Al	Fe ³⁺				Al	Si	
Berthierine No. 11 of Brindley (1982)	0.730 (1.460) trivalent = 1.928	0.234 (0.468)	0.215 (0.430) bivalent = 3.750	1.660 (3.320)	0.161	0.643 (1.286)	1.357 (2.714)	13.29 (+ 1.29)
Phyllite V, French Guiana	0.581 (1.162) trivalent = 2.556	0.697 (1.394)	0.849 (1.698) bivalent = 2.258	0.280 (0.560)	0.593 (1.186)	0.091 (0.182)	1.909 (3.818)	12.18 (+ 0.18)
Phyllite V, Senegal	0.72 trivalent = 2.38	1.66	2.03 bivalent = 2.63	0.60	-	0.41	3.59	12.41 (+ 0.41)

* Empty sites.

observed in several samples could be the signature of an inherited chloritized mica substrate. On heating, the main peak disappears, a characteristic feature of 7 Å minerals.

Bulk chemical analyses show that iron is abundant, and is essentially present in the ferric form. Silica is very high and alumina relatively low, implying little Al substitution in the tetrahedral sites. Magnesium content is high. On the basis of structural formulae calculations, phyllite V appears to be equally trioctahedral and dioctahedral.

Phyllite V is clearly distinct from berthierine in bulk chemistry and in the composition of the tetrahedral and octahedral sites. Contrary to recent suggestions, therefore, phyllite V is not a berthierine. This mineralogical distinction corroborates the morphological evidence: berthierine in ironstones generally occurs in oolitic form, whereas oolitic verdine grains have not been observed. As Hayes (1970) pointed out, "clay minerals, like most other minerals, record the physical and chemical conditions under which they formed". One may, therefore, conclude that phyllite V forms in an environment different from those required for the formation of berthierine and previously described chlorites, including chamosite. The main characteristics of these minerals are compared in Table 4-6.

In his study of the polytypism of chlorite in sedimentary rocks, Hayes (1970) considered the trioctahedral chlorites of the 1bd to 1b ($\beta = 97^\circ$) polytype as characteristic of the initial stages of crystallization in sediments. Although he considered that this largely develops in the domain of burial diagenesis, he did not reject the possibility that it could occur in a more surficial environment, prior to halmyrolysis, in sea water. Phyllite V is probably the first described example of this very possibility.

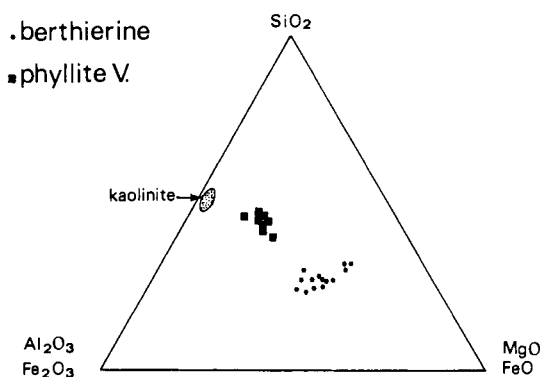


Fig. 4-10. Triangular diagram comparing chemical composition of berthierine (Brindley, 1982) with that of phyllite V. The domains of the two minerals are clearly distinct, and the influence of the valency state of the iron is clear. The difference in chemistry reflects major differences in the depositional environment of ancient oolitic ironstones and present-day verdine.

TABLE 4-6

Comparative mineralogical data for phyllite V and possible related species. “Chlorites” constitute a family of species, most of which are trioctahedral, although dioctahedral varieties have been reported from soils. In these cases, however, the main cation is aluminium. “Chlorite Fe” refers to the two iron-rich chlorites, bavalite and veridite. The latter is relatively rich in ferric iron, although the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio is around 5, and both species are trioctahedral. Several researchers have created “ferric berthierine” and “ferric viridite” by artificial heating, but the conditions of formation are obviously dissimilar to those of phyllite V, so that the products cannot be compared to the natural mineral from a sedimentological viewpoint

Mineral	X-ray diffraction		Heating behavior		Chemistry		
	(001) peak			(060)	Octahedra	Main cation	Al substitution for 2 tetrahedra
	14 Å	7 Å					
(14 Å) Chlorites	present	acute	stable	1.54 Å (peak)	typically trioctahedral	Mg (Al)	< 0.5 – 1
(14 Å) Chlorite Fe	low to very low	very high	7 Å stable	1.54 Å (peak)	trioctahedral	Fe^{2+}	0.5 – 1
(7 Å) Berthierine	no	acute	14 Å increases	1.54 Å (peak)	triocta >> diocta	Fe^{2+}	0.5 – 0.9
Phyllite V	? unclear	broad but clear	7 Å destroyed	1.55 – 1.49 Å (dome)	diocta ≈ triocta	Fe^{3+} Mg	≤ 0.2

*Glaucony**Terminology*

Compared to phyllite V, the minerals which comprise glauconitic grains have been extensively studied, and their characteristics are much better known. There is a con-

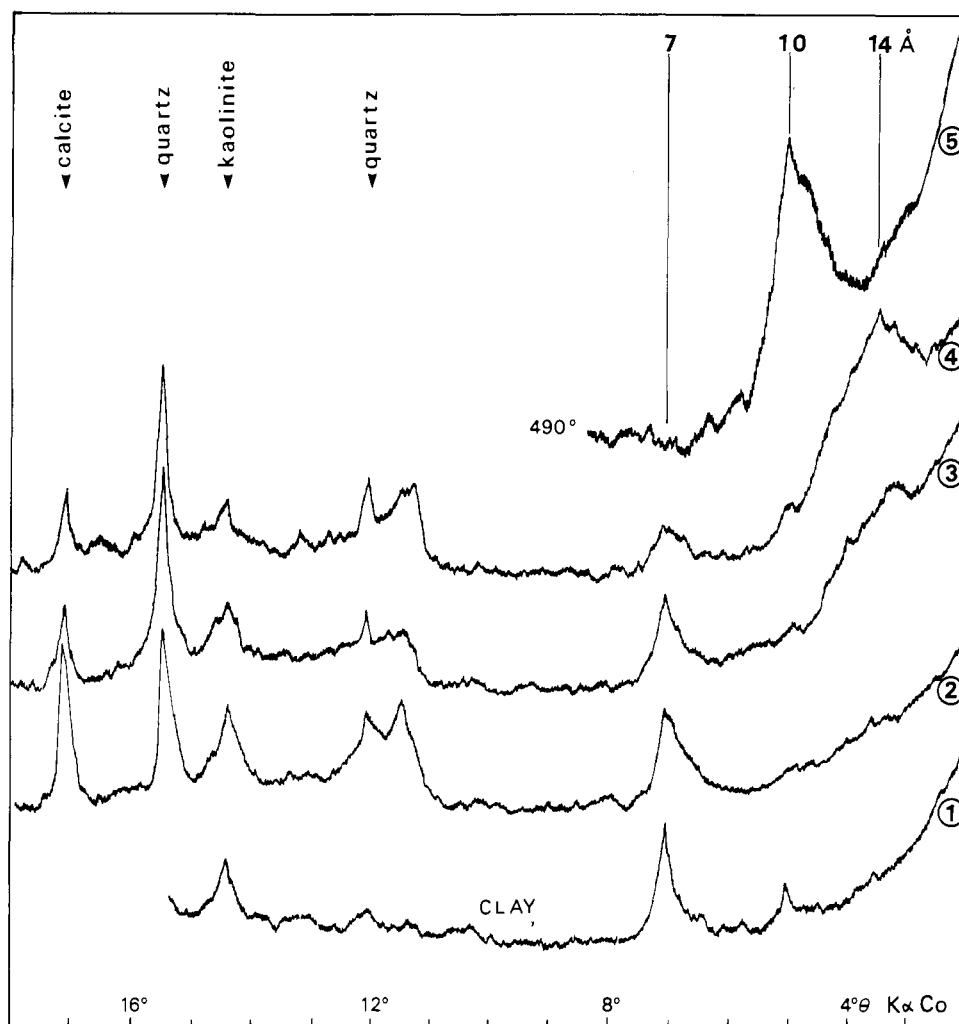


Fig. 4-11. The XRD patterns showing different stages of glauconitization. 1 = clay fraction; 2 = grey grains, not attracted in magnetic separator; 3 = grey-green grains, attracted at 0.6 Å; 4 = green grains, attracted at 0.47 Å; 5 = as 4, heated to 490°C for 4 h. All fractions are from one sample recovered in the Gulf of Guinea (Giresse and Odin, 1973). Inasmuch as glauconitization is hosted by faecal pellets (consisting of kaolinite with minor calcite and quartz, see trace 2), there is similarity between the grey particles and the associated clay fraction. The authigenic minerals are glauconitic smectites, with a peak at 14 Å which shifts to 10 Å on heating. There is disappearance of the kaolinite substrate concomitant with development of the authigenic minerals (traces 3 and 4).

siderable amount of confusion in the literature, however, over the term “glaucinite”. This term has been widely misused, in that it is commonly applied to both the grains themselves and the authigenic minerals found within such grains, irrespective of whether these components actually correspond to any particular mineral. Because of this confusion, it is necessary to distinguish the grains from their authigenic components. The terms “glaucinitic grain” or “glaucony” (Odin

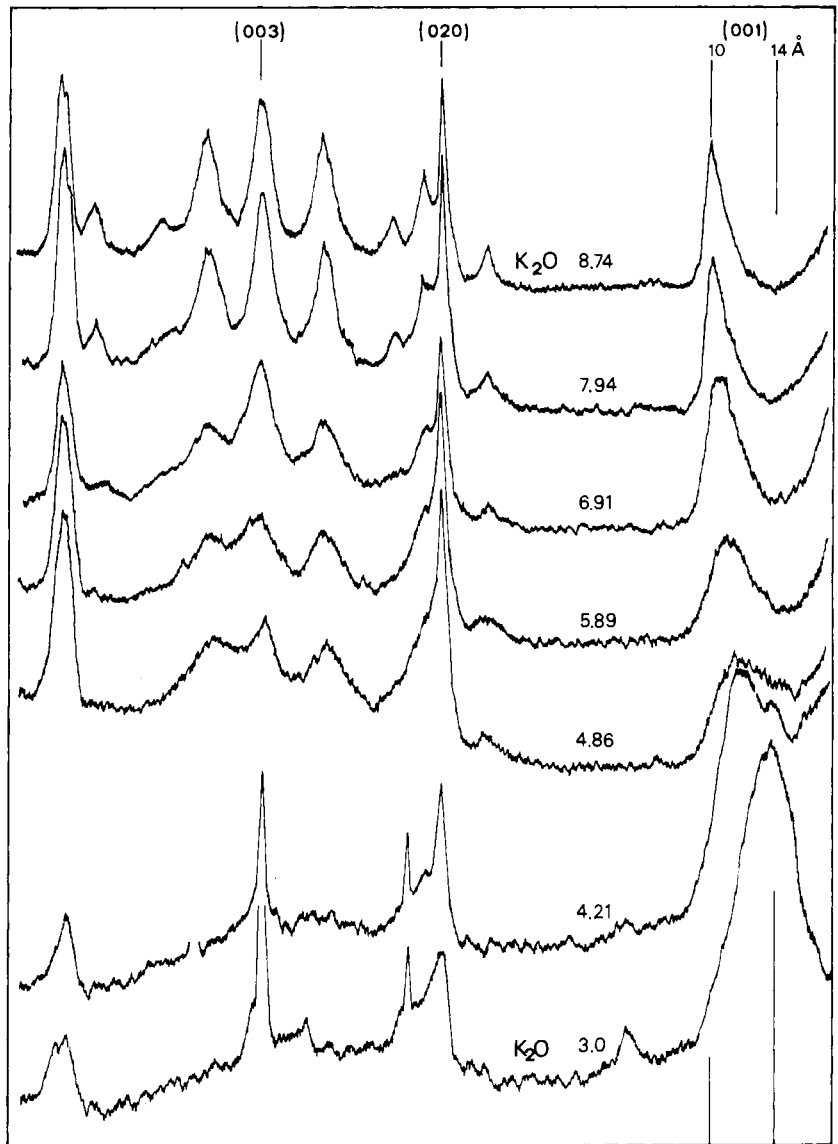


Fig. 4-12. The XRD patterns of various randomly oriented specimens of glaucony, compared with their potassium content.

and Matter, 1981), therefore, are used to describe the facies, and the term "glaucinitic mineral" (qualified by its mineralogical affinity, e.g., glauconitic mica) is used to describe its authigenic component.

X-ray diffraction

As with verdine, it is often difficult to know which peaks to assign to the substrate and which to the authigenic mineral, particularly in the early stages of glauconitization. For this reason, a bulk analysis is generally of little use; considerably more information is obtained from the study of individual fractions. Figure 4-11 shows the progressive evolution of the peaks in different fractions of the same sample. The series of diagrams show both the disappearance of the original substrate and the increase in authigenic components as evolution progresses. Because oriented samples tend to bias the results in favor of the thinnest crystals, which SEM study shows are the least evolved, XRD analyses are best carried out on powder mounts. A comprehensive set of XRD traces is shown in Fig. 4-12.

The first-order basal reflection (001) lies between 14 and 10 Å. Its shape usually depends on the nature of the fraction examined. For example, the bulk sample shows broader peaks than individual fractions. With simple glycolation, the (001) peak hardly shifts, even if initially at 14 Å. The swelling behavior is enhanced, however, if, prior to glycolation, K is removed by cation exchange. On heating to 490°C for 4 h, the peak is displaced to 10 Å, showing that all glauconitic minerals essentially have a 2 : 1 structure.

The most consistent peak in both position and shape is the (020) reflection at 4.53 Å. This reflection serves as a useful internal reference point to evaluate the position of the (001) peak. The distance from the middle of the (020) peak to the middle of the (001) peak has proved to be a valuable indicator of the mineralogy of the grains, as it provides a useful and easily determined estimate of their potassium content (Odin, 1982), as shown in Fig. 4-13. Obviously, care is needed if this method is applied to studies of poorly evolved grains which have a K-rich initial substrate. In general, however, the technique has proved to be very useful, particularly in selection of suitable fractions for radiometric dating, because grains with high K contents are less susceptible to alteration of the isotopic equilibrium.

There are a number of other notable features. Several peaks show distinct changes during the glauconitization process. As the mineral evolves from a smectite-type mineral with an (001) peak at 14 Å to a mica-type mineral with an (001) peak at 10 Å, the (023) peak first appears, followed by (in order) the (021), the (11 $\bar{1}$) and the (11 $\bar{3}$) peaks. Providing that goethite is absent, the shape of the (11 $\bar{1}$) and (021) peaks are useful indicators of the degree of evolution. As with all iron-rich 2 : 1 structures, the (002) reflection is rather muted. According to Bentor and Kastner (1965), the shape and size of the (112) and (11 $\bar{2}$) reflections on either side of the (003) reflection is a reliable measure of the order-disorder of the layer silicate lattice. However, rather than actually disappearing when the lattice is disordered, as suggested by Bentor and Kastner (1965), the peaks tend to decrease in height.

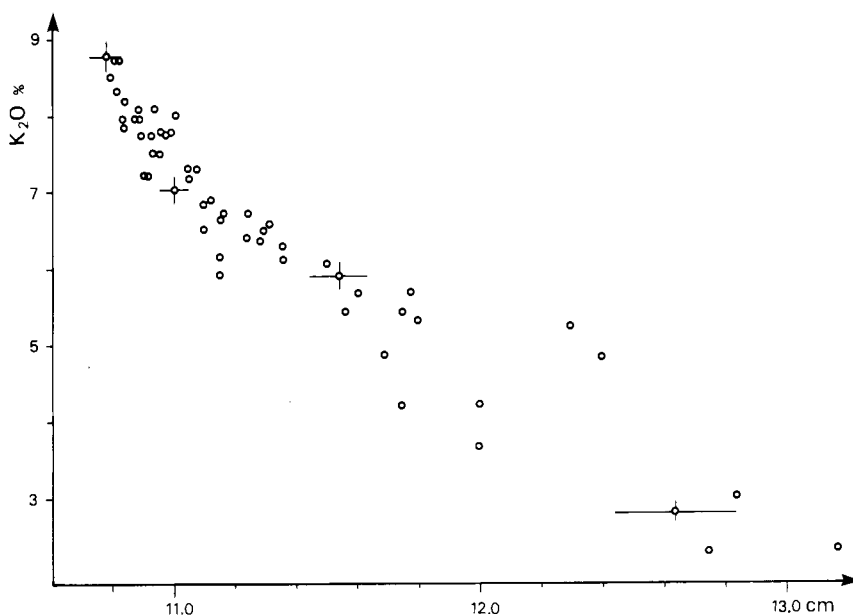
In brief, XRD indicates that the authigenic components of glauconitic grains comprise a crystallographic family ranging from a green smectite end-member, here termed "glaucinitic smectite", to a green mica end-member, called "glaucinitic

mica'', the latter being the glauconite *sensu stricto* of the mineralogists. The two pure end-members are rarely encountered in nature. Glauconitic smectite characterizes grains which are very little evolved, or nascent, such as those found in Recent sediments where the process has just begun, and also occurs as a diffuse pigment in hardgrounds. Highly evolved grains consist of glauconitic mica: they are not found in Recent sediments, but are present as relict grains in some parts of the present-day continental shelf, and also in ancient rocks, where they are particularly associated with major breaks in deposition. Glauconitic mica has not been found as a diffuse pigment.

Chemistry

There is now a considerable amount of published information on the chemical composition of glaucony grains. Consequently, one can define with some certainty the range in chemistry of glauconitic minerals and study the relationships between cation contents. It should be remembered, however, that glaucony grains not only consist of authigenic minerals, but also of the initial substrate, and it is not always possible to achieve perfect separation of the glauconitic minerals. Also, alteration may have taken place. These factors are taken into account in the subsequent discussion.

The SiO_2 contents remain fairly constant, lying between 47.5 and 50.0% (Odin



and Matter, 1981), in common with results obtained by Hendricks and Ross (1941) and Smulikowski (1954).

The Al_2O_3 contents lie between 3.5 and 11% in 54 of the samples discussed by Odin (1975a, p. 43). Hendricks and Ross (1941) and Smulikowski (1954), however, have reported values in excess of 12%, and Foster (1969), in a study of 32 samples, found 6 with values between 12 and 15%. Twenty samples studied by Cimbalnikova (1971a) gave values in a narrow range between 6 and 10%. Shutov et al. (1970) quoted extremely high values, in excess of 20%, from Palaeozoic glauconies, but these probably resulted from post-depositional diagenetic processes.

The Fe_2O_3 contents lie between 19 and 27% in 75 of the samples described by Odin (1975a, p. 41), with the highest values (those above 26%) being linked to early stages of oxidation. Twenty samples of Cretaceous age analyzed by Cimbalnikova (1971a) fall within the range 19–23.5%. Foster (1969) derived similar results, although recorded values below 19% in rare grains with “extremely high” alumina.

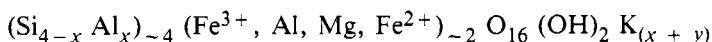
The FeO contents are very consistent, falling between 1 and 3.2% in virtually all published examples. This feature is one of the main characteristics of the glauconitic minerals, and together with the Fe_2O_3 contents reflect the very homogeneous nature of the genetic environment in time and space.

The MgO contents of 56 glauconies given by Odin (1975a) lie between 2 and 5%, comparing well with values published elsewhere. The relative consistency of MgO values again reflects the homogeneity of the depositional environment in time and space.

The K_2O is particularly significant, because, as discussed in the section on pp. 16–18, it is the main control on the behavior of glaucony under XRD. The lowest value which can be attributed with certainty to the authigenic phase is in the region of 3%. Lower contents of potassium have been found, but these occur in grains containing a substantial amount of substrate material. The highest values recorded lie between 8.6 and 8.9%, from relict Neogene deposits on the present-day continental shelf and from Cenomanian sediments (Odin and Matter, 1981). Values close to 9% have also been recorded by Foster (1969) and Lamboy (1976).

Other cations, such as Ca, P, Ti and Mn, are invariably present in glaucony, but it is difficult to determine the proportions actually contained in the structural lattice. The trace elements Rb and Sr are of interest, because of their potential value in geochronology. The Rb content of evolved grains usually falls between 230 and 290 ppm. Leaching has little effect on these values: consequently, they are characteristic of the authigenic phyllite structure. Conversely, Sr contents generally fall with moderate acid leaching, from initial values between 15 and 25 ppm to values between 1.5 and 9 ppm. This indicates that some of the strontium is an easily exchangeable, “polluting” component (Pasteels et al., 1976), and that only the content measured after leaching may be considered to be structurally bound.

A simplified structural formula for the glauconitic minerals may be written thus:



where x varies from 0.2 to 0.6, and y (the sum of the divalent octahedral cations)

ranges from 0.4 to 0.6. This indicates that the glauconitic minerals have a ferric 2 : 1 structure, are mainly dioctahedral, and have potassium in the interlayers.

As shown in Fig. 4-14, there is a marked compositional break between the glauconitic minerals and the illitic minerals, even when data from ferric illites, indicative of restricted hypersaline conditions (Kossovskaya and Drits, 1970) are included. The ferric nature of the glauconitic minerals essentially distinguish this group from other three-layer silicates. Takahashi and Yagi (1929) first recognized that glaucony is characterized by a high iron content even in the earliest stages of evolution. Ehlmann et al. (1963) noted that the iron content is independent of the intensity of the green coloration, and recognized that iron is abundant in the earliest infillings of foraminiferal tests, an observation subsequently confirmed by Pratt (1963, p. 100) and Seed (1968, p. 230). Foster (1969), Velde and Odin (1975), and Birch et al. (1976) have shown that the iron content is not related to the content of interlayer cations, and that iron is fixed in the structure prior to the incorporation of potassium.

The presence of potassium is related to the marine origin of glaucony, and the potassium content appears to govern most of its physical properties, including the X-ray patterns (Fig. 4-12), the amount of expandable layers (Velde and Odin, 1975), the density of the grains (Shutov et al., 1970), the refractive index (Cimbalnikova, 1970), the ion-exchange capacity (Cimbalnikova, 1971b), and the paramagnetic

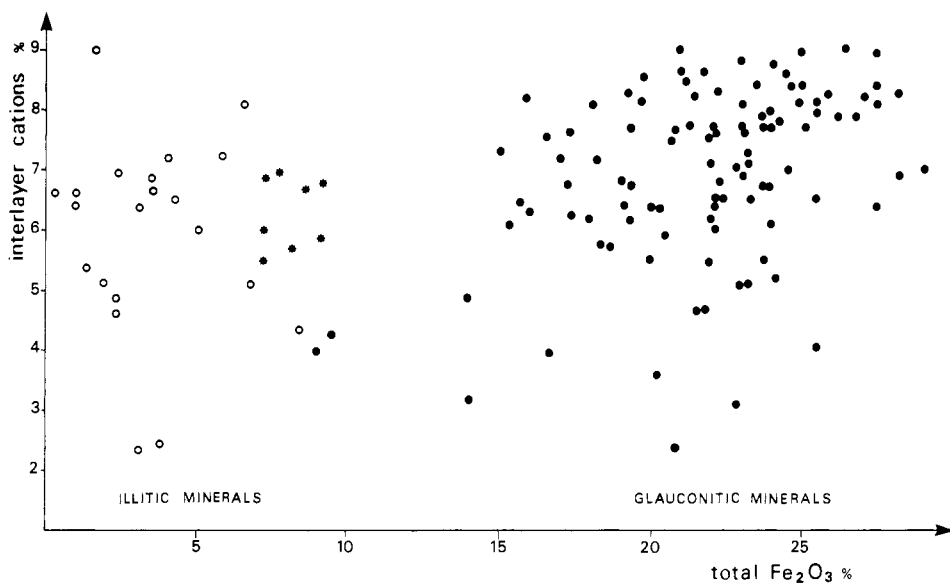


Fig. 4-14. Iron content as a function of interlayer cation content in 2:1 minerals. Filled dots: glauconitic minerals, taken from Hower (1961), Parry and Reeves (1966), Cimbalnikova (1971a) and Odin and Matter (1981). Open dots: illitic minerals, taken from Hower and Mowatt (1966). Stars: ferric illites from hypersaline environments, taken from Kossovskaya and Drits (1970). Two distinct mineral families may be distinguished, indicating separate lines of evolution in different genetic environments. (Modified from Odin, 1975a, p. 54.)

behavior. Inasmuch as potassium content increases during the evolution of glaucony, all these properties can be used to identify the degree of evolution.

Comparison with celadonite

Celadonite also has a 2 : 1 structure and contains high proportions of Fe_2O_3 and K_2O , and is consequently sometimes mistaken for glauconitic mica. Celadonite forms in a completely different geological setting, usually coating mineral grains or infilling small vesicles in volcanic rocks. Rarely, it may be found infilling large vacuoles or as large-scale veins. The best-known outcrops are in the Monte Baldo area of northern Italy. These outcrops were known in Roman times, and were extensively quarried until the first World War, with the crushed celadonite being extensively used in the painting of frescoes. Distinction of celadonite and glauconite minerals in such frescoes has been studied by Odin and Delamare (1986).

Celadonite and glauconitic mica are easily distinguished by XRD. Figure 4-15 compares a glauconitic mica with a K-rich celadonite from northern Italy, and shows that the celadonite peaks are much better defined, being both sharper and generally more intense. Also, the ratio of the height of the (023) peak to the height of the (130) peak is much higher for celadonite. On the basis of these criteria, it is actually possible to estimate the relative proportions of celadonite and glauconitic

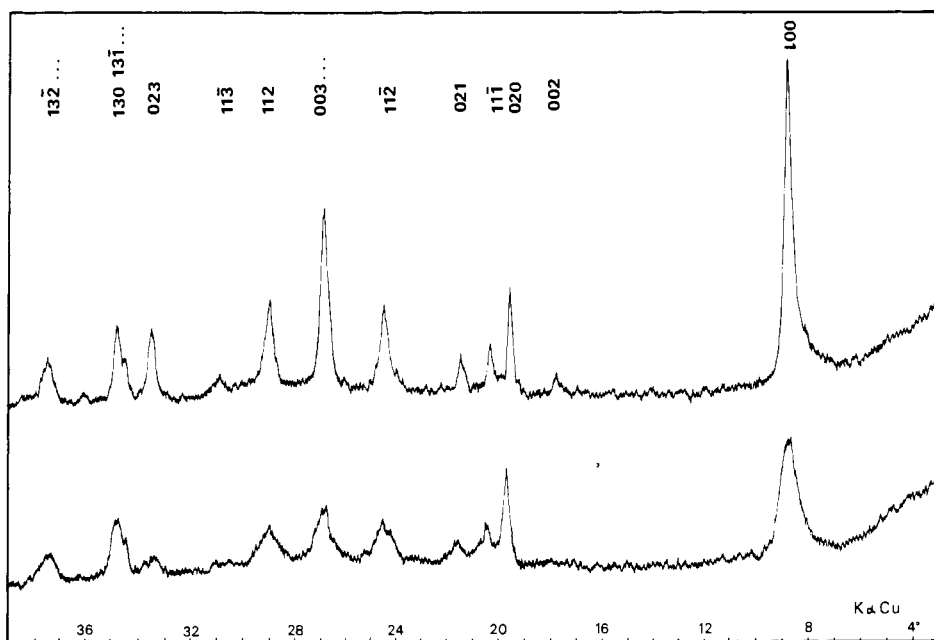


Fig. 4-15. The XRD patterns of randomly oriented celadonite (top) and glauconitic mica (bottom) produced under identical machine conditions. The celadonite has $\text{K}_2\text{O} = 9.60\%$, whereas the glauconitic mica has $\text{K}_2\text{O} = 8.75\%$. There are general differences in peak shape, especially the (001), (003), (112) and (112) peaks, even though their positions are similar. There are also differences in relative heights of the (020) and (003) peaks and of the (023) and (130) peaks.

mica in mixtures of the two. Archeological investigations have shown that such mixtures were used in the painting of Roman frescoes. There are less obvious differences when glaucony is compared to K-poor celadonite, but SEM observations show such celadonites to have a very specific appearance (Fig. 4-16), which helps to recognize the pigment.

Celadonite and glauconitic mica also differ in chemistry and crystallography. According to Hendricks and Ross (1941), Smulikowski (1954), Pirani (1963), and Foster (1969), SiO_2 contents are between 52 and 56%, appreciably higher than in glauconitic minerals. The MgO values are also higher, always exceeding 5% in celadonite. Foster (1969) demonstrated that the two minerals belong to different crystallographic domains, and that there could be no homonymy on mineralogical grounds. Following Hendricks and Ross (1941) and Foster (1969), therefore, it is recommended that the two separate terms are maintained.

This is also sensible from a geological standpoint: the two minerals have quite distinct parageneses, with celadonite forming in hydrothermal conditions in conjunction with zeolites, and glauconitic mica forming in the low-temperature marine environment. It is possible that some problems in distinction may occur, for example in cases of volcanic rocks dredged or drilled from the sea floor. In such cases, the mineral should be referred to as a “green micaceous pigment” until detailed mineralogical investigations prove its true nature.

VERDISSEMENT PROCESS

Layer lattice theory

The model for the genesis of glaucony proposed by Burst (1958) and Hower (1961), namely the “layer lattice theory”, became widely accepted in the 1960's.



Fig. 4-16. Celadonite laths viewed under the SEM. Individual laths are about $3\ \mu\text{m}$ long. Glauconitic minerals never show this habit.

This model proposes that glaucony growth takes place by the transformation of a degraded layer silicate, with the authigenic mineral retaining a “memory of past structure”. According to this model, therefore, a precondition for glauconitization is that the mineral to be transformed must have a similar crystal structure to that which is generated (illite or smectite).

Odin and Matter (1981) have listed seven observations which are incompatible with the layer lattice theory:

(1) Glauconitization of detrital mica is quoted as an example of the layer lattice theory. Odin (1972), however, has shown that verdissement of detrital mica takes place through growth of glauconitic minerals *between* the mica sheets, and that the mica sheets themselves remain unaltered for a considerable period. This shows that glauconitization requires neither the crystal architecture nor the ions of the initial mica.

(2) In many cases, verdissement proceeds on granular substrates which are wholly calcareous, a situation which the layer lattice theory cannot explain.

(3) Similarly, most glauconitized hardgrounds in ancient formations are limestones (Aubry and Odin, 1973; Juignet, 1974).

(4) Two fundamentally different authigenic clays can be generated from the same substrate. For example, biotite undergoes glauconitization off northwestern Spain and California, but undergoes verdinization off Sarawak and French Guiana. Similarly, in different parts of the Gulf of Guinea, glaucony and verdine have both been generated from faecal pellets, composed largely of kaolinite.

(5) In areas where the sea floor is muddy, verdissement only proceeds in the faecal pellets, not in the diffuse clay. The process is clearly governed by the physical nature of the substrate, rather than its chemistry.

(6) If illite or smectite were specifically favorable substrates for glauconitization, the authigenic clays would frequently display a continuum between aluminous 2 : 1 and ferric 2 : 1 structures, and this is not the case (Fig. 4-14). Similarly, there is no continuum between kaolinite and phyllite V.

(7) The layer lattice theory postulates that the octahedral layer loses aluminium at the same time as it gains ferric iron. The similarity in geochemical behavior of these two ions makes this difficult to achieve.

The layer lattice theory, therefore, does not adequately explain the glauconitization process. In the following section, the verdissement process is discussed in the light of new information gathered since the layer lattice theory was first proposed.

Mechanism of verdissement

Most of the information regarding the verdissement process has been gathered during studies of glaucony (Odin, 1975a; Odin and Matter, 1981), but as discussed above, verdine and glaucony are generated by similar mechanisms, with the major differences in their mineralogy being a result of differences in their genetic environment.

Understanding of the mechanism of verdissement depends on two critical observations:

(1) Evolution only begins and proceeds close to the water – sediment interface.

Surficial cores invariably show that glaucony grains occur over a relatively thin zone, less than 10 m maximum, immediately below the sea bed.

(2) The mechanism proceeds more efficiently, and often exclusively, where the sediment is in granular form. Consequently, glaucony and verdine are both found mainly in granular form.

The SEM observations are particularly useful in understanding the verdissement process. As already discussed, the starting material is generally granular, and is highly porous. Crystal growth begins in these pores, which may extend across an entire grain. Studies of glauconitized mica and echinoderm debris have shown that the newly formed minerals grow as blades attached to internal surfaces or as minute lepispheres in the pores. By growing in pore space, the glauconitic minerals mould the initial texture of the substrate on an intimate level. Grains, therefore, commonly show ghosts of the initial substrate texture, a feature frequently observed in thin-section. Clearly, the porosity of the particles is an important factor. Because the grains have porosity, they contain internal surfaces, which play a critical role by allowing ions to interact. The grains essentially act like a sponge, favoring geochemical reactions.

The development of new minerals soon imparts a green coloration to the grains. Even at this early, or *nascent*, stage, the clay is iron-rich and characteristic of the glauconitic mineral family: K_2O contents are of the order of 2–4%. Because the minerals of the substrate are in geochemical disequilibrium with sea water, they are

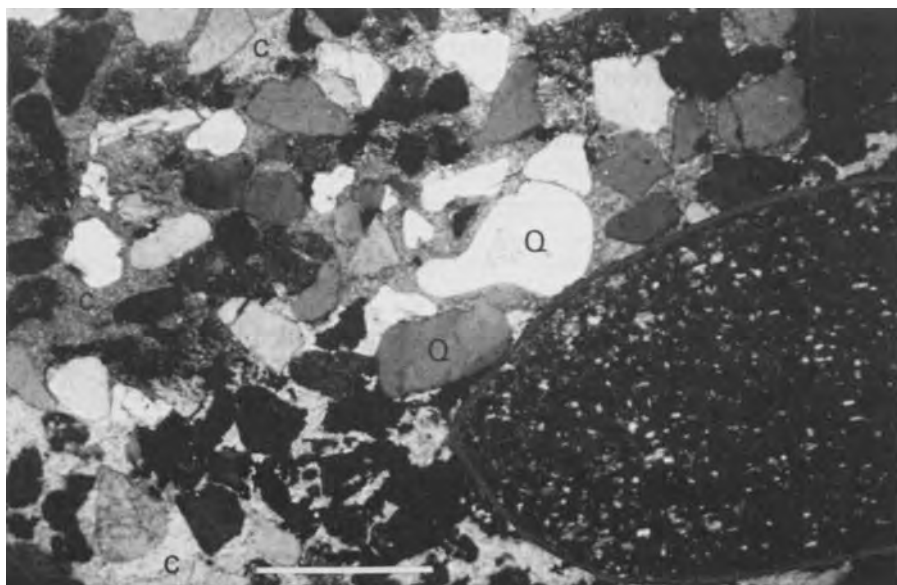


Fig. 4-17. Thin-section photomicrograph of Lower Albian calcite-cemented glauconitic quartzose sandstone, from the Boulonnais – Paris Basin, illustrating verdissement of detrital quartz. The verdissement tends to exploit grain fractures. In the bottom right-hand corner, a large glaucony grain displays remnants of its original granular quartz substrate. Scale bar = 0.1 mm, Q = quartz grains, C = carbonate cement.

unstable and become progressively destroyed as verdissement proceeds. The more stable the substrate, the longer it takes to disappear (Lamboy, 1976). Calcareous substrates, being least stable, are, therefore, easily and rapidly replaced by authigenic clays. Consequently, residual carbonate is rarely observed in ancient glauconies, although, as discussed above, the original calcareous nature of the substrate may be diagnosed by the internal texture of the grains. Conversely, micas and especially quartz are much more stable, and remnants of these materials are commonly found in ancient glauconies, even in evolved grains (Fig. 4-17). As the substrate is destroyed (Fig. 4-4), it leaves a new system of pores that, in turn, become filled with authigenic clays, developing as blades or rosettes. At this stage, an individual grain largely consists of glauconitic minerals, K_2O contents are between 4 and 6%, and the glauconitic minerals show globular, caterpillar-like or blade-like habits (Fig. 4-3): the grain is said to be *slightly evolved*.

With continuing evolution, a series of recrystallizations takes place, tending to obscure the initial textures of the grains. Recrystallization and crystal growth cause an increase in volume of the grains, producing two different effects, depending on the initial nature of the substrate. Many grains develop external cracks at this stage, a feature earlier described as a result of dehydration with reduction in volume, due to potassium enrichment. SEM shows this to be erroneous. Because the grain interiors are more favorable for crystal growth than the surfaces, the larger and better-organized crystallites are found at the grain centers. Because growth is more rapid at the center compared to the margin, cracks appear at the surface. A different effect occurs with recrystallization of glauconitized mica flakes. Here, the growth of authigenic clay between the individual sheets causes the flakes to open into accordion-like folds. At this stage, K_2O contents are between 6 and 8%, and the grains are said to be *evolved*.

If environmental conditions remain suitable, the cracks created in the preceding

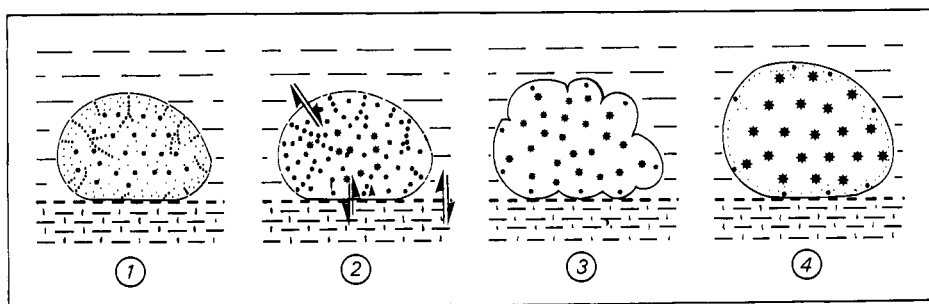


Fig. 4-18. Scheme of evolution of glaucony grains at the sea bed. Four points in the evolutionary continuum are represented. *Nascent glaucony* (1) is a porous granular substrate in which glauconitic smectite (small stars) originate by crystal growth. *Slightly evolved glaucony* (2) still contains remnants of the substrate, and the glauconitic minerals are more evolved in the center (large stars) than in the margin. Cations feeding the growth of the authigenic minerals come from the sea, the interstitial pore water of the sediment and, when adequate, from the substrate itself. In *evolved glaucony* (3), the more efficient crystal growth at the centre of the grain compared with the margin provokes superficial cracks. In *highly evolved glaucony* (4), substrate components have disappeared, and authigenic minerals are mainly glauconitic micas. After burial, further recrystallization processes may result in a fifth stage of evolution.

stage are filled, imparting a smooth aspect to the grains. This is typical of *highly evolved* grains, in which K_2O contents exceed 8%. The minerals filling the cracks are generally less rich in potassium than the rest of the grain, again illustrating that the surface of the grain is less favorable for clay authigenesis than the interior. The general scheme of evolution of glaucony grains is shown in Fig. 4-18.

The evolution process may be halted at any stage if the environment becomes unsuitable. Two main factors appear to be involved: marine regression and burial. A regression phase may introduce the grains to a more oxidizing environment, provoking alteration. Although in porous sediments verdissement may still proceed at depths up to a meter from open sea water, burial below this level rapidly halts the process. Consequently, a high rate of detrital influx will inhibit or entirely prevent glauconitization.

The verdissement process is not only concerned with the growth of the authigenic phyllite, but also with the disappearance of the initial substrate. A knowledge of the behaviour of the substrate minerals is particularly important when radiometric dating of glaucony is undertaken, because the isotopes of the substrate could significantly affect the apparent age. Up to a point, the amount of remaining substrate can be estimated using XRD and SEM observations, but once K_2O contents exceed 5%, the substrate is rarely detectable. To estimate this possible contribution, the writers measured the ^{40}Ar content of Recent glaucony at different stages of evolution (Fig. 4-19). The samples used came from the continental shelf

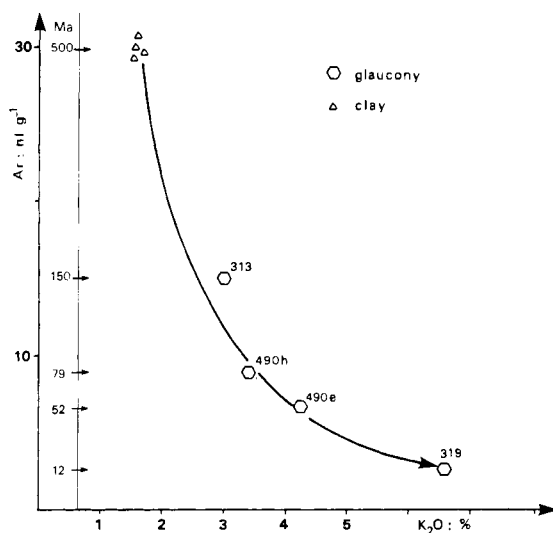


Fig. 4-19. Evolution of argon content during glauconitization of mud coprolites from Recent sediments of the Gulf of Guinea. The essentially kaolinitic mud is rich in inherited radiogenic argon, probably located in mica or poorly crystallized feldspar. As the green grains become more potassium-rich as authigenesis progresses, the argon of the original substrate is progressively removed. Even in the evolved glaucony of the area (with $K_2O = 6.6\%$), however, inherited argon is still present, indicating the continued presence of mineralogically undetectable substrate components.

off Congo, for three reasons. Firstly, the substrate consists mainly of faecal pellets; secondly, a full range of evolution had been detected; and thirdly, the muds which comprise the initial substrate are rich in inherited isotopes, showing an apparent K – Ar age of about 500 Ma. This study (Odin and Dodson, 1982) showed that even grains with a K_2O content of 6.6% (sample G.319) still contains 9% of the initially inherited ^{40}Ar . Although the nature of the component able to retain argon through such a strong geochemical evolution is still uncertain, it is clear that the apparent K – Ar age of a slightly evolved glaucony may be noticeably older than its time of genesis. The effect is reduced in cases where the initial substrate is less rich in radiogenic isotopes, as with samples from Senegal, where the substrate has a high apparent age (450 Ma) but a low potassium content. The same effect occurs in Rb – Sr dating: for example, radiogenic Sr from the initial clay has a significant effect on the apparent Rb – Sr dates of Recent glaucony from the Gulf of Guinea (Keppens et al., 1984). Not one Recent glaucony from the Gulf of Guinea has given a zero apparent age, either by K – Ar or by Rb – Sr dating. Only one case of zero apparent age glaucony is known as yet in present-day sediments. This date was determined on a Recent evolved glaucony collected off California (Odin and Dodson, 1982). This sample contains 7.5% K_2O , and the grains occur as infillings of foraminiferal tests and as replacements of detrital micas. Consequently, if the composition of the initial substrate is not known precisely, confidence can only be attached to radiometric dates obtained from evolved grains. Grains with less than 7% K_2O are likely to have had a positive apparent age at the time of burial. The possibility of inheritance of radiogenic isotopes may be assessed by measuring apparent ages from several fractions of the same sample, because different fractions are at different stages of evolution. These data can be used to generate a curve of apparent age as a function of potassium content, the form of which provides information on the degree of inheritance. A good estimate of age can thus be obtained, although the errors may be large (Odin and Dodson, 1982; Kreuzer et al., 1982, p. 755). In general, the best estimate of age of deposition is given by the most evolved grains.

Detailed studies of areas such as the Gulf of Guinea have provided valuable information on the duration of the evolution process (Fig. 4-19). Substrates, which have been exposed to sea water for less than 20,000 years (that is, those at depths shallower than 110 m), have maximum K_2O contents of 5%. Consequently, this stage of evolution is apparently reached in a period of the order of 10^4 years. Grains at depths between 200 and 400 m have maximum K_2O values of 6.5 – 7.5%, and the most highly evolved grains (those with $K_2O > 8\%$) are relict, of Pliocene or Pleistocene age. It appears that highly evolved glaucony requires a period of some 10^5 – 10^6 years to develop.

The processes involved in the evolution of verdine are less easy to ascertain than in glauconitization, because there are no comparable mineralogical progressions, such as changes in XRD behavior or in potassium content. Consequently, as yet there are no criteria by which the stage of evolution can be defined. By analogy, however, one can assume that color is a guide, as the grains change from light to dark green. Similarly, rare grains display cracks comparable to those of evolved glaucony, and others have a smooth bright appearance similar to highly evolved

glaucy. Their paramagnetic behavior appears to confirm that this sequence corresponds to a progressive evolution, as the more paramagnetic the grain, the darker it appears. Given these observations, and the fact that verdine is essentially a granular facies, it seems likely that verdine develops in a similar fashion to glaucy, that is, by crystal growth followed by recrystallization.

It is noteworthy that verdine and goethite are frequently found in close association, because this implies that verdine forms close to the zone of highly oxygenated waters, possibly even within it. It is possible, for example, that verdine forms at very shallow depths (about 10–20 m) in a muddy substrate of faecal pellets rich in organic matter. In this situation, the abundance of organic matter would maintain the reducing conditions necessary for verdinization, even though the sea water is highly oxygenated. As soon as the organic matter is destroyed, conditions become oxidizing, and goethite forms as an alteration product of the verdine. Verdine may be protected from alteration in a transgressive setting, so that the oxidizing zone moves away from the site of formation, or by transportation into deeper water. Because highly evolved verdine is present on parts of the continental shelf flooded since the last regression 18,000 years ago, the entire process appears to be much more rapid than glaucitization, probably being completed in less than 10,000 years.

The role of confinement

As emphasized by Odin and Matter (1981), a fundamental factor in the verdissement process is the degree of “confinement”, that is, the extent to which the mineral-forming reactions occur in chemical isolation from sea water. The preferential location of growth of glaucitic minerals inside microfossil tests, in pores and fissures within particles, or in burrows in hardgrounds is taken as an indication that verdissement requires a degree of confinement. Confinement creates a microenvironment which is different both from the surrounding sea water and from the enclosing sediment.

It is generally true that grains with diameters less than 100 μm are less well evolved than larger grains with diameters between 200 and 400 μm . It would seem that the interiors of small grains are relatively unconfined, leading to excessive exchanges with ambient fluids, inhibiting crystal growth. Similarly, the most effective crystal growth takes place in the center of a grain, rather than the periphery, which is more open to exchange with the ambient fluid. It is also important, however, that confinement is not so great that ionic exchanges are prevented. Obviously, growth of a silicate inside a carbonate requires passage of ions into the grain from the exterior, and, similarly, the ions composing the substrate must be permitted to depart. The large volumetric increases which occur in the late stages of glaucitization testify to the introduction of ions from the exterior. Very coarse sedimentary particles, such as gravel-sized grains, are only glaucitized on the surface, because their interiors are too confined to allow complete verdissement.

A key factor in the verdissement process, therefore, is the presence of a *semi-confined* physical environment where ions may enter and leave, but where exchange is not too rapid. Ions are fed from the sea water, from the interstitial fluids in the

sediment, and from the substrate itself, with the porosity of the substrate acting as a controlled passageway providing the optimum condition for interaction of the relevant ions. Within mica flakes, such favorable semi-confinement is found between the cleavage flakes. In microfossil tests, semi-confinement is created by the wall of the test which acts as a semi-permeable barrier for migrating ions. In hard-grounds, semi-confinement is controlled by the porosity of the medium: according to Juignet (1974), glauconitization of chalks occurs over a wider zone (up to 1 cm) than in less porous rocks, such as phosphates or cherts (less than 1 mm). Grains which are mobile on the sea floor are particularly susceptible to verdissement, because motion facilitates the renewal of the ion source. As soon as the substrate is buried, grains become isolated from sea water, the main source of the cations, and exchange becomes more restricted because water circulation diminishes. At this stage, the favorable zone of semi-confinement may transfer from the grain interiors to the pore spaces between grains, thus allowing the formation of a layer of green silicates around grains. This frequently observed layer is known as the peripheric oriented rim or the fibroradiated cortex (Collet, 1908; Zumpe, 1971; Odin, 1975a; Lamboy, 1976). Following this, verdissement halts altogether.

OCCURRENCE AND PALEOGEOGRAPHIC SIGNIFICANCE OF GREEN PARTICLES

Verdine

Verdine grains have not, as yet, been recorded with certainty from ancient sediments. This may, in part, be a problem of terminology, as discussed in the section on p. 222. It is possible, for example, that some grains described as chamosite or berthierine are actually composed of phyllite V. It is, however, erroneous to relate directly berthierine of ancient oolitic ironstones to present-day verdine, as Van Houten and Bhattacharyya (1982) did, because their morphology, mineralogy and geological significance are all quite distinct. As yet, the only possible pre-Quaternary example of verdine is the Miocene "chamosite" described by Porrenga (1976a). He regarded these as similar to the surficial grains cored in the Niger Delta area, which are now known to be composed of phyllite V. In the absence of XRD data on this Miocene sample, the validity of this assignment cannot be judged.

All other recorded occurrences of verdine are from the present-day sea floor, although some of these are relict. The distribution of verdine is shown in Fig. 4-20 and summarized below.

Atlantic Ocean

Most of the verdine occurrences known to date are from the Atlantic Ocean, both offshore west Africa (Senegal, Ivory Coast, Nigeria, Gabon, and Congo) and offshore eastern South America (Venezuela, Surinam, and French Guiana). Off Senegal, phyllite V has been observed both north and south of Cap Vert. North of Cap Vert, verdine occurrences are sporadic and confined to the depth range of 25 – 180 m. In this area, coprolites, originally consisting of a clay rich in kaolinite and smectite, form the substrate. Consequently, the distinction between the com-

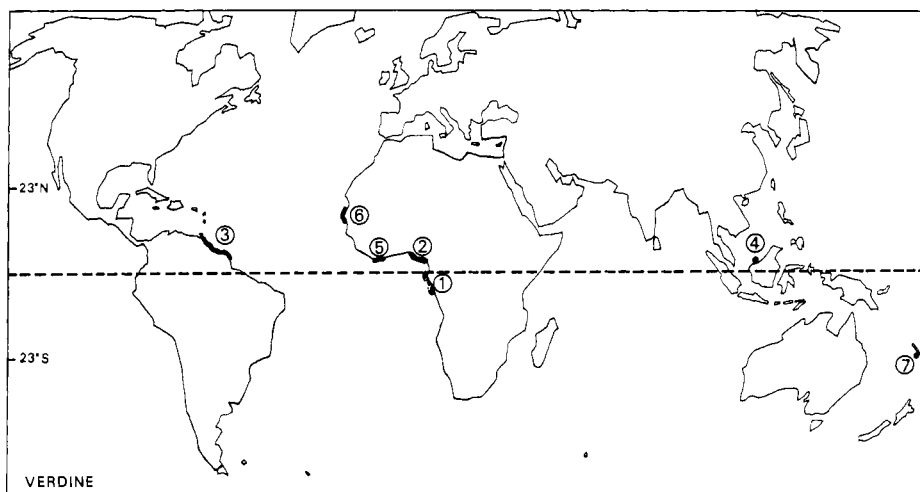


Fig. 4-20. Distribution of verdine on present-day continental platforms, numbered in order of documentation. 1 = Ogooué-Congo, 2 = Niger Delta, 3 = Orinoco-Amazon Delta, 4 = Sarawak, 5 = Ivory Coast, 6 = Senegal, and 7 = New Caledonia. Areas 1 and 3 are now known to be wider than initially described, but the precise extension of areas, 1, 4, 6 and 7 awaits further systematic mineralogical studies. Not shown on this map are the recently confirmed occurrences in the Casamance Estuary (South Senegal), off Guinea, and in Mayotte Islands (Comoro, Indian Ocean).

ponents of the substrate and the authigenic mineral by XRD is difficult. The presence of slightly evolved glaucony is a further complication. South of Cap Vert many surficial samples collected by Masse (1968) are rich in verdine. The grains were originally described as glaucony, but subsequent studies have shown them to consist of relatively pure phyllite V. They mainly consist of internal moulds of calcareous microfauna, with the result that XRD can easily distinguish the authigenic mineral from the substrate; there has been little oxidation. Grains found at depths shallower than 110 m have formed in the last 18,000 years. The age of the grains found deeper is not certain, but they are undoubtedly Quaternary.

Von Gaertner and Schellmann (1965) also examined Recent sediments from off Guinea, and considered that grains comprising the magnetic fraction were chamosite, which had developed after deposition by replacement of goethite. Subsequent examination of new samples from Guinea has shown that verdine is present in the area. Verdine has also been identified from two areas in the Casamance Estuary (South Senegal) and in the Mayotte Islands (Comoro, Indian Ocean).

A study by Martin (1973, pp. 241–264) of the offshore area of the Ivory Coast revealed the presence of verdine in the depth range of 20–40 m. Martin (1973) regarded this as berthierine on the basis of chemical and XRD studies. The substrate consists of highly kaolinitic coprolites. This and the substantial degree of oxidation shown by the grains, particularly those from the shallower parts of the outcrop, makes the precise identification of the authigenic mineral difficult.

As already discussed, one of the first records of verdine is that made by Porrenga

(1967b) from offshore Nigeria. Green grains, regarded by him as chamosite, were found in water depths greater than 65 m, with the total length of the outcrop exceeding 500 km. Kaolinitic faecal pellets form the main substrate, and as in Ivory Coast there has been considerable oxidation, with goethite commonly occurring. Porrenga (1967a) made a significant observation regarding the genesis of verdine when he noted that the area where green grains are common coincides remarkably well with the area where the upper water mass is in contact with the sea floor.

At depths of between 5 and 60 m off Gabon and Congo, Giresse and Odin (1973) have recorded the occurrence of a green phyllite, originally described as berthierine (Giresse, 1965) but now termed phyllite V. The substrate largely consists of faecal pellets, and many grains have been oxidized. The main occurrences are over a zone some 100 km long north of the mouth of the River Congo and in a patch of some 30 km diameter at the mouth of the River Ogooue. There may be intermediate occurrences, but the kaolinitic nature of the substrate masks any trace of phyllite V on XRD traces.

On the western margin of the Atlantic, a number of authors have documented the occurrence of green grains offshore from the mouth of the River Orinoco and in the Gulf of Paria (Van Andel and Postma, 1954; Nota, 1958, and Koldewijn, 1958, both quoted in Porrenga, 1967a; Hirst, 1962). In the absence of XRD analysis, these grains were regarded as glauconite until Porrenga (1967a) recognized their similarity with the so-called "chamosite" from Nigeria. Porrenga also pointed out that they occur for some 750 km along the continental shelf as far as Guyana.

Verdine has also been recorded farther east, from offshore Surinam (Hardjoesastro, 1971). The grains show diverse habits, occurring as replacements of faecal pellets, as internal moulds of microfossil tests and as accordion-like shapes.

Following the identification of "glaucony" offshore French Guiana (Moguedet, 1973; Bouysse et al., 1977), Rénié (1983), Chagnaud (1984) and Pujos et al. (1984) concluded, on the basis of detailed XRD work, that green grains that occur above 150 m depth are not glauconitic, but show a 7 Å peak and have all the characteristics of verdine. Verdine occurs between 20 and 150 m, forming between 1 and 10% of the total sediment. Close to the shore, the substrate consists mainly of chloritized biotite flakes, but internal moulds of microfossil tests become progressively dominant offshore. Oxidation is extensive in the deeper areas, and occurs sporadically in other parts of the platform.

The occurrences offshore eastern South America are the most extensive yet discovered, with verdine probably common over a distance of some 1400 km from the Orinoco Delta to the mouth of the river Oyapock, although detailed mineralogical studies are lacking over a large part of this area.

Pacific Ocean

The only other verdine localities known to date lie in the Pacific Ocean. Porrenga (1967a) describes abundant "chamosite", often oxidized to goethite, at depths between 20 and 60 m offshore Sarawak (Malaysia). Substrates include microfossil tests and faecal pellets, and chloritized biotite flakes are especially favorable. Porrenga noted that verdinization of chlorite involves the progressive disappearance of the 14 Å peak concomitantly with an increase in the 7 Å peak. The 7 Å peak disappears

after heating to $450^{\circ} - 550^{\circ}\text{C}$. Consequently, the “chamosite” found by Porrenga (1967a) in the offshore Sarawak locality is directly comparable to phyllite V of French Guiana. Porrenga, however, does quote a single chemical analysis with $\text{FeO} = 17\%$ and $\text{Fe}_2\text{O}_3 = 4\%$. This differs markedly from all modern data on verdine presently gathered. Keller (pers. commun., 1966, quoted in Porrenga, 1967a) discovered what he took to be similar Recent “chamosite” 1000 km west of Sarawak, between Sumatra and Malaysia. The significance of this awaits further investigation, particularly considering the common occurrence of glaucony in the region. Green grains from the Makassar Strait (South Borneo) are now known to be glaucony.

The final example of Recent verdine is from the southern part of New Caledonia, and is still under investigation (Odin and Froget, in prep.). A comparison of the seven known outcrops of verdine is given in Table 4-7.

Glaucony

Although glaucony has been found in sediments of practically all ages, its first appearance in the geological record being at about 2000 Ma in the USSR (Polevaya et al., 1961), Australia (Webb et al., 1963) and China, certain periods appear to be more favorable for its formation than others. The Albian–Cenomanian and the Cenozoic are particularly notable, with glaucony development on a global scale. True in-situ glaucony has only been recorded from marine sediments, but several anomalous non-marine occurrences have been reported. For example, Millot (1949) suggested that authigenic “glaucony” was present in lagoonal deposits at Pechelbronn (France); Djadtchenko and Khatuntseva (1955) reported “glaucony” in eluvial deposits from the Ukraine (USSR); and Keller (1956) claimed that volcanic ash in the lacustrine Morrison Formation of Colorado (USA) had undergone transformation to “glaucony”. Kossovskaya and Drits (1970) reviewed the occurrences of so-called “continental glaucony”, concluding that the minerals concerned are not strictly comparable to the glauconitic minerals, being significantly poorer in iron, and referred to them as “ferric illite”. Besides these reports of authigenic non-marine “glaucony”, there are records of true marine glaucony reworked into continental sediments (Triat et al., 1976; Odin and Rex, 1982).

TABLE 4-7

Characteristics of outcrops of verdine

Location	Latitude	Depth (m)	Length of the outcrop (km)
Ogooue – Congo	$0 - 5^{\circ}\text{N}$	down to 80	750 (locally)
Niger Delta	$4 - 5^{\circ}\text{N}$	10 – 65	600 (continuous)
Orinoco – Amazon	$2 - 10^{\circ}\text{N}$	20 – 150	1650 (probably)
Sarawak	$3 - 3.5^{\circ}\text{N}$	20 – 60	100 (continuous)
Ivory Coast	5°N	down to 60	400
Senegal	$15 - 16^{\circ}\text{N}$	30 – 200	250 (locally)
New Caledonia	22°S	20	15 (minimum)

Glaucy occurs principally in sandstones, siltstones, mudstones and limestones, but is never associated with evaporitic deposits or other chemical deposits, such as the magnesium-rich clays of the sepiolite–attapulgitic group. The nature and geographical distribution of glaucy in late Neogene and Recent surficial sediments is summarized below.

Western margin of the Atlantic Ocean

Information regarding distribution of glaucy on the eastern seaboard of the United States has been published by Ehlmann et al. (1963), Bell and Goodell (1967) and Goodell (1967). From Cape Hatteras (North Carolina) in the north to Florida in the south, Recent glaucy is present in quantities up to 70% of the sediment. Grains occur mainly as internal moulds of microfossil tests, pale green in color, and have an optimum development at about 200 m depth.

Off South America, glaucy is present from Venezuela and Trinidad (Porrenga, 1967a) to French Guiana (Moguedet, 1973; Chagnaud, 1984), that is, over the same interval as verdine. The glaucy occurs at depths greater than 150 m, in deeper water than verdine, and appears to be a relict deposit along the entire length of the outcrop from the mouth of the Orinoco to the mouth of the Amazon, probably older than 20,000 years B.P. Farther to the south, Bell and Goodell (1967) have recorded abundant glaucy (up to 35% of the sediment) on the Scotia Ridge, in water depths of between 200 and 3000 m, and Collet (1908) recorded it between the Malvinas Islands and the Rio de la Plata.

Eastern margin of the North Atlantic

The most northerly record of glaucy offshore Europe is that of Bjerkli and Östmo-Saeter (1973), who described Holocene glaucy infilling microfossil tests in water depths of some 270 m off Norway. Glaucy is present in the Irish Sea and the English Channel, but is probably reworked.

Authigenic, but mostly relict, glaucy occurs in great abundance off northwest Spain (Lamboy, 1976). The glaucy shows a great diversity in substrate type, and grains comprise up to 50% of the sediment over a depth range of 100–300 m. The relict glaucy dates as far back as the Pliocene. Glaucy is present in minor amounts off Portugal (Monteiro, 1970) and southern Spain, in water depths between 100 and 200 m, and is probably of relict origin.

Glaucy appears to be present along virtually the entire Atlantic coast of the African continent (Bell and Goodell, 1967; Mathieu, 1968; Emelyanov, 1970; Tooms et al., 1970). Off Morocco, glaucy occurs at depths between 140 and 200 m. In the region from Casablanca to Essaouira, the grains, which occur as internal moulds of microfossil tests, comprise less than 10% of the sediment. They are of Pleistocene–Holocene age, and were partially oxidized during the last regression 18,000 years ago. South of Essaouira, off Agadir, glaucy is more common, forming between 15 and 85% of the sediment, with faecal pellets acting as the main substrate. Again, the grains are relict and highly oxidized.

Correns (1939, p. 383) indicated the possible presence of glaucy between Cap Blanc (Mauritania) and Cap Vert (Senegal). Subsequent work, however, has shown that only those grains in water depths greater than 200 m off Senegal can be termed

glaucy. In deeper water (> 1000 m) offshore Senegal and Guinea, coring has revealed glauconitic horizons of Miocene–Quaternary age close to the sea bed. Coprolites form the initial substrate here, and the grains appear to have been transported from shallower water.

Glaucy is widespread throughout the Gulf of Guinea, having been recorded from Ivory Coast (Martin, 1970, 1973), from the Niger Delta (Porrenga, 1967a, b), from Cameroon (Emelyanov, 1970), and from between the mouth of the River Ogooue (Gabon) and the mouth of the River Congo (Bezrukov and Senin, 1970; Giresse and Odin, 1973). In this area, glauconitic grains, the result of the verdissement of kaolinitic faecal pellets, occur in situ at depths between 80 and 300 m, but are present at greater depths locally. Grains which occur at depths shallower than 120 m were formed within the last 18,000 years. At 110 m, there is an oxidized zone composed of grains altered at the time of the last regression 18,000 years ago.

A detailed study of the shelf between Congo and Gabon by Giresse and Odin (1973) has greatly increased the understanding of the verdissement process. As water depths pass from shallow (80 m) to deep (300 m), glauconitization of the coprolitic substrate becomes more and more evolved. This is because grains in deeper water have been exposed to sea water for a longer period as the most recent transgression, initiated 18,000 years ago, proceeded (Giresse, 1975; Odin and Giresse, 1976).

Glaucy has been reported from many locations between Congo and South Africa (Caspari, 1910; Lloyd and Fuller, 1965; Calvert and Price, 1970; Bezrukov and Senin, 1970), but according to Simpson (1970, p. 163) most of this has been reworked from the Cretaceous, and only the glaucy which fills foraminiferal tests is Recent. This is supported by Birch (in Dingle, 1973), who noted that the distribution of glaucy in the Quaternary sediments of Agulhas Bank described by Collet (1908) matches the outcrop of the glauconitic Eocene. Further work (Birch et al., 1976) showed that many glauconitic grains from the South African continental shelf possess a high K_2O content (8.0–8.5%), suggesting that they are reworked from Cretaceous and Tertiary sediments. Several of these samples were dated radiometrically by Odin (1985b) to test the reworking hypothesis. A small number proved to be of Cretaceous–Eocene age, and several gave an apparent Miocene date. A large proportion, however, gave comparatively young dates, between 8 and 3 Ma, indicating that they can be considered in-situ types, but of relict origin.

Pacific Ocean

Glaucy is well known from the west coast of the U.S.A., occurring between 43 and 10°N (Murray and MacIntosh, 1968). It also occurs farther south, off Peru and Chile. Odin and Stephan (1981) reviewed the distribution of glaucy in the eastern Pacific (Figs. 4-21 and 4-22). The localities off California have been extensively studied (Galliher, 1935; Emery, 1960; Uchupi, 1961; Pratt, 1963). On the basis of his studies, Galliher (1935) proposed that glaucy developed by transformation of biotite mica on the sea floor. Hein et al. (1974), however, reassessed their work, showing that the substrates for glauconitization were more diverse than Galliher had suggested, and that his model was, therefore, not tenable, supporting the contention of Odin (1972).

Most of the glaucy occurrences off the west coast of America lie at depths of

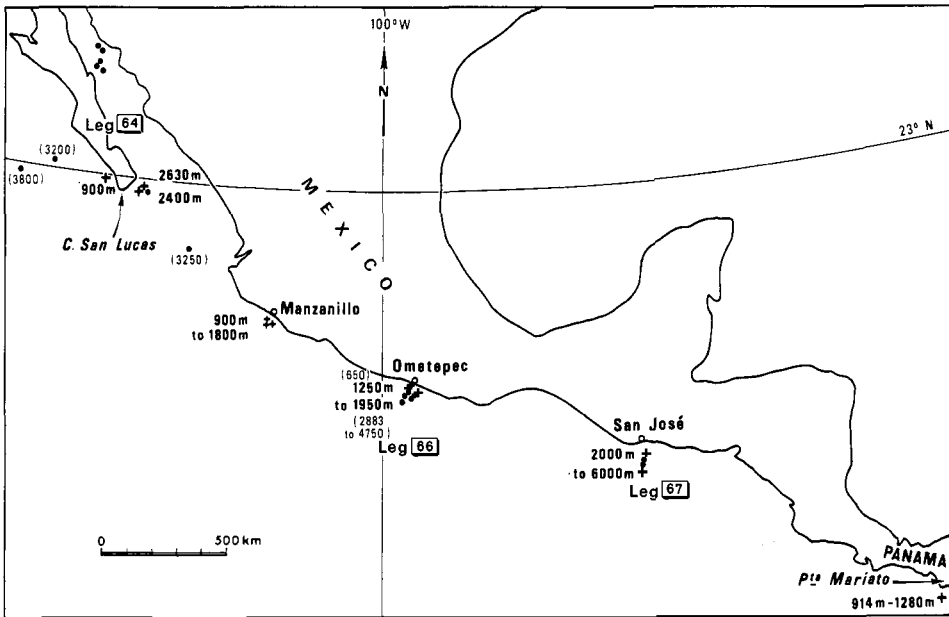


Fig. 4-21. Distribution of glaucony in surficial sediments off Central America (after Odin and Stephan, 1981). Glaucony is also likely to be present in areas between the investigated points. There is wide diversity of water depth compared with the great concentration of outcrops at between 100 and 300 m depth on the passive Atlantic margins. Key as in Fig. 4-22.

some 100–300 m, but Odin and Stephan (1981) showed that a substantial number of Quaternary–Recent samples occur in water depths greater than 1000 m, apparently in situ (Figs. 4-21 and 4-22).

Elsewhere in the Pacific, records are more scarce. Takahashi and Yagi (1929) described green grains off Japan, but little is known of their precise composition. Off New Zealand, glaucony, probably relict, occurs between 250 and 2000 m depth on the Chatham Rise (Norris, 1964; Cullen, 1967; Seed, 1968). Collet also quoted “glaucony” off Australia and Japan, but gave no mineralogical details.

Other occurrences

Glaucony is relatively common in shallow-water surficial sediments of the Mediterranean Sea (Thoulet, 1912; Dangeard, 1928; Leclaire, 1964, 1972; Caillère and Monaco, 1971). Murray (in Collet and Lee, 1906) also records glaucony in deep-water sediments, but these could well have been transported from shallower areas. Glaucony is also present in surficial Wurmian sediments of the Aegean Sea (Robert and Odin, 1975).

Records of glaucony in the Indian Ocean are scarce. Collet (1908) noted green particles off South Africa, and Houbolt (1957) and Von Lange and Sarnthein (1977) found glaucony in sediments of the Persian Gulf down to depths of some 110 m. Popov and Sval’nov (1982) encountered widespread glaucony on the outer part of

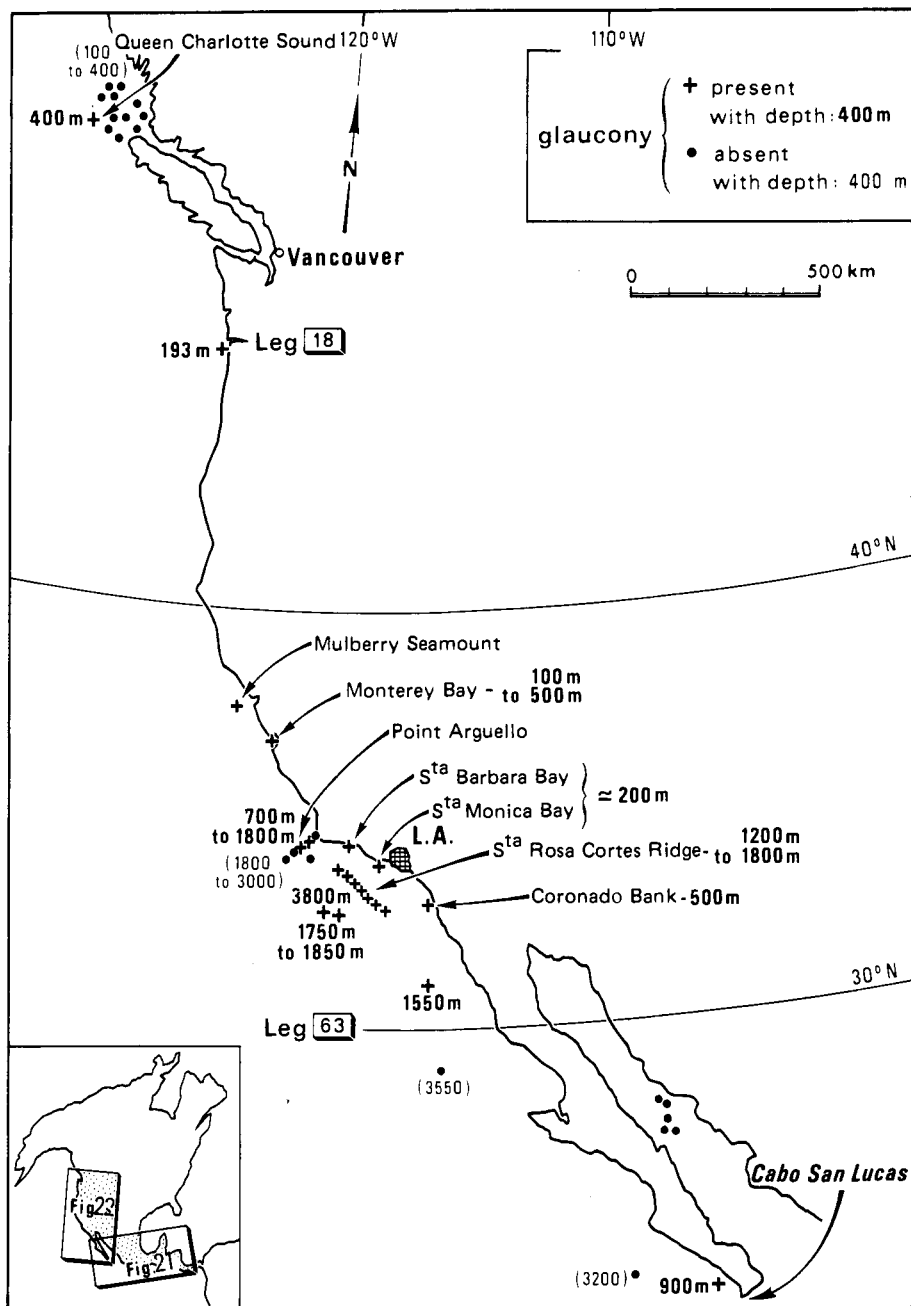


Fig. 4-22. Distribution of glaucony in surficial sediments off western North America (after Odin and Stephan, 1981). Crosses indicate localities where glaucony has been quoted in the literature, especially in Deep Sea Drilling Project reports.

the continental shelf in many areas around the Indian Ocean, notably off western Madagascar, around Sri Lanka, and off Hindustan, Burma, and Australia. Glaucony from the Kerguelen–Heard Plateau (South Indian Ocean) has been studied recently by Odin and Fröhlich (in prep.).

Environment of verdissement

Verdine

In virtually every case, verdine is associated with input from major river systems in the tropical belt along passive continental margins. Verdine deposits are found along the Atlantic coast, the Senegal River, Niger River, Ogooue River, Congo River, Amazon River, and Oyapock River (Fig. 4-20). The size of the deposit appears to be a function of the size of the river, although it is not yet certain what factors specifically control this. As pointed out by Odin and Matter (1981), the facies seems to develop best in the presence of cold currents and zones of upwelling. For example, verdine only occurs to the south of the ancient Senegal River mouth, not to the north. This testifies to the importance of the interaction between the cold surface-water currents flowing to the south and river discharge. This causes the river output to be deflected to the south, creating a suitable environment for phyllite V development. The South American case is similar: here, the massive output of the River Amazon has been deflected westward, and this, combined with the output from the Orinoco and many other relatively small rivers, has created a particularly favorable setting for verdinization. The result is that verdine occurs over a very large area of the continental shelf, some 1400 km long. Until very recently, verdine had not been reported from tectonically active areas. Although the New Caledonia discovery modifies the picture somewhat, the locality is nevertheless in the vicinity of an emergent landmass, which appears to be the main determining factor.

The distribution of verdine is particularly depth-dependent, being found in situ in water depths between 10 and 50 m. As discussed earlier it may actually form within the highly oxygenated water zone at about 10–20 m depth. In some areas, verdine is found at greater depths, as off Senegal where it occurs down to 200 m, but such occurrences are believed to represent relict deposits formed prior to the Recent transgression. Fully evolved verdine grains have been generated since this last transgression, some 18,000 years ago; therefore, the verdinization process can be regarded as relatively rapid, probably requiring a period of the order of 6000–7000 years.

Glaucony

On present-day passive continental margins, glaucony is common in surficial sediments over a wide latitudinal range, from 65°N to 55°S (Fig. 4-23). In many areas, however, it is relict (as, for example, are most glauconies collected north of 35°N and south of 35°S in the eastern North Atlantic) and, thus, is not characteristic of present-day environmental conditions. Nevertheless, the latitudinal distribution of Recent authigenic glaucony is greater than that of verdine, although, as with verdine, tropical areas are particularly favorable. Authigenic glaucony has yet to be recorded from subpolar regions.

The bathymetric distribution of glaucony is similarly wider than that of verdine. Glaucony is particularly characteristic of the continental shelf at depths between 60 and 500 m, forming up to 90% of the sediment. The optimum depth is about 200 m at the present day, but this could have changed through geological time. Accumulation of glaucony on the outer part of the shelf apparently results from a balance between detrital influx and winnowing by bottom currents. Close to the shore, particularly in the vicinity of river mouths, detrital influx exceeds erosion, producing high accumulation rates which prevent glaucony formation. Below about 60 m depth, the continental influence is less, and winnowing causes continual redistribution of sedimentary particles. Consequently, grains are exposed at the sea floor for long periods, sufficient to allow glauconitization, and winnowing facilitates ionic exchange between the substrate and sea water. Below 200 m, energy is less, and sediments accumulate more rapidly, again inhibiting glauconitization. Most of the glaucony found below 200 m, therefore, is likely to have been transported from shallower water. Locally, however, strong bottom-water currents even in the deep ocean basins simulate the conditions found on the outer shelf, allowing genesis of glaucony in very deep water, such as that formed at depths of 1600–2500 m during the Miocene to the southwest of Rockall Plateau, Northeast Atlantic (Morton et al., 1984).

Away from the passive margin setting, active tectonic highs such as Chatham Rise or the Scotia Ridge (500–1000 m depth) also seem favorable for glauconitization. These occurrences further demonstrate that depth need not be an important factor. More important factors seem to be local input of iron, presence of bottom currents,

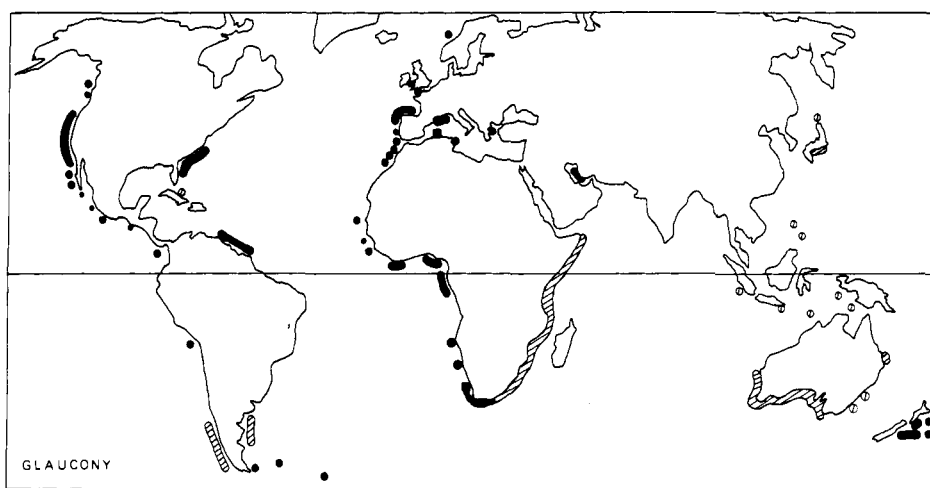


Fig. 4-23. Distribution of glaucony on the present-day sea floor (modified after Odin and Matter, 1981, and Odin and Stephan, 1981). Hatching indicates areas of unidentified green grains, presumably glaucony. There is high frequency of occurrence of glaucony on the eastern margin of the Atlantic and Pacific oceans. There is also lack of detailed information on outcrops east of Africa and between Japan and south Australia; this is urgently required in view of the identification of verdine in this area (Sarawak and New Caledonia), as shown in Fig. 4-20.

and occurrence of favorable substrates such as microfossil tests, much the same as the factors governing the deep-water Northeast Atlantic occurrence.

In the geological record, the base of a transgressive sequence is frequently marked by a highly glauconitic layer. Although transgression itself is not a prerequisite for glaucony formation, it does bring together many of the factors which favor the process. Firstly, during a transgression, particles such as shell debris, mineral grains, and faecal pellets, formerly deposited in the zone above wave base, find themselves at depths favorable for glauconitization. Secondly, a transgression causes a diminution of sediment supply by encroaching onto the continental landmass, so that sediments at the sea floor are not rapidly buried. This, in turn, gives the reactions a longer time to proceed. Thus, a transgression has three important effects: (1) it produces suitable substrates; (2) it places the substrates at depths where the reactions are most efficient; and (3) it prevents rapid burial providing sufficient time for the reaction.

Two further points regarding the environment of glauconitization should be discussed here, these being the common association of glaucony with phosphate and of glaucony with goethite. Studies of the present-day continental shelf have revealed that, although there is a close relationship between glaucony and phosphate, the two processes are not concomitant. In some areas, phosphatization post-dates glauconitization, as off northwest Spain (Lamboy, 1976) and southwest Africa (Collet, 1908; Emelyanov, 1970; Parker, 1975), whereas in other areas, such as Chatham Rise off New Zealand (Cullen, 1967), Chile, and the straits of Florida (Bentor, in Odin and Létolle, 1980), the reverse is true. Although their conditions of formation are not greatly dissimilar, therefore, the two facies are not in thermodynamic equilibrium with sea water at the same time. The lack of a common environment for the genesis of glaucony and phosphate has previously been emphasized by Collet (1908).

normal sequence	glauconies	phosphates	clay minerals
EVAPORITES			Mg FIBROUS CLAYS
CARBONATES			Al SMECTITES
OXIDATES			Fe GLAUCONITIC MINERALS
HYDROLYSATES			PHYLLITE V
RESISTATES			

Fig. 4-24. Glaucony, verdine and phosphate in the normal geochemical evolutionary sequence. (Modified from Odin and Létolle, 1980.)

The relationships between glaucony, verdine, and phosphate can be considered in terms of the classical normal evolutionary sequence of Goldschmidt, as revised by Millot (1964, p. 91). In this scheme, the sequence consists of five members: (1) coarse residues (the detritus carried from the continental landmass to the sea) at the base, overlain successively by (2) hydrolyzates (the fine-grained detritus of continental origin), (3) oxidates, (4) carbonates, and (5) saline deposits, the last two being strictly of chemical origin associated with hypersaline conditions (Fig. 4-24). Glaucony development may be essentially linked with the oxidate member of the sequence, although it can be associated with the detrital and carbonate members, excluding the carbonates of chemical origin. Verdine, as demonstrated earlier, occurs nearer shore than glaucony, and can be linked with the detrital member of the sequence. Phosphate development, however, is more of a purely chemical process, requiring less of a continental input. It would appear, therefore, that if geochemical evolution followed the classical sequence, glauconitization would precede phosphatization.

The frequent association of glaucony with goethite is the result of subsequent oxidation. During the Quaternary, there have been major changes in sea level, and this has led to the sporadic exposure of the shallower parts of the continental shelf. A good example may be found off West Africa, where a red hydroxide belt is widespread at about 100–110 m depth, corresponding to the maximum level of regression 18,000 years ago.

The geochemical behavior of iron in the sea: An integrated view

Integrating the information now available on the genesis of verdine and glaucony with what is known about the distribution of other iron-bearing minerals in the marine environment, a global picture of the geochemical behavior of iron in the sea emerges. There are two main sources of iron in the sea: (1) fluvial, transported from the continental landmasses, and (2) juvenile, either as a direct input at mid-ocean ridges, or indirectly, from alteration of deep-sea basalts (Fig. 4-25). Five main zones can be defined following Odin (1975b):

Zone 1 is the area of deposition of detrital iron, which immobilizes much of the fluvial input of iron near the continent. In the presence of organic matter during early diagenesis, however, iron is reduced and becomes soluble. It thus either becomes available for local reprecipitation as pyrite or migrates into sea water to feed other zones.

Zone 2 is essentially confined to warm coastal climates, and is the zone where goethite forms, through biochemical–chemical precipitation or alteration of previously formed material.

Zone 3 is characterized by the verdinization process. Two subzones may be defined: zone 3a is located on the continental shelf in the immediate vicinity of a river mouth, and zone 3b is located on tectonic ridges in the vicinity of emergent islands.

Zone 4 is where glauconitization occurs. Again, two subzones may be defined: zone 4a is located on the outer part of the continental shelf of passive margins, at depths between 60 and 500 m, and zone 4b occurs on tectonic highs, on the borders of active margins, or in the deep ocean basin, at depths up to 2500 m.

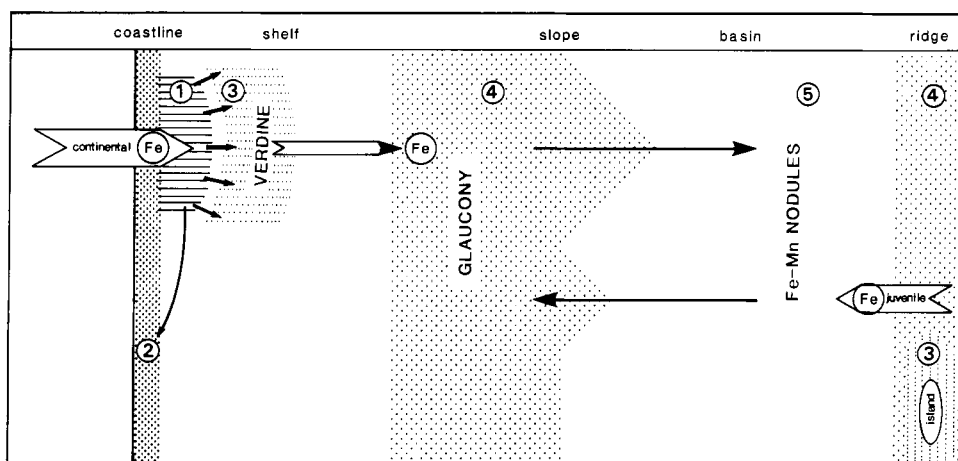


Fig. 4-25. Glaucony and verdine in the geochemical path of iron in the sea. (After Odin, 1975b.)

Zone 5 covers great expanses of the deep sea floor, and is the area where juvenile iron is incorporated into ferromanganese nodules and into iron smectites frequently colored green.

This fundamental arrangement is only a general model, and cannot cover the anomalies brought about by local variations in conditions. Furthermore, it is an instantaneous view: over geological time, the zones may become mixed, and may be found at levels which are not characteristic of their site of formation. The major Quaternary phase of transgression–regression is a specific example of a process which can cause such mixing.

CONCLUSIONS

Particles consisting of authigenic green phyllites, characteristic of marine sediments, show a wide variety of composition. It is of primary importance, therefore, that studies of such particles include the precise identification of the facies and that correct terminology is employed. The use of the term “glauconite” to describe such particles is at best inadequate and is frequently misleading. The usage of the term should be discontinued except in its strictest mineralogical sense.

Three main types of green particles occur:

Verdine has been known for some time, but has been incorrectly described as consisting of chamosite or berthierine, from which it differs both in habit (never occurring as oolitic grains) and in mineral chemistry. The mineralogy of the authigenic phyllite which constitutes verdine grains has not been fully described, and so the mineral has been given the informal term *phyllite V*. Its main XRD characteristic is a broad 7 Å peak, indicating that it either has a 7 Å (serpentine) structure or that it has a 14 Å (chlorite) structure in which the (001) reflections are small due to its high iron content. The mineral is essentially ferric, and is equally dioctahedral and

trioctahedral, neither character being normally associated with serpentine or chlorite. Although verdine does not show a recognizable mineralogical evolution, progressive changes in color, morphology, and paramagnetic behavior occur. It occurs in nearshore facies, restricted to the tropical zone, and seems to form very quickly, in the order of a few thousand years.

Glaucony grains are characterized by a variety of authigenic minerals which have in common a 2 : 1 structure, a high potassium content, and a ferric nature. They form a continuous family termed the *glaucconitic minerals*. The XRD shows a main peak anywhere between 10 and 14 Å, which shifts to 10 Å on heating. Glaucony shows both a morphological and a mineralogical evolution, enabling the identification of several stages of evolution, from nascent to highly evolved. It occurs in open-sea facies and its genesis is favored by tropical conditions, although at the present day it is found between 65°N and 55°S. Formation of glaucony requires longer periods of non-deposition than does verdine: nascent glaucony takes about 10^4 years to form, whereas highly evolved glaucony requires some 10^5 – 10^6 years.

Chlorite is characterized by two sharp peaks at 14 and 7 Å on XRD traces, and a subsidiary peak at 10 Å is sometimes observed, representing the original substrate. Genesis of this type of chlorite in the marine environment has not yet been demonstrated, and green particles of this type are detrital, representing alteration of mica in a continental setting. Such grains are commonly altered to verdine and glaucony in the marine environment.

Glaucony and verdine are the result of *verdissement* of previously deposited substrates, which are in most cases granular in form. The process involves crystal growth and recrystallization in the semi-confined environment within the substrate, and only occurs at the sediment–water interface. Verdissement takes place, therefore, during halmyrolysis, the very earliest stage of diagenesis. The genesis of glaucony cannot be explained in terms of the previously proposed layer lattice theory, but takes place through crystal growth processes.

Although glaucony is widespread in ancient sediments, only one pre-Quaternary occurrence of verdine has yet been described. Is this simply the result of inadequate research into the mineralogy of ancient green particles, or does verdine undergo evolution to another phase, such as berthierine or chlorite, in later diagenesis? One of the directions that research into marine green particles must follow in the future is to determine the reasons for this anomaly.

NOTE ADDED IN PROOF

Phyllite V has now been found to consist of a pure 7 Å clay mineral (in young deposits) or of a mixture of this mineral with a 14 Å clay mineral (a chlorite), a rare interlayered 7 and 14 Å structure, and probably a 10 Å phase. The 7 Å phase has been shown to be a previously non-identified mineral, named “odinite” by Bailey (in press), which is a new dioctahedral–trioctahedral Fe^{3+} -rich, 1 : 1 clay mineral. A typical formula for this mineral is $(\text{Fe}_{0.96}^{3+} \text{Mg}_{0.96} \text{Fe}_{0.40}^{2+} \text{Al}_{0.20}) (\text{Si}_{1.8} \text{Al}_{0.2}) \text{O}_5 (\text{OH})_4$, with Fe^{3+} between 0.75 and 1.0, Fe^{2+} between 0.25 and 0.40, Mg between 0.75 and 1.0, Al^{VI} between 0.2 and 0.6, and Al^{IV} between 0.05 and 0.20.

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