TEXTBOOK

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Introduction to Applied Mineralogy

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Introduction

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Mineralogy deals with the predominantly crystalline building blocks of the geological matter surrounding us, the minerals. Since this geological matter served as a natural environment for humans from the beginning of their existence as a habitat and source of raw materials, the study of minerals as raw materials, building materials, materials and jewelry has always been a vital necessity. Mineralogy from this point of view is one of the oldest sciences. The increasing production and use of technical materials led to the fact that the concept of minerals today has also been extended to synthetic products.

Modern mineralogy is defined as the material-related geoscience. It investigates the chemical, physical and biogenetic properties of matter and their role in the processes of the Earth system. In addition, its methods and concepts are equally aimed at the study of natural and synthetic substances and their application.

Modern economics and research led to the development of a sub-discipline within mineralogy, applied or technical mineralogy. This sub-discipline is primarily concerned with practical aspects, e.g. with problems of mineral raw materials or the study of minerals that play a decisive role in technical processes, such as in ashes, slags, ceramic materials or high-performance materials. Thus, applied mineralogy mainly comprises the application of typical mineralogical methods to technical processes and products for analytical process control and quality assurance, product development, manufacturing and application technology, as well as waste management and disposal.

Applied mineralogy is located at the intersection of natural sciences and engineering sciences/technology and deals with the entire line from raw material – extraction/preparation – processing – material – disposal. Inevitably, this results in points of contact with a number of neighbouring disciplines such as geology, physics, chemistry, biology, medicine or the materials and engineering sciences, and close cooperation with colleagues from other disciplines is imperative (Fig. 1.1).

In professional practice, geoscientific knowledge is increasingly taking a back seat to materials science knowledge for mineralogists today, and an industrial

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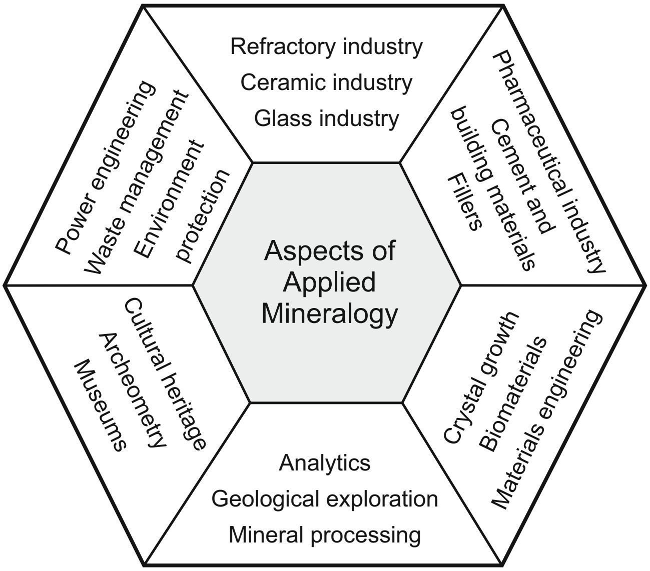

Fig. 1.1 Aspects of modern mineralogy/applied mineralogy

occupation is the normal career path for a mineralogist. The main areas of employment are the extraction and processing of raw materials, the ceramics industry, the glass industry, the building materials industry, the metallurgical industry, the chemical industry, electrical engineering/electronics, energy technology and environmental and waste management.

In the present textbook, important aspects of applied mineralogy are compiled and individual subfields are discussed in separate chapters. Due to the limited scope, the basics of mineralogy, crystal chemistry, crystallography and phase theory, solid state physics and chemistry are assumed and only referred to. This textbook is primarily aimed at Bachelor's and Master's students of geosciences, but is also suitable for related disciplines.

Introduction to Materials and Substance Systems

2

In applied mineralogy, the relationships between chemical composition, crystal structure and physical properties play an essential role. For practical reasons, an ambivalence is found when considering the individual aspects: If materials are considered from the point of view of crystallography and symmetry, crystal chemistry recedes into the background. The lattice, the unit cell and thus the symmetry elements and operations are the focus of the considerations.

If aspects of crystal chemistry are relevant, one considers coordination polyhedra and chemical variability. Here the strictly defined symmetry recedes into the background, the described polyhedra such as tetrahedra or octahedra are not necessarily to be seen in the strict geometrical sense, distortions from ideality are accepted.

Clear formulations help to avoid misunderstandings. This is essential, especially when different disciplines are in dialogue. However, it is difficult to use too many specialist terms, as the colleague with a different specialist background often does not know them. In petrology, for example, terms such as “granoblastic microstructure with grain interlocking” are commonly used when describing microstructures. In materials science, however, a description as “coarsely crystalline dense microstructure” would be more readily understood. The same applies vice versa: terms such as “dry or wet sintering” are common in the ceramic field. The geoscientist, however, would rather speak of “sintering without or with the presence of a melt”. The principle of “know your partner and use his language” is both helpful and wise.

Finally, it must be distinguished whether single crystals or ceramics are considered. The aspects of synthesis are dealt with in detail in Chap. 10 “Crystal Growth”.

2.1 Single Crystals

In the case of single crystals, the defined chemical composition and structural perfection are the key characteristics for the material.

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The question of whether chemical deviation from ideality and structural perfection are desired or should be avoided is clearly decided by the application aspect. However, it is crucial to find reproducible conditions for the synthesis of the chosen product with suitable properties.

2.1.1 Chemical Deviation From Stoichiometry

In principle, any material allows the incorporation of contaminating components. The decisive question is only the quantity. There are different understandings of the terminology for chemical variability in the various disciplines of natural and material sciences. The following classifications have proven useful:

- Doping: incorporation of foreign ions up to several percent
- Phase width: incorporation of foreign ions up to 10%
- Solid solution: incorporation of foreign ions up to several tens of percent
- Complete solid solution series: no limit to miscibility

Although this classification is not common in all disciplines, it gives a clearer idea of the chemical variations present. When describing a defined composition, it is still useful to speak of the "member of the phase width or solid solution series". Stoichiometry gives integer ratios of components in chemical reaction equations as the result of the formation reaction. On this basis, the stoichiometric composition of a compound is then considered to be the ideal integer formula. Deviations from the integer describe the chemical variation, the "non-stoichiometry". In this respect it is not meaningful to speak of stoichiometric mixtures, even if they satisfy integer ratios of the components. The statement "mixture of the stoichiometric composition of phase XY" is clearer and more exact.

The incorporation of ions that deviate from the stoichiometry or that add a new component to the compound can in principle be done in two ways:

- diadoch replacement on lattice site or
- incorporation on interstitial sites.

In any case, electrochemical neutrality must be ensured and, if necessary, a charge balance must take place. Ideally, ions with the same charge and comparable ion radius (in relation to the coordination number) replace each other on the same lattice site. Frequently, a necessary charge balance is realized by vacancies, often also by means of vacancies in the anion lattice. However, it should be noted that the anion lattice represents the "framework" of the crystal structure, so to speak, and defects there are to be regarded as the exception rather than the rule. A difference of about +/−10% of the ion sizes of substituted and substituting ions shows the variation possibilities. The incorporation of foreign ions on interstitial sites usually requires a crystal structure that allows this spatially and thermodynamically. Some of these

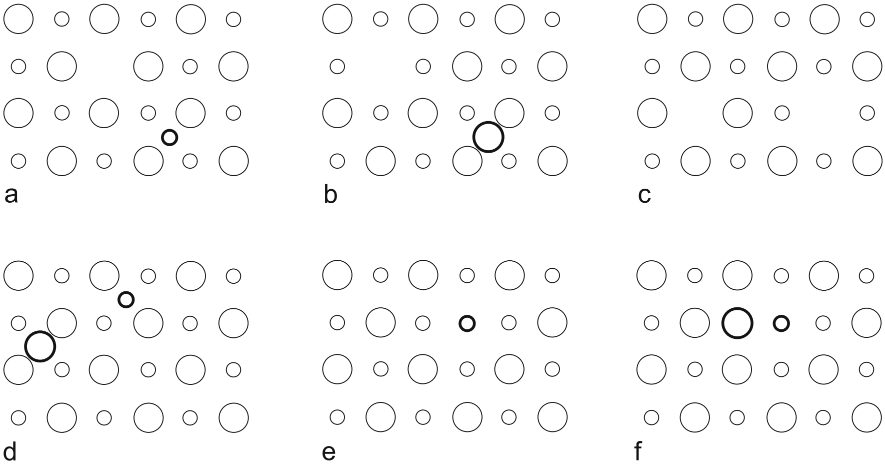


Fig. 2.1 Schematic representation of point defects in binary ionic crystals. (**a**) Frenkel defect: vacancies in the cation lattice and cations on interstitial sites; (**b**) Anti-Frenkel defect: vacancies in the anion lattice and anions on interstitial sites; (**c**) Schottky defect: vacancies in the cation and anion lattice; (**d**) Anti-Schottky defect: cations and anions on interstitial sites; (**e**) Anti-layer defect: cations replace anions or vice versa, these defects change the stoichiometry; (**f**) Anti-structure defect: place exchange between cations and anions. (Modified after Kleber et al. 1998)

possibilities are described by the point defects in binary ion crystals, keywords are e.g. Frenkel and Schottky defects (Fig. 2.1).

However, there are phase widths that cannot be described unambiguously with the usual models of substitution, such as in the case of magnetite in equilibrium with calcium ferrites in systems of interest in the iron and steel industry. Here, magnetite incorporates several mass percent of Ca^{2+} under suitable redox conditions and temperatures at normal pressure. However, the incorporation of such a large cation into the spinel structure represents a phenomenon that is difficult to explain. There are probably massive distortions in the crystal structure that make this possible.

Chemical variation certainly has a significant effect on distortions in the crystal structure. Sometimes this changes with variation in chemical composition.

2.1.2 Structural Defects

If one considers the aspect of structural defects, the crystal chemistry recedes into the background. A crystal can be described as a lattice composed of unit cells. A wide variety of defects can occur in the form of dislocations.

If one takes the crystal growth model of Kossel and Stranski as an approximate basis for understanding the growth, one finds different attachment possibilities for the individual building blocks on the so-called Kossel crystal (Fig. 2.2).

The energy gain of the system during the transition to the stable state of a crystalline solid with suitable parameters is decisive for the accumulation. Position

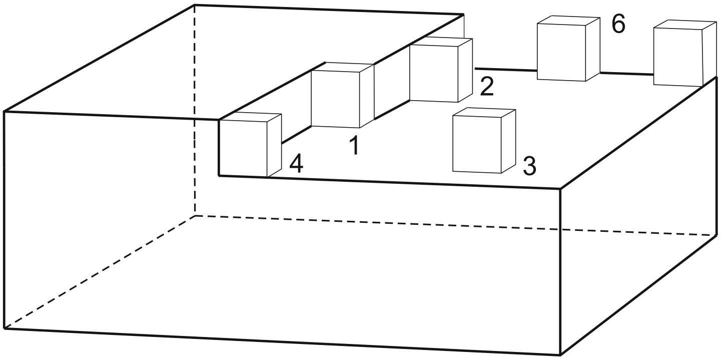


Fig. 2.2 Attachment possibilities of lattice blocks to a cube surface; the relative energy gain is qualitatively expressed as decreasing from position 1 to 6. (Modified after Kleber et al. 1998)

1 in Fig. 2.2 represents the highest energy gain and position 6 the lowest. This model implies a cyclic growth in which the formation of a surface nucleus (position 3) is kinetically inhibited, but the total surface grows out increasingly faster once this exists.

According to this model of the building blocks that make up a crystal, a distinction is made between different crystal faces (facets) of the crystals (Fig. 2.3):

- F-surfaces: *flat faces*
- S-faces: *stepped faces* with uniform step height *(stepped faces)*
- K-faces: unevenly stepped *faces (kinked faces)*

The notion of a three-dimensional lattice can be used to describe various lattice construction errors.

In the case of a step dislocation, an additional mesh plane is inserted in the grid and distorts or widens the grid there along the dislocation line (Fig. 2.4).

In the case of a screw dislocation, the lattice distortion winds three-dimensionally around a central axis in the respective direction of this dislocation (Fig. 2.5). The lattice distortion is found here along the screw axis.

According to the crystal growth model of the lattice building blocks, the problem of the formation of a surface nucleus would thus be circumvented. However, theories that generally attribute crystal growth to screw dislocations could not be confirmed in real crystals.

Another structural defect are small angle grain boundaries. In these cases, two lattices of the identical material are transferred into each other by inserting additional lattice planes tilted against each other (Fig. 2.6).

Lattice distortions form in all structural defects. These influence the physical properties. In the case of phase transformations, such local lattice distortions can initiate or hinder the transformation, depending on the material. Furthermore, in the region of these lattice distortions, foreign ions can be preferentially incorporated locally, which, due to this local agglomeration, cause chemical heterogeneities and significantly influence the overall property of the crystal.

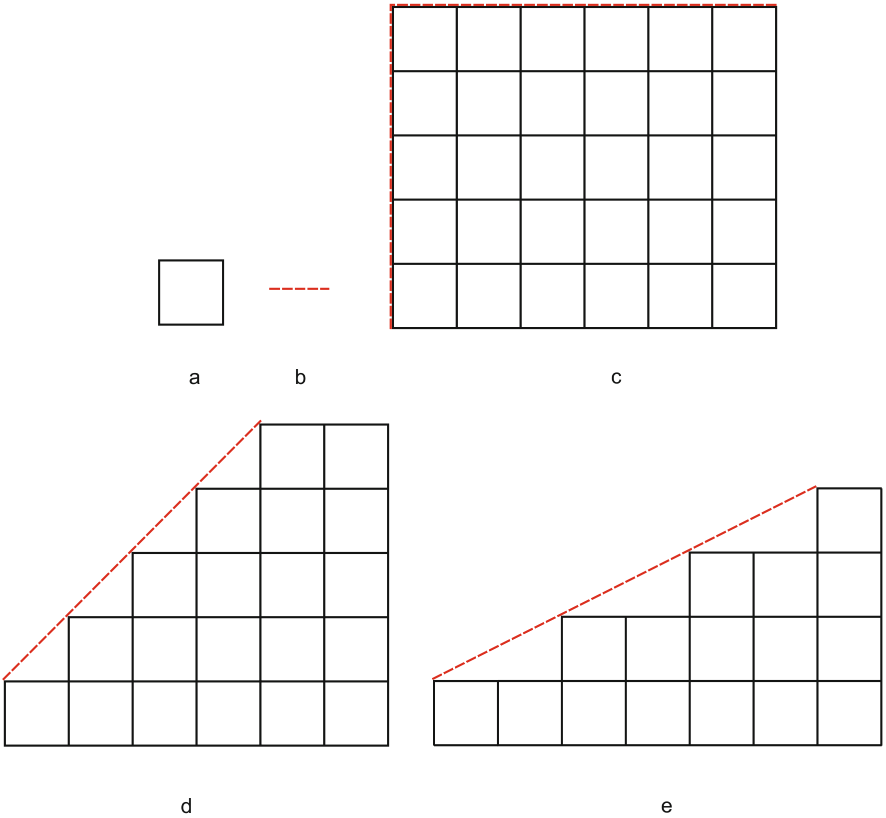


Fig. 2.3 Representation of different types of crystal faces. (**a**) Lattice element; (**b**) Crystal face; (**c**) F face; (**d**) S face; (**e**) K face

The physical properties of materials are closely related to symmetry. Thus, isotropic properties are found only in cubic materials, such as the indicatrix as a three-dimensional representation of the refractive index. In terms of crystal growth, isotropy does not exist because spherical crystals do not exist. If materials show, for example, a kidney-shaped, rounded formation, this is due to small, radially intergrown needles whose surface gives the kidney-shaped, rounded impression. These are parallel intergrowths with small angle displacements, not single crystalline individuals. Glass is an amorphous solid, which can be regarded as a solidified melt. However, glass is also optically isotropic, although there is no symmetry. Isotropy, however, basically means nothing more than the equality of the property in all spatial directions. This also applies to glass – the same statistical disorder in all directions.

If one performs a spherical growth experiment, the absence of isotropic growth becomes clear (Fig. 2.7).

If a single crystal, e.g. silver, is ground into a sphere and this is allowed to grow electrolytically as a seed crystal under suitable conditions, many different growth

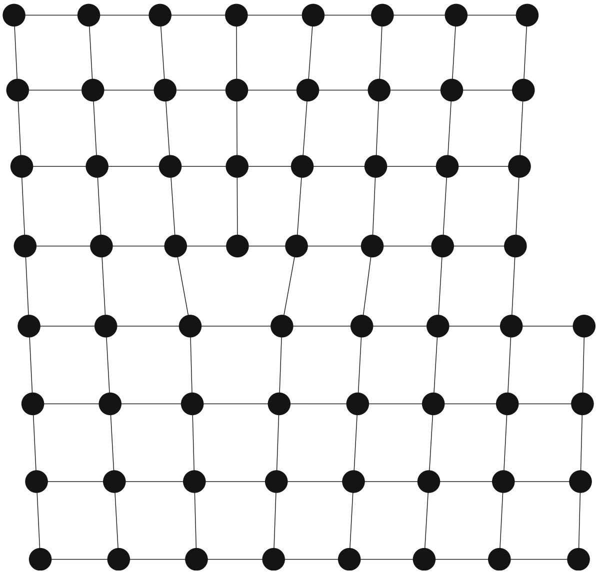


Fig. 2.4 Step dislocation in a cubic primitive lattice. (Modified after Kleber et al. 1998)

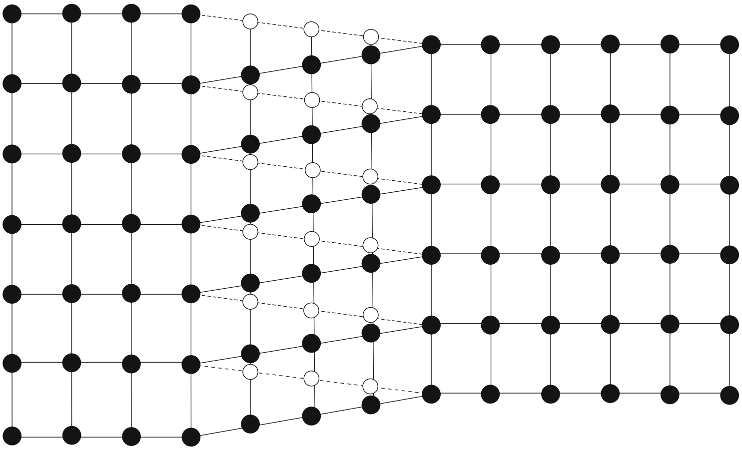


Fig. 2.5 Screw dislocation in a cubic primitive lattice. (Modified after Kleber et al. 1998)

facets will form. This applies analogously to growth from aqueous solution and melts. According to the material and thus the thermodynamics of this compound, certain facets will increase dominantly over time, while others will disappear. At the stage of the beginning of the sphere growth experiment, all growth directions are equal. The direction of the facet that forms dominantly will grow more slowly compared to other directions that become edges or corners. The corner direction, on the other hand, grows fastest due to its greater distance from the original state. This is specific to the material. For example, rock salt crystals from aqueous solution

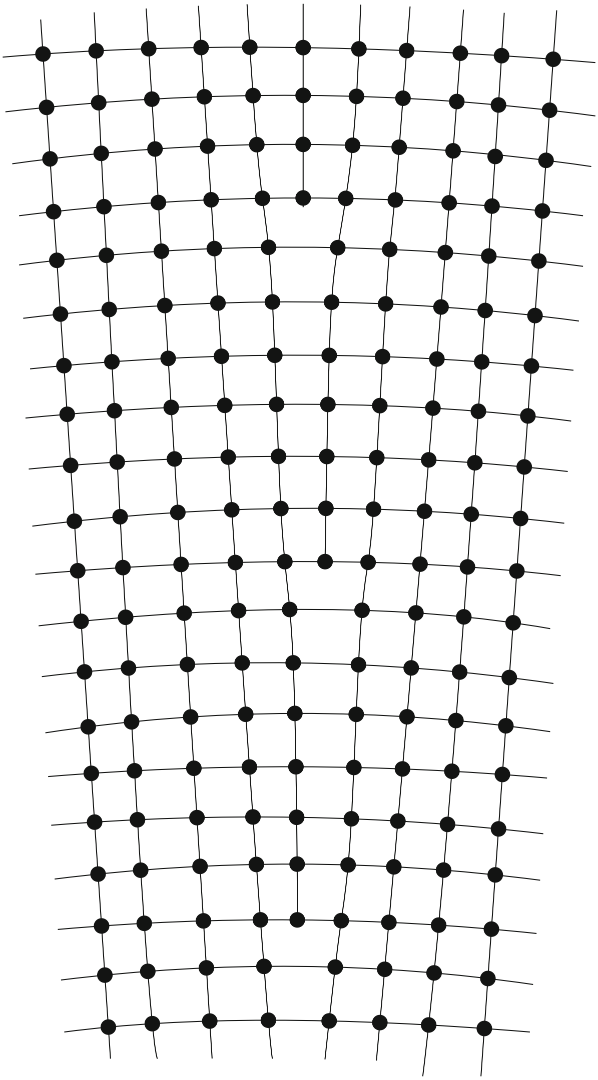


Fig. 2.6 Schematic representation of small angle grain boundaries. (Modified after Kleber et al. 1998)

form cubes, while alum crystals form octahedra. The same applies to growth in melts, which are actually also solutions. If, however, substances are present in the solution which, due to their attachment to the growing crystals, impede the growth rate in certain directions without being incorporated themselves, the crystal morphology is changed by them. Urea in the solution, for example, changes the crystal form of alum from an octahedron to a cube.

Changes in boundary conditions, such as pressure or temperature, can also affect crystal morphology. In diamonds, both natural and synthetic, the temperature (and pressure) during formation influences the morphology. At about 1300 °C (and

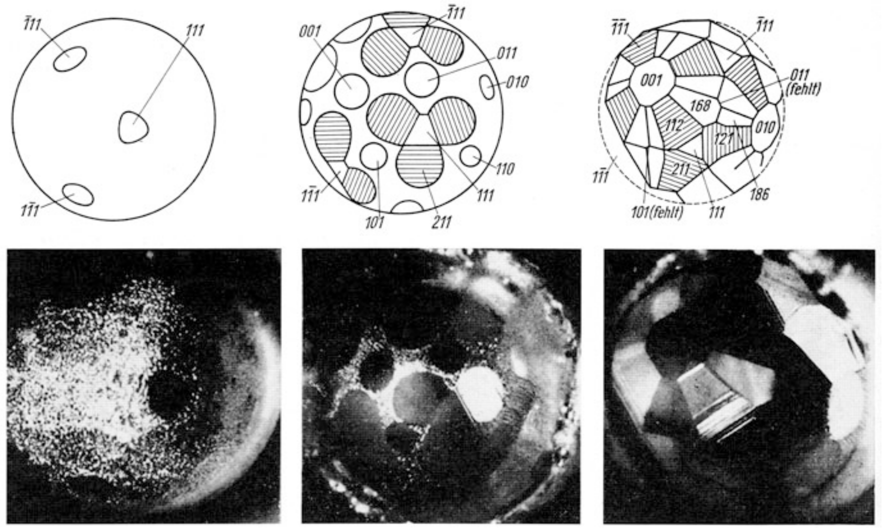


Fig. 2.7 Electrolytic growth of a spherical crystal of silver from a nitric acid silver nitrate solution in three successive stages of growth. (Modified after Kleber et al. 1998)

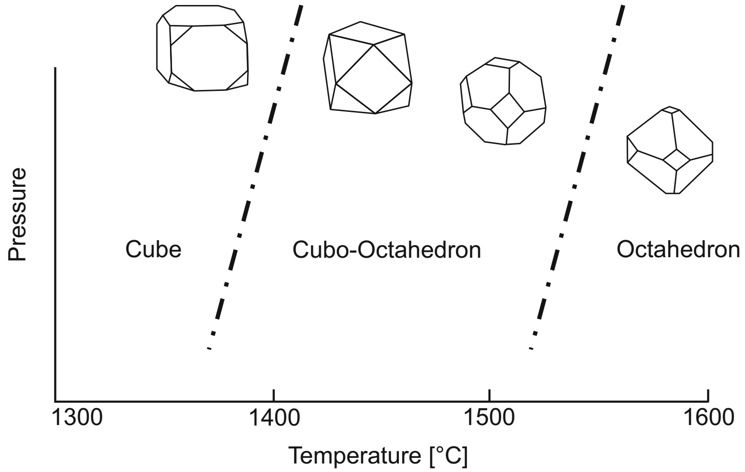


Fig. 2.8 Dependence of diamond morphology on pressure and temperature during formation

increased pressure) cubes are more likely to be found, and at about 1600 °C octahedra (Fig. 2.8).

2.2 Ceramics

Ceramic materials, along with polymers and metals, represent the third major group in the system of materials as inorganic and non-metallic materials.

The so-called component notation is often used to simplify chemical formulas. The following abbreviations are common:

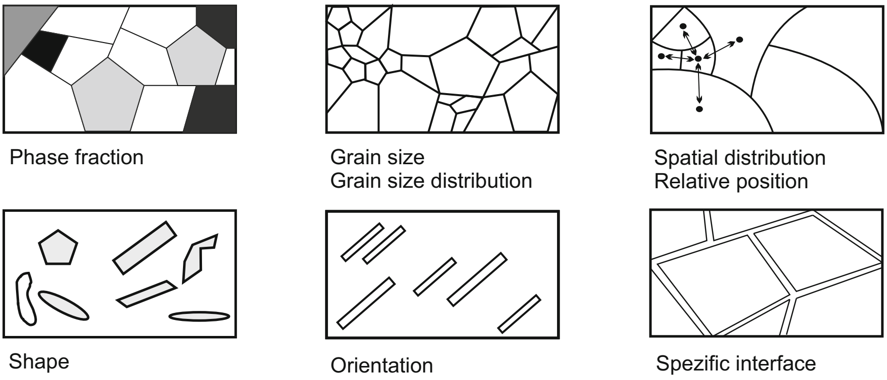
A – Al_2O_3
C – CaO
F – Fe_2O_3
f – FeO
K – K_2O
M – MgO
N – Na_2O
S – SiO_2
$\bar{S}$ – SO_3
etc.

Such would be: anorthite $CaAl_2Si_2O_8$: CAS_2, gehlenite $Ca_2Al_2SiO_7$: C_2AS, etc.

A ceramic is determined by the chemistry and the properties of the grains that build it up. In addition, the microstructure and the existing pore space must also be included in the considerations. The microstructure describes the repeating characteristics of a solid (Fig. 2.9).

Ceramics can be regarded as rocks of technical origin. Consequently, formation conditions, thermal and chemical overprinting and corrosion can also be identified and described from the microstructure.

Ceramics are either single-phase or multi-phase plus a possible pore space. The individual grains are not necessarily monocrystalline and in the case of multiphase ceramics not necessarily single-phase. A grinding process of ceramics leads to single-phase monocrystalline grains only in exceptional cases.


Phase fraction

Grain size
Grain size distribution

Spatial distribution
Relative position

Shape

Orientation

Spezific interface

Fig. 2.9 Parameters for quantitative microstructure description

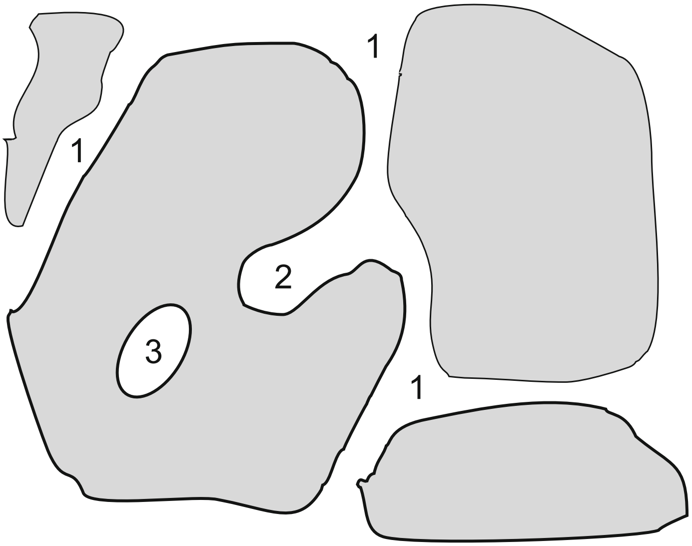


Fig. 2.10 Schematic representation of porosity: *1* open, flow-through pores; *2* open, non-flow-through pores (so-called blind pores); *3* closed pores

The aspects of single crystals described above also apply here in relation to the small crystallites. In addition, one must also take into account the formation of the grain structure by "intergrowth" of the grains with each other. At the grain boundaries there are sometimes large lattice distortions due to clearly different orientations of the often differently phased microstructural constituents. Therefore, impurities are frequently found at the grain boundaries. If the microstructure forms in the presence of a melt, the grain boundaries and spandrels are the last areas to crystallize. In the case of melting, the first melt is also formed in the spandrels and then at the grain boundaries. The glassy (non-crystalline) fraction in ceramics can vary over wide ranges, from $<1\%$ in some oxide ceramics to $>60\%$ in porcelain, for example.

In principle, microstructures can be classified on the basis of the different phases. As soon as one speaks of a microstructure, polycrystallinity is present. Furthermore, it must be decided whether a microstructure is single-phase or multi-phase. In this case, porosity is not to be referred to as a phase, but it must be described. Likewise, it must be noted whether segregation occurs in individual phases in the individual crystallites. Finally, it must be noted whether homogeneous or inhomogeneous texturing is present.

Porosity can be divided into open and closed porosity (Fig. 2.10). In addition, one also speaks of pores that can be flowed through and pores that cannot be flowed through. Porosity is a fundamental property of ceramics, as it directly and indirectly influences a number of physical properties.

2.3 Material Systems

In petrology, we move in the description of rocks and mineral formations or dissolution phenomena in complex polynary systems in pressure and temperature space. If we consider only granite with the simple main minerals feldspar, quartz and mica, we find at least six oxide components without the accessory and chemical features:

Mineral	Chemical formula	Oxide components
Quartz	SiO_2	SiO_2
Feldspar	$(K,Na)[AlSi_3O_8]$ and $Ca[Al_2Si_2O_8]$, respectively.	K_2O, Na_2O, CaO, Al_2O_3, SiO_2
Mica e.g.	$KAl_2[(OH)_2/(AlSi_3O_{10})]$	K_2O, Al_2O_3, H_2O, SiO_2

Therefore, mineral formations or decompositions in petrogenetic networks are considered as defined compositions in pressure and temperature space.

In the field of applied mineralogy, the pressure aspect plays a subordinate role. Here polynary systems are temperature-dependent and with consideration of redox reactions of importance. To simplify complex phase relationships, components are often combined or neglected altogether.

The knowledge and practical application of phase theory to relevant systems is a unique selling point of the mineralogist.

The following basic knowledge and its determination from the phase diagram are assumed in the following:

- Congruent melting point: At the transition from the crystalline to the molten state, the solid changes into a melt of identical composition. In the ternary system, the composition of the phase lies in its primary precipitation field.
- Incongruent melting point: During the transition from the crystalline to the molten state, the solid passes into a melt and a solid phase, both of which have a different composition to each other and to the original phase. In the ternary system, the composition of the phase is not in its primary precipitation field.
- Solidus (-line): The first melt forms at the solidus during the transition to higher temperatures. Conversely, the last residual melt solidifies during the transition to lower temperatures. The temperature range below the solidus is called the sub-solidus range.
- In the sub-solidus there exist 3-phase fields separated by 2-phase lines. If one (or both) of the coexisting phases shows a phase width, these 2-phase lines can be formed as 2-phase fans.
- Liquidus (-line): During the transition to higher temperatures, the last solid phase melts at the liquidus line. Conversely, the first crystal forms during the transition to lower temperatures. The temperature range above the liquidus line is called the hyper-liquidus range. Between the solidus line and the liquidus line lies the liquidus region.

- Eutectic: In the eutectic, the solid phases of the sub-solidus relations and the melt of eutectic composition are in equilibrium. Mathematically, the eutectic represents the absolute minimum of the liquidus lines.
- In ternary systems, the temperatures of all three field boundaries fall into the eutectic.
- Peritectic: The peritectic is an invariance point such as the eutectic. Here the incongruent melting solid phase is present alongside the phases in equilibrium into which it decays. Mathematically, the peritectic represents a relative minimum of the liquidus lines.
- In ternary systems, the temperature of one or two field boundaries falls into the peritectic and of two or one field boundaries falls out of the peritectic further into an eutectic.
- Tie line: Line in the phase diagram of a mixture connecting state points in phase equilibrium. Each tie line in the subsolidus region must have a corresponding field boundary in the liquidus region.
- The temperature on the field boundary falls in the direction away from its associated tie line. If the tie line and the field boundary intersect, this intersection represents a saddle point from which the temperatures fall.

Although single-component systems (e.g. SiO_2) and two-component systems (binary systems, e.g. Al_2O_3-SiO_2) can be significant in technical systems, phase relationships are predominantly represented in three-component systems (ternary systems). In applied mineralogy, ternary systems provide important information on melt formations, crystallization paths, etc (Bergeron and Risbud 1984). The designation of a ternary phase diagram begins with the lower left component and moves counterclockwise.

2.3.1 Example System CaO-Al_2O_3-SiO_2

In the following, the ternary system **CaO-Al_2O_3-SiO_2** will be fundamentally considered as the most important system for the ceramic field and for understanding the use of refractory materials and of cements or related construction chemical products (Fig. 2.11).

In the ternary system, both the sub-solidus phase relations and the liquidus relations are represented. Therefore, the system is somewhat confusing. It has long been accepted practice to colour-code and edit the contents and statements of phase diagrams, although in the twenty-first century this may be considered outdated by non-practitioners. In Fig. 2.12 the areas for industrially significant materials in the phase diagram are colour-coded.

This system is also relevant for the consideration of melting events and phase formation in porcelain and ceramics. An important raw material here is clay, e.g. kaolinite $Al_2[(OH)_4/Si_2O_5]$. As it is subjected to a thermal process usually above 800 °C in industrial processing, the H_2O component evaporates. It is converted to the ternary system CaO-Al_2O_3-SiO_2.

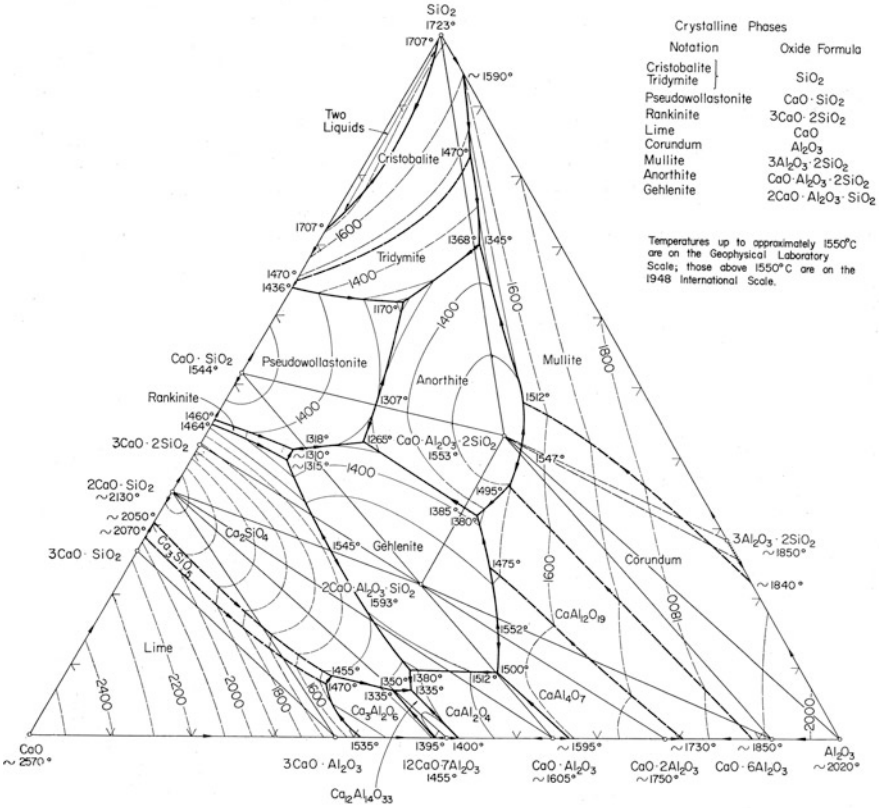


Fig. 2.11 The CaO-Al_2O_3-SiO_2 ternary system. (Figure from American Ceramic Society, Phase Diagrams for Ceramists, Vol. I, Fig. 630, reprinted with permission from the American Ceramic Society (1964))

The course of a consideration of a ternary system is as follows:

- Step one:
  - Which atmospheric or redox conditions are the basis? Either this is noted in the description or, if not stated, air is assumed.
  - Are the figures in mole% or mass%? Industry almost always thinks in terms of mass percentages, research tends to think in terms of mole percentages. If this is not specified, a simple test applies: take a suitable compound and check whether its quantity proportions of the components correspond to a mass or mole fraction.
- Step two:
  - Marking of the occurring phases with melting points and melting behaviour and the tie line relations (Fig. 2.13).

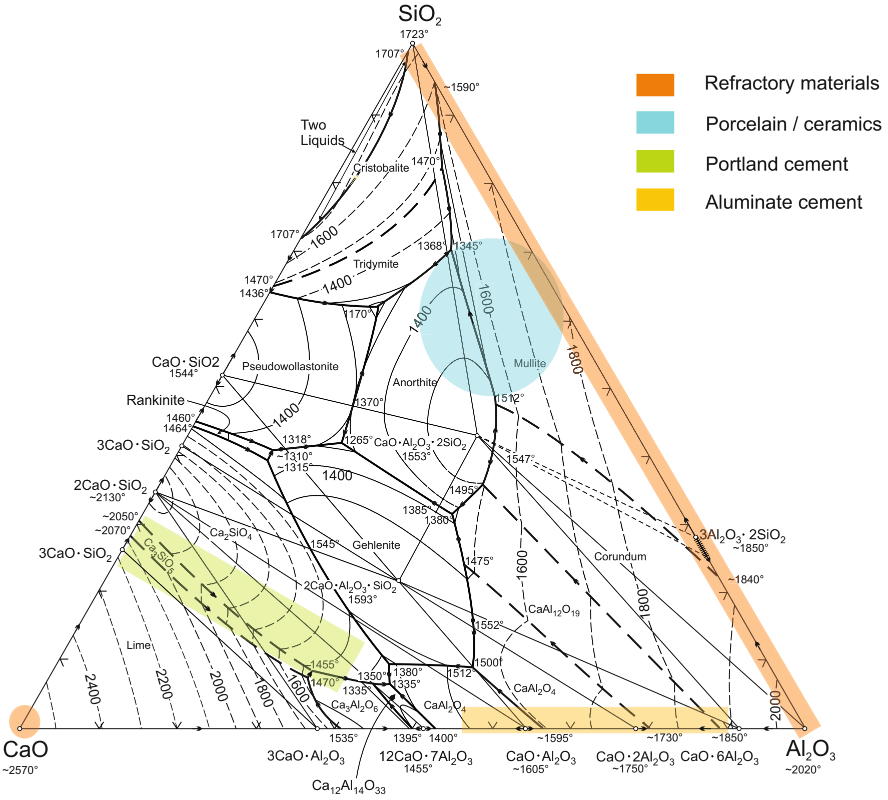


Fig. 2.12 The CaO-Al_2O_3-SiO_2 ternary system with the location of technically important products. (Modified from American Ceramic Society, Phase Diagrams for Ceramists, Vol. I, Fig. 630, reprinted with permission of the American Ceramic Society)

- Step three:
  - Determination of the solidus temperatures of the 3-phase fields (Fig. 2.14). For this purpose, the temperature is read at the invariant point, which is the common corner of the primary precipitation fields of the phases coexisting in the 3-phase field under consideration. This invariant point does not necessarily have to lie in the 3-phase field of the sub-solidus.

With this plot it becomes very clear how the temperature for the occurrence of the first melt drops dramatically into the ternary system starting from the pure components or the binary phase relations.

The representation in the ternary system is also very helpful for the prediction of crystallization processes. Based on the initial composition of the melt, the crystallization sequence and the coexistence of phases can be determined via the stability ranges of the individual phases.

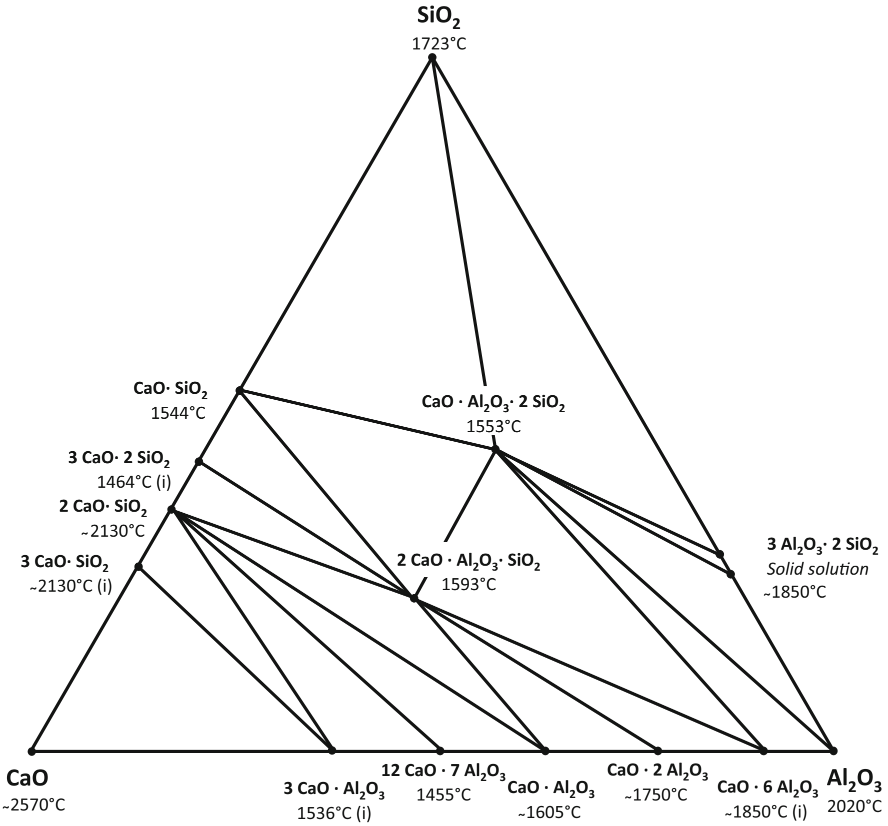


Fig. 2.13 The ternary system CaO-Al_2O_3-SiO_2 reduced to the occurring phases with melting points, melting behavior and tie line relations in the sub-solidus. *i* incongruent melting point

Notes

Often the processes upon temperature increase are interesting, e.g. when clarifying the question at which temperature which melt of which composition occurs. To do this, first determine the point of the composition to be considered from the components. Finally, one determines the crystallization process with decreasing temperature. This is now reversed and the course of crystallization is observed with increasing temperature. The attempt to directly derive the melting behaviour with increasing temperature often fails, as this method opens up too many possibilities.

Phase diagrams are important tools for learning to understand industrial processes. However, some things have to be considered when transferring them to practice:

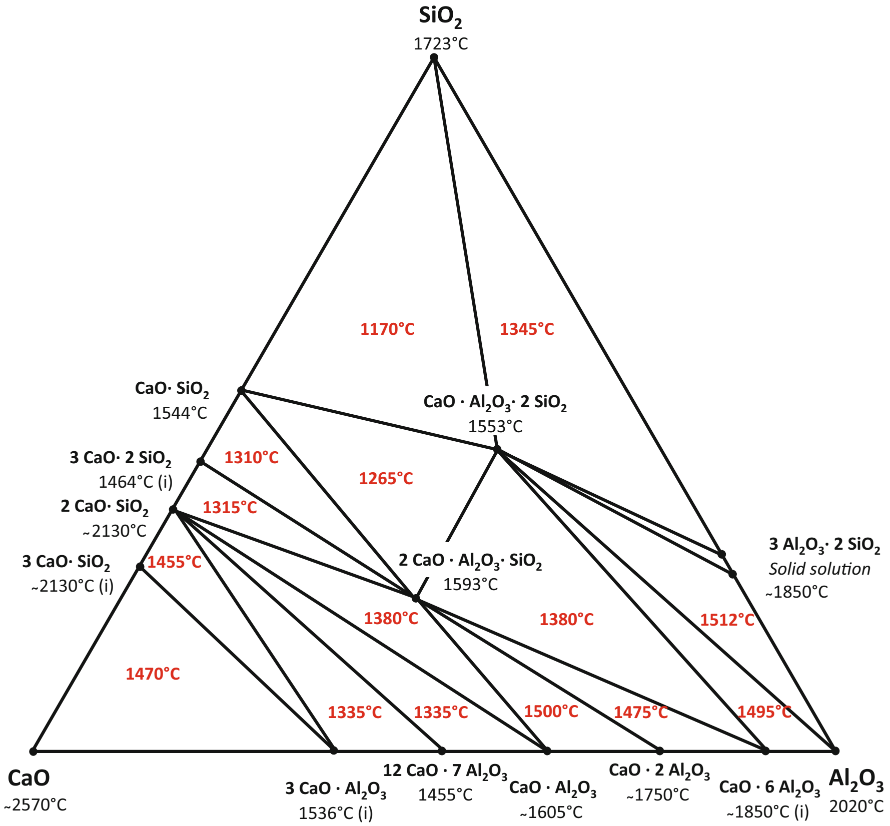


Fig. 2.14 The ternary system $CaO\text{-}Al_2O_3\text{-}SiO_2$ reduced to the occurring phases with melting points, melting behaviour, conode relations in the sub-solidus and registration of the solidus temperatures of the 3-phase fields. *i*: incongruent melting point

- All phase diagrams are subject to errors, no matter how carefully they are studied: +/−20 °C and +/−3% still represent excellent quality.
- Raw materials used in industry – especially in the construction chemicals and stone and earth industries – are not products of the highest chemical purity. Impurities of +/−3% or higher contents of Fe, K, Na, etc. are common and are reflected in temperature reductions of up to 50 °C. A transfer of phase diagrams to practice can therefore only give good indications.
- Further, in practice, the components are so diverse that one often has to make a chemically meaningful reduction by combining components, e.g. Na_2O and K_2O or Al_2O_3 and Fe_2O_3, etc.

2.4 Material Properties

At the beginning of the chapter it was already pointed out that for single crystals and ceramic materials there is a fundamental relationship between chemical composition, crystal structure and physical properties. In polycrystalline ceramic materials, the microstructure plays a dominant role, since a cumulative effect of the properties of the individual components occurs here. Without going into detail, some important properties of inorganic non-metallic materials will be discussed below.

2.4.1 Mechanical Properties

Various strength parameters are decisive for the industrial use of ceramic materials. Depending on the stress requirements, these are primarily *compressive, flexural and tensile strength* (Fig. 2.15). In general, ceramic materials exhibit a high compressive strength, but show a lower flexural strength (brittle behaviour) and, depending on porosity and cracks, usually a very low tensile strength.

The compressive strength can reach similar and even higher values compared to natural rocks (Table 2.1).

Figure 2.16 shows some of the factors that influence the strength properties of ceramic materials. The diagram illustrates the complexity of the influencing factors.

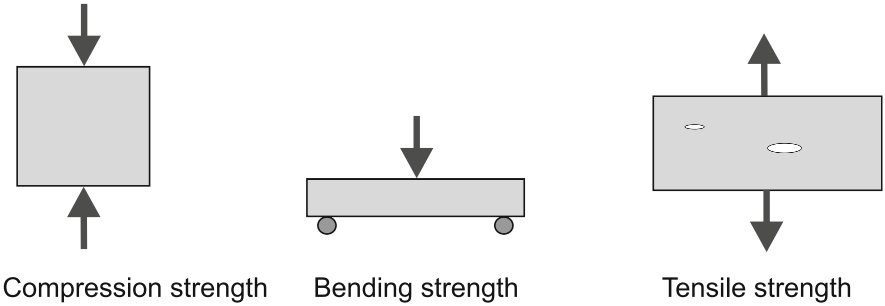
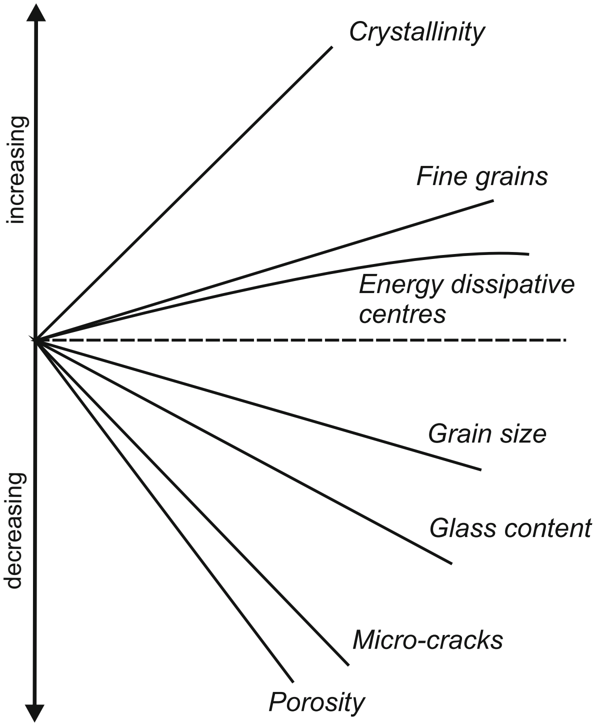


Fig. 2.15 Schematic representation of various strength parameters

Table 2.1 Compressive strength of different materials

Material	Compressive strength in MPa
Coarse ceramics (bricks)	10–25
Refractory ceramics	30–100
Fine ceramics (porcelain)	400–600
Oxide ceramics	1000–3000
Granite	210–250
Basalt	160–190
Granulite	180–350
Marble	110–150
Sandstone (12% porosity)	10–40

Fig. 2.16 Influence of various factors on the strength of ceramic materials



2.4.2 Thermal Properties

Important thermal material properties are, for example, the thermal load capacity, the thermal conductivity, the coefficient of thermal expansion (CTE) or the thermal shock resistance (TSR). They represent important quality parameters, especially for the practical use of materials at elevated and/or changing temperatures.

The melting temperature of the components is, of course, an important reference point for the thermal load capacity. In two- and multi-component systems, however, more complex conditions are sometimes encountered due to the occurrence of eutectics. In particular, the reduction of the melting temperatures due to the effect of fluxes (e.g. alkalis) must be taken into account.

The thermal conductivity of materials is extremely determined by the prevailing microstructure, especially the porosity. A low thermal conductivity and thus good thermal insulation can be achieved by increasing the porosity. In building materials, this is implemented in aerated concrete, for example.

The coefficient of thermal expansion (CTE) of polycrystalline multiphase materials is influenced by a number of factors and thus shows very complex dependencies. On the one hand, there is a superposition of the CTE of the different phases, on the other hand, the microstructure again plays an important role, since, for

Table 2.2 Directional coefficients of thermal expansion of various materials (10^{-6} m K^{-1})

Material	$\alpha \perp$ c axis	$\alpha \parallel$ c-axis
SiO_2 (quartz)	140	90
$Zr[SiO_4]$ (zircon)	37	62
$Na[AlSi_3O_8]$ (albite)	40	130
3 Al_2O_3–2 SiO_2 (mullite)	45	57
Al_2O_3 (corundum)	48	56
BN (hex.)	7	75
$CaCO_3$ (Calcite)	−60	250

example, the orientation of the individual phases or the porosity have an influence on the CTE (Table 2.2).

The conditions for thermal shock resistance (TSR) are similarly complex. Here, material-specific (e.g. different thermal conductivity and CTE of the phases) and structure-specific factors (e.g. ratio of crystalline to vitreous phase, microcracks, grain structure, porosity) overlap, so that a calculation is not possible. For this reason, standardized test procedures are used to estimate the CTE.

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Inorganic Non-metallic Raw Materials

3

Mineral raw materials are components of the earth formed by geological processes, sufficiently explored and usable due to their utility properties. They are the blood of the economy and represent the link between geosciences and engineering/technology. Modern industry cannot exist without a solid base of raw materials (Lefond 1983; Kužvart 1984). In general, mineral raw materials can be divided into three main groups based on their properties and fields of application: Energy raw materials (e.g. coal, oil/natural gas), elemental raw materials (e.g. ores) and property raw materials (e.g. natural stones, industrial minerals) (Fig. 3.1).

Inorganic non-metallic property raw materials, also often referred to as stones, earths and industrial minerals, play a special role here. Developments in recent decades show that the demand for non-metallic raw materials is higher and growing faster than the demand for metallic raw materials (Fig. 3.2).

If one follows the trends in the international feedstock industry, a development with a similar trend as the population development is visible. This development is mainly caused by the industrialization of former developing and newly industrializing countries. While the per capita raw material consumption in developing countries is only about 2100 kg a^{-1}, modern industrialized countries consume on average about 12,600 kg raw materials per year.

Various steps are being taken to secure the supply of raw materials in the future. These activities include:

- Intensification of the search for and exploration of raw material deposits in areas that are geologically well explored (analogy search),
- Geological search on poorly explored territories (undeveloped areas, marine areas),
- Improving territorial development with the aim of using previously unexploited raw materials,
- Improvement of extraction, processing and refining technologies,
- Complex use of raw materials (accompanying raw materials),

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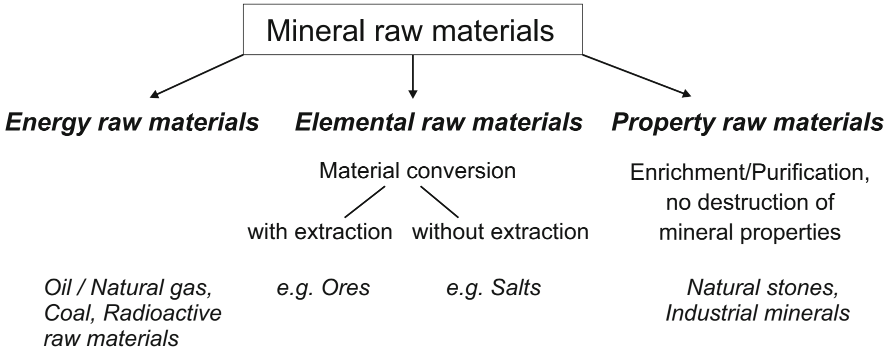


Fig. 3.1 Classification scheme of mineral raw materials

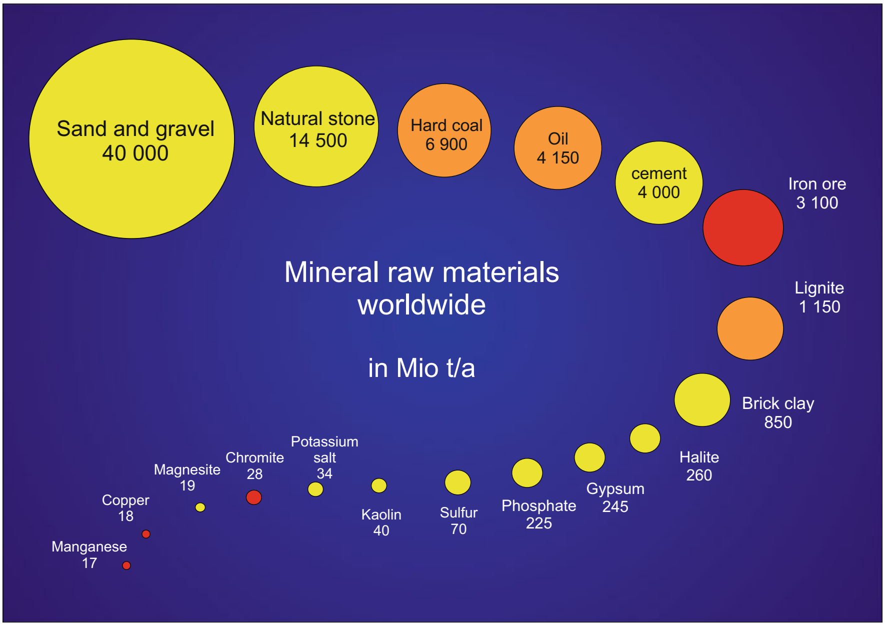


Fig. 3.2 Order of quantities of mineral raw materials in world consumption (*yellow* stones/earths/industrial minerals, *orange* energy raw materials, *red* metals). (Data source: USGS 2012)

- Substitution possibilities of raw materials (and materials) as well as
- Use of secondary raw materials, recycling.

For an effective management of the raw material base and an optimal use of mineral raw materials, above all the knowledge of the properties of these natural materials is necessary (Lorenz and Gwosdz 1997, 1998, 1999, 2003). This is the only way to achieve an optimal process sequence from raw material exploration to mining, processing and use. In particular, the growing demands of raw material users for specific raw material properties require a fundamental knowledge of the mineralogical properties of inorganic non-metallic raw materials. In the following, this issue will be discussed with reference to some selected mineral raw materials. An overview of important stones, earths and industrial minerals is given and the relationships between mineral properties and technical use are discussed using these examples.

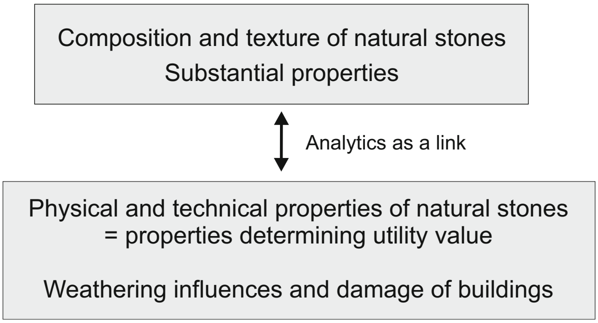
3.1 Natural Stone

Natural stones are among the most important mineral raw materials, with an annual world consumption of several billion tonnes. In terms of the quantity used, approx. 5–10% are currently used as natural stones in a fixed form and dimension (so-called ashlars) and 90–95% as crushed natural stones (e.g. for road construction, track construction, aggregate for the construction industry, etc.). Due to the extraction situation and utilisation properties, surficial deposits of carbonate and silicate rocks are preferred.

The usable rocks with mono- and polymineral variable grain structure are representatives of the property raw materials, i.e. the primary physico-chemical and technical properties are decisive for the technical use (Fig. 3.3).

An important factor for the characterization of natural stones is mineralogical-geochemical analysis. Whereas in the past only a few relevant technical properties such as compressive strength and water absorption capacity were investigated, today a wide range of geoscientific investigation methods are used. This is due to the close dependence of the utility value on material composition and microstructure. The decisive factor for the selection of the analytics used is in particular the question of whether the material is fresh natural stone (application properties for industrial use) or already installed material (weathering influences, structural damage).

Fig. 3.3 Relationship between properties and utility value of natural stone



3.1.1 Composition and Microstructure of Natural Stones

The chemical composition does not play a decisive role for freshly quarried natural stones, but it can be very important for the assessment of the state of preservation of the building material. Much more decisive, however, is the primary (and secondary) mineral composition of natural stones. Here, of course, the major rock-forming minerals of the earth's crust play a dominant role (Fig. 3.4). Experience shows that rarely more than six rock-forming minerals are found in one type of natural stone.

Some general characteristics can be noted for the weathering behaviour of the most important rock-forming minerals. In general, dark (mafic) minerals are less resistant to environmental influences than light (felsic) ones, and plagioclase is less resistant than potassium feldspar. Quartz is the most stable major mineral. Among the carbonates, only anhydrous minerals form rocks, i.e. hydrous carbonates are always indicators of weathering processes.

In addition to the mineral composition, the microstructure is an important influencing factor for the service properties of natural stones. The rock fabric describes the repeating characteristics of a rock body, i.e. phase proportions and size distribution, shape, orientation and local distribution of the mineral phases and

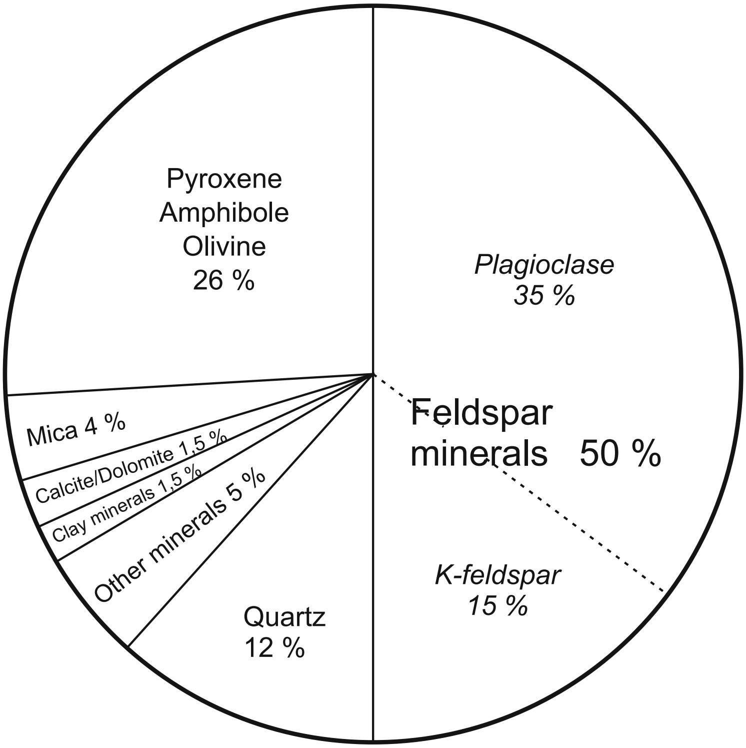
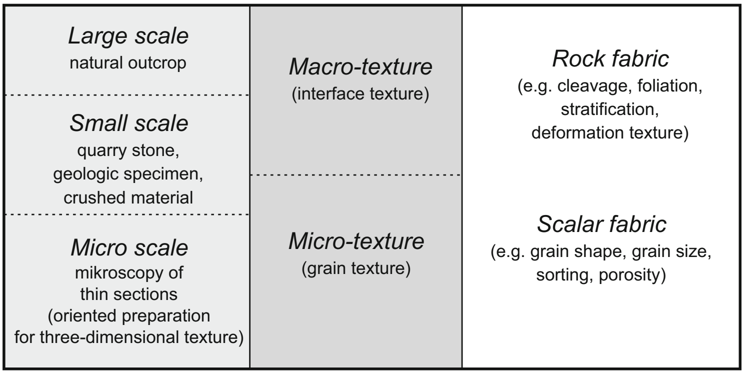


Fig. 3.4 Proportion of the most important rock-forming minerals in the rocks of the Earth's crust



<table>
<tr><td>Large scale
natural outcrop</td><td rowspan="2">Macro-texture
(interface texture)</td><td rowspan="2">Rock fabric
(e.g. cleavage, foliation, stratification, deformation texture)</td></tr>
<tr><td>Small scale
quarry stone, geologic specimen, crushed material</td></tr>
<tr><td>Micro scale
mikroscopy of thin sections (oriented preparation for three-dimensional texture)</td><td>Micro-texture
(grain texture)</td><td>Scalar fabric
(e.g. grain shape, grain size, sorting, porosity)</td></tr>
</table>

Fig. 3.5 Different types and magnitudes of textural features in natural stone

specific interfaces. Textural features occur in different orders of magnitude (Fig. 3.5).

The formation of the minerals (grain size, shape, etc.) and the grain bonding (direct, indirect) have a decisive effect on various strength parameters. In sedimentary rocks, for example, the type (clayey, carbonate, siliceous) and formation of the binder can significantly change the compressive strength (Fig. 3.6).

3.1.2 Physical-Technical Properties

A number of physical-technical properties influence the utility value of natural stones to varying degrees. These differences become clear, for example, when comparing the two scalar properties density and porosity. While density is only used in a few cases for natural stone evaluation, porosity directly and indirectly determines almost all properties such as water absorption, heat conduction or strength properties. Porosity contributes decisively to the reactive surface and is therefore also an important parameter for the assessment of weathering resistance, as this starts at the surface. Therefore, measurements of porosity and pore size distribution are essential for the utility value of natural stones.

Porosity describes the proportion of void space that can be occupied by mobile phases (gases, liquids) (Fig. 3.7). A distinction is made between the total porosity and the apparent porosity, which only includes the communicating pore space. The porosity can be determined by optical methods (microscopy) or mercury porosimetry. However, microscopy can only be used to assess a two-dimensional section through the rock. Therefore, preparations representative for all spatial directions are necessary. Mercury porosimetry, on the other hand, provides direct information on the open pore volume.

Hygric properties, i.e. properties that determine the interaction with water or moisture, play a very important role for the use of natural stones in outdoor areas. These properties include water absorption, saturation coefficient, moisture and

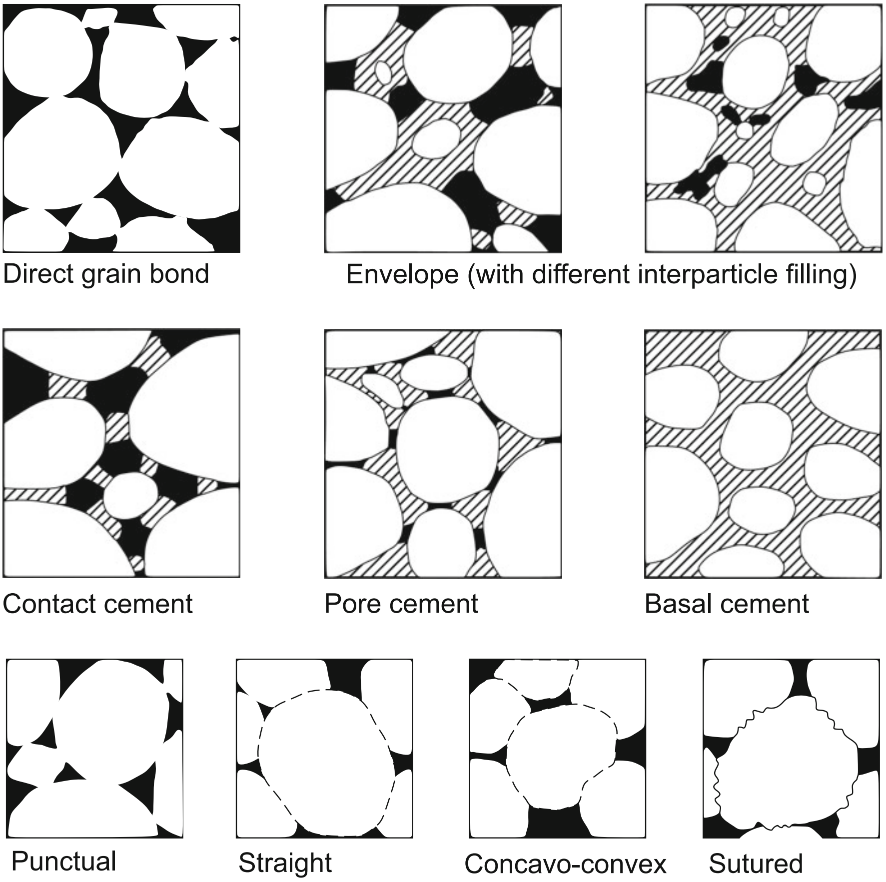


Fig. 3.6 Grain-binding modes in clastic sedimentary rocks. (*White:* grains, *black:* pore space, *hatched:* binder). (Modified after Peschel 1983)

adhesive water content, permeability and capillarity (capillary rise). While water absorption only characterises the water content when water is stored until saturation, the coefficient of saturation is characterised by the quotient of voluntary water absorption to water absorption under pressure and is thus an important measure of the weathering and frost resistance of natural stones (Fig. 3.8).

Strength properties are important criteria for the characterization of natural stones, as they essentially determine the application parameters. Strength is generally defined as the resistance to a certain force. Important factors influencing the strength are, for example, the state of preservation of the rock-forming minerals, grain-size distribution, grain bonding (intergrowth ratios) and orientation of the mineral phases, the pore space or also residual stress states of the rock. A distinction is made between:

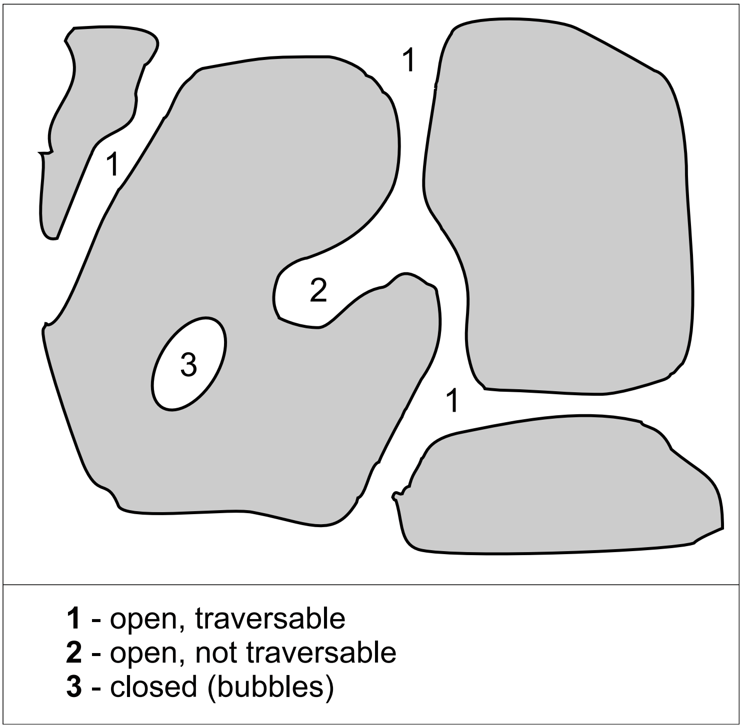


Fig. 3.7 Schematic representation of porosity

Water uptake

$$w_i = \frac{m_2 - m_1}{m_1} \cdot 100\ \%$$

m_1 = Mass of dry sample
m_2 = Mass after water storage

Saturation coefficient

$$S = w_i / w_{id}$$

w_{id} = Water uptake at 15 MN/m^2

$S < 0.75$ weathering- and frost-resistant
$S > 0.90$ not weathering- and frost-resistant

Fig. 3.8 Determination of water absorption and saturation coefficient in rocks

- static strength (compressive, bending, tensile and shear strength) = stress due to continuously acting forces
- dynamic strength (hardness, impact and grinding strength) = change of acting forces.

The static strength is an important parameter for use in structural engineering, while dynamic strengths are to be considered above all in traffic and civil engineering. A

	Compressive strength in MN/m^2	***Porosity*** in %
Granite	210 - 245	
Basalt	160 - 190	
Granulite	175 - 350	
Marble	110 - 150	
Sandstone	10 - 40	12 - 20
	80 - 110	4 - 8
	180 - 270	1.5 - 3

Fig. 3.9 Equipment for determining the compressive strength of formatted natural stone samples

fundamental parameter for the technical classification of solid rock is the compressive strength. It is carried out on compression presses (Fig. 3.9) with formatted test specimens (cubes, cylinders, prisms) until fracture. The rock fabric is one of the main factors determining the compressive strength of rocks. Figure 3.9 lists the compressive strengths of some selected rocks.

Dynamic strengths are often characterized by the wearability of the rocks. For example, the loss of material due to abrasion on a grinding wheel or under the action of a sandblast is measured under defined conditions and converted into corresponding characteristic values.

It is more difficult to characterise the technical properties of crushed natural stones such as crushed sand (0.063–2 mm), grit (2–20 mm) or crushed stone (20–63 mm). The complex action of different forces (tension, compression, bending, shearing) on the aggregate results in the superposition of the different effects (Fig. 3.10). For this reason, the properties are simulated on the aggregate, e.g. the determination of the ballast and crushed stone compressive strength in the pressure pot with pressure stamp.

Another parameter for characterizing crushed natural stone is the adhesion of binders (e.g. bitumen, cement) in industrial use. Bitumen adhesion, which is particularly important for use in road construction, is characterised by the degree of coating of the grain surface. Greywacke is the preferred material for this application due to its good surface properties. The adhesion of the binder cement, on the other hand, is somewhat more complex, since in addition to the adhesive forces, chemical reactions with the aggregate also have an influence on the strength. Consequently, due to its chemical consistency, limestone is a suitable aggregate for combination with cement in the construction industry.

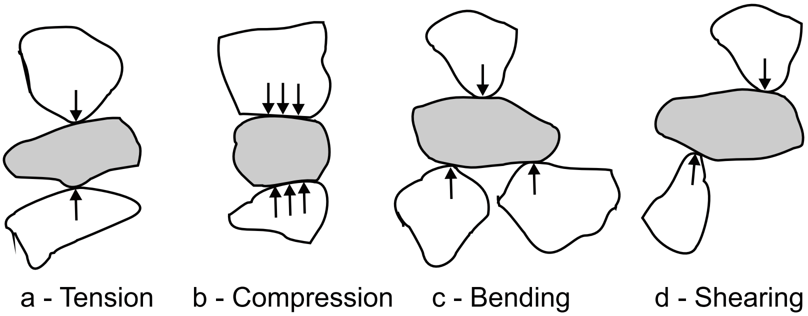


Fig. 3.10 Scheme of complex stressing of mineral grains in crushed stone or grit

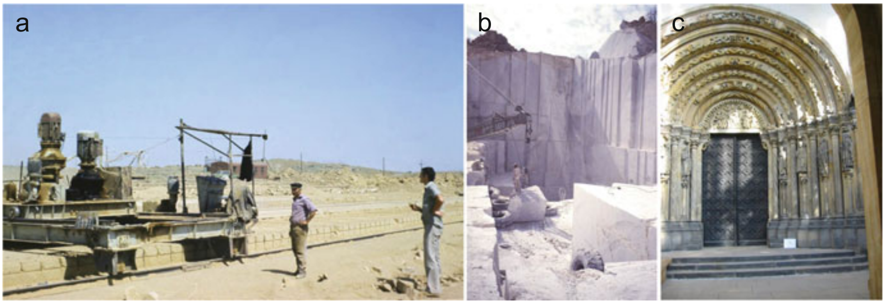


Fig. 3.11 Quarrying and use of various natural stones: (**a**) Tuff quarrying in Yerevan (Armenia); (**b**) Quarrying operation of white marble in Palissandro (Namibia); (**c**) Golden portal of the Freiberg Cathedral (Saxony, Germany) made of Grillenburg sandstone

3.1.3 Exploitation and Use of Natural Stone

Rocks from all geological environments are used as natural stones worldwide. In history, mainly rocks from local deposits were used, which can thus dominate the respective cityscape or entire regions. Economic considerations have led to natural stone material from all over the world being used today. In addition to the properties of use, aesthetic considerations often play an important role in the selection of suitable ashlars.

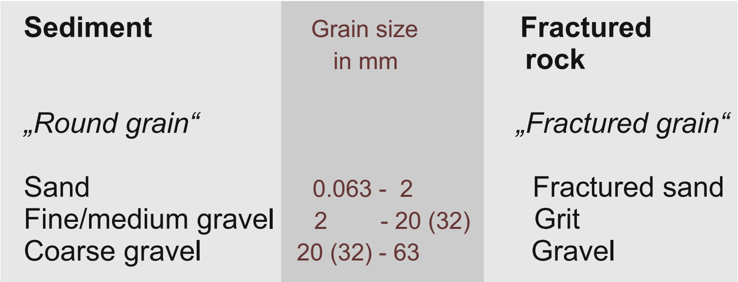
Among the plutonites, granites, granodiorites and gabbros are popular natural stone materials, while rhyolites, basalts and tuffs dominate among the volcanic rocks (Fig. 3.11a). The range of metamorphic rocks used is wide, from crystalline schists to gneisses, granulites, serpentinites, quartzites and marbles (Fig. 3.11b). Sedimentary rocks are also popular natural stones, with sandstones being processed in particular as ashlars (Fig. 3.11c), while greywackes and limestones are currently preferred as crushed natural stones.

3.2 Sand and Gravel

The seemingly unlimited occurrence of sands and gravels in vast sand deserts, on beaches or in river courses often leads to the assumption that they are arbitrarily available and therefore relatively worthless. However, if you look at sand and gravel in terms of raw materials, it is a highly sought-after natural product. Measured in terms of the amount extracted, gravel sands are, along with natural stones, the most important mineral raw materials in the world, with more diverse uses than almost any other raw material. Special requirements are placed on sands and gravels, some of which are only met in selected raw material deposits.

From a sedimentary petrographic point of view, sands and gravels belong to the unconsolidated sediments; as a mineral raw material they belong to the group of property raw materials. Since the definition of sand and gravel is of a purely grain-size nature, in addition to the naturally occurring sands and gravels (so-called round grains = uncrushed mineral grains), crushed natural stones (so-called crushed grains) are also counted as sands and gravels in the industrial sense, which are widely used e.g. as aggregates (Fig. 3.12).

Although in colloquial usage the terms sand and gravel are usually understood to mean quartz-rich sediments, the designation is actually independent of the material composition or genesis. All naturally occurring sands consist of different minerals. If a sand is predominantly composed of only one type of mineral, it is called monomineral sand. Such sands may be heavy mineral sands, such as rutile sands or cassiterite sands. Pure quartz sands are also to be counted among the monomineral sands, since they consist almost entirely of quartz grains. Quartz sand and quartz gravel are sands and gravels with SiO_2 contents >85 mass-%. The term industrial sand is defined as silica sand with >98 mass-% SiO_2 (pure quartz sand).



Sediment	Grain size in mm	**Fractured rock**
„Round grain“		*„Fractured grain“*
Sand	0.063 - 2	Fractured sand
Fine/medium gravel	2 - 20 (32)	Grit
Coarse gravel	20 (32) - 63	Gravel

Fig. 3.12 Classification of sand and gravel according to DIN 4022 (EN ISO 14689–1)

3.2.1 Formation and Types of Deposits

Sand and gravel deposits belong to the group of clastic sediments. The genesis of the deposits is essentially determined by the type and intensity of weathering (including erosion) and the transport and depositional conditions (glacial, aeolian, fluvial, marine). These factors are thus important for the mineral composition and properties of the sands and gravels and ultimately determine the raw material quality as well as the type of deposit. Low chemical weathering and mechanical reworking result in sands with complex mineral compositions, while pure quartz sands are mainly produced by intensive chemical weathering and mechanical reworking.

Fluvial deposits account for the largest proportion of industrially used gravel sands. These are mostly recent and fossil river courses in areas of former glaciation or in large river systems. In deposits of the marine coastal area (littoral sands), high-purity sands are generated by natural processes of processing, which represent sought-after industrial raw materials. Such special sands of high purity and favourable grain size distribution were geologically formed in Central Europe mainly during the Upper Cretaceous and the Tertiary. The four largest German deposits in Haltern, Weferlingen (Upper Cretaceous), Frechen and Hohenbocka (Tertiary) can also be assigned to this geological environment (Fig. 3.13).

3.2.2 Mineral Composition and Chemical Properties

The material composition (= mineralogical and chemical composition) of the sands and gravels is an essential characteristic value, as the industrial user receives information on the usability of the raw materials. On the other hand, conclusions can also be drawn concerning supply areas and stratigraphic correlations as a basis for geological modelling. Only the detailed knowledge of these material parameters (e.g. characteristics of impurities) guarantees an effective processing and an optimal use of the mineral raw materials.

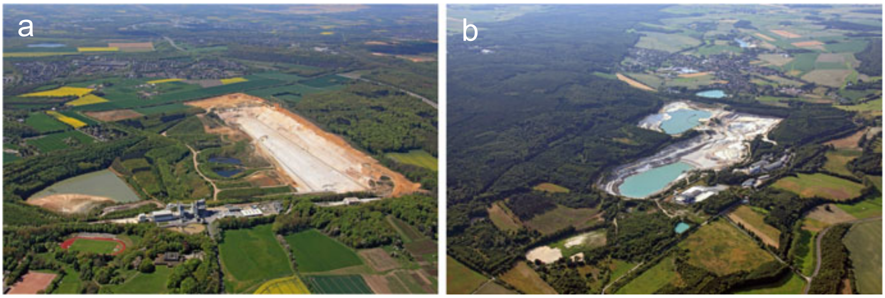


Fig. 3.13 Deposits of high-purity quartz sands at Frechen (**a** Palaeogene) and Weferlingen (**b** Upper Cretaceous). (With the kind permission of Quarzwerke GmbH, Frechen)

Although the composition of sands and gravels can be very complex, some components can be singled out as main constituents that also influence the chemical composition. These include:

- Rock fragments
- SiO_2 (quartz, chalcedony, opal)
- Feldspar minerals
- Clay minerals or phyllosilicates (especially kaolinite, illite, montmorillonite, chlorite)
- Heavy minerals (density >2.9 g cm^{-3})
- Organic substances (especially humic substances)
- (Fe/Mn minerals, carbonates)

Of the SiO_2 modifications, quartz is the most common mineral in sands and gravels. Quartz has a relatively high hardness and is chemically resistant. Therefore, at the end of the geological weathering and sedimentation chain in sands and gravels, the mineral quartz is preferentially enriched as a detrital component. In general, the raw material quality for most industrial applications increases with increasing quartz content. The alkali-reactive behaviour of cryptocrystalline and amorphous silica (chalcedony, opal) is particularly important for use in the construction industry.

Increased amounts of non-quartz components can have a decisive influence on the raw material quality of high-quality sands. Although heavy minerals usually only occur as accessory minerals (usually <1 mass-%), they can, for example, represent non-melting refractory particles in the glass batch or carriers of colouring chemical elements (e.g. Fe, Ti, Mn, Cr) in the glass industry. In the construction industry, sulphides in particular can cause damage through secondary oxidation processes.

In industrial sands and gravels of particularly glaciofluvial and fluvial formations, a number of clay minerals (kaolinite, illite, montmorillonite) may be accumulated in the "elutriable" fraction (<63 μm) and occur either finely distributed or stratified. Such constituents of clayey substances can impair the setting behaviour and strength of concrete. Particularly in high-quality sands (foundry and glass sands), even small quantities of clayey constituents can result in important quality restrictions (negative influence on binder properties, carrier of colouring elements, etc.).

Organic substances are carried into fluvial and glaciofluvial systems by flowing water; on the other hand, organic substances (xylites, humic substances) play an important role in sands and gravels, which are closely associated with the formation of lignite. A characterization of the organic substances is difficult, because they can occur in different forms (solid, liquid), grain size (in the clay fraction partly as clay-humus complexes, larger coal particles and xylites) and degree of polymerization. When present in the aggregate, they can retard the setting behaviour in fresh concrete, reduce the flexural strength of hardened concrete or cause long-term damage due to acid reactions. In the foundry industry, organics can have negative effects on various binders in moulding materials. In the glass industry, elevated $C_{org.}$ contents lead to undesirable coloration of special glasses due to their reducing effect on metal ions already present in the glass. In addition, humic substances are preferred carriers of coloring chemical elements (especially Fe).

3.2.3 Granulometric Properties

Grain size distribution and shape of the grains influence the use of gravel sands in various industries. Grain size is also the most important petrographic characteristic for the classification of gravels and sands and is usually determined by sieve analyses. Determinations by sedimentation analysis, optical methods or laser granulometers are also possible. The analytical results are presented as a frequency distribution or cumulative curve (Fig. 3.14), from which various parameters such as mean grain diameter or sorting can then be determined for further characterisation.

3.2.4 Extraction and Processing

Important parameters of sand and gravel deposits that determine the mining conditions are their size, shape and the raw material quality. Mining can be carried out dry with various dredgers above the groundwater level or after lowering the water level. Mining with floating and suction dredgers is realized below the water table in recent rivers or open pits.

The processing management depends on the geological conditions within the deposit and the industrial requirements for the raw material. In general, it is possible to produce a high-quality raw material from almost any raw product using the appropriate processing methods, although economy and ecology are limiting factors. While raw materials for construction sands and gravels are often used directly from

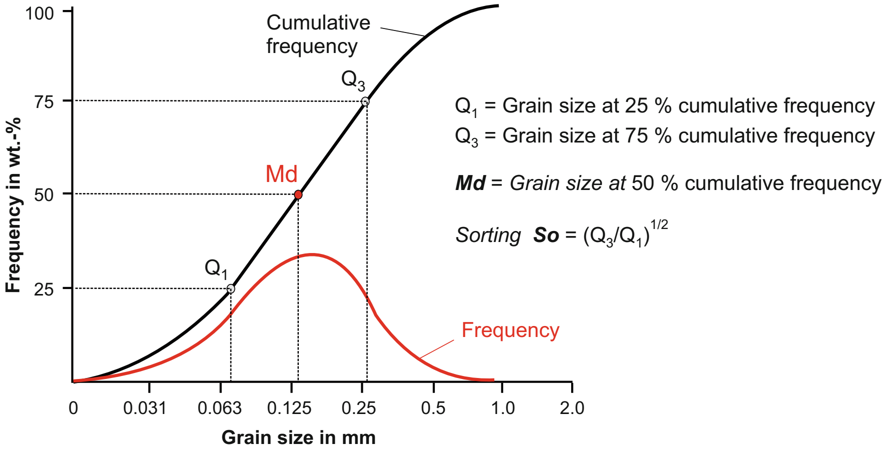


Fig. 3.14 Presentation of grain size distribution and specific granulometric parameters

Table 3.1 Compilation of important processing methods for quartz sands/gravels

Procedure	Processing effect
Washing process	Desludging, removal of clayey-silty and carbonaceous components
Sizing (e.g. sieving, hydrocyclone)	Narrowing of the grain-size distribution, removal of impurities in fine and coarse fractions
Attrition	Abrasion of the impurities on the grain surfaces
Density separation	Separation of heavy minerals
Magnetic separation	Separation of ferromagnetic minerals
Electrostatic separation	Separation of mica, Fe minerals, etc.
Flotation	Utilization of surface properties of light and heavy minerals for separation
Chemical treatment	Dissolution and volatilisation methods, essentially for the removal of Fe carriers
Microbial leaching	Removal of oxidic iron minerals and grain coatings
Drying, thermal treatment, grinding	Post-treatment of the raw material for specific properties

the quarry or are only processed by water washing or sieving, sophisticated processing technologies must be used for high-quality special sands (e.g. glass industry) (Table 3.1). The special treatment strategy always depends on the kind and quantity of impurities.

3.2.5 Use of Sands and Gravels in Industry

Various requirements are placed on gravels and sands depending on the industrial fields of application. In terms of quantity, the main area of application is the construction industry, but there is also a whole range of applications for high-purity quartz sands:

- Construction industry
  - Building construction (aggregate for concrete, mortar and sand-lime bricks)
  - Civil engineering (frost protection, base layer gravel, gravel chippings)
- Metal fabrication
  - Foundry (moulds)
  - Si metal, ferrosilicon
- Glass industry
  - Float glass, hollow glass, glass fibres
- Chemistry
  - Water glass
- Ceramics
  - ceramic materials, enamel
  - Silicon carbide

- Filter
  - Water filter, air filter, drainage
- Other
  - Cleaning (blasting, scouring, polishing agents)
  - Adhesion improvement (e.g. grit)

In the construction industry, the specific requirements mainly include grain size, proportion of crushed material, clay content, content of organic substances, contents of sulphur and chlorine compounds, and alkali sensitivity. Special sands, on the other hand, are characterized by very good granulometric properties (especially grain-size distribution) and high chemical purity.

3.3 Clay Raw Materials

The term clay is taken from sedimentary petrography and, according to nomenclature, includes minerals with grain sizes <2 μm. Clay minerals in the technical sense are also characterized by plastic properties, which are of decisive importance for industrial use (Jasmund and Lagaly 1993). Natural clays and clay deposits are generally fine- to very fine-grained weathering products of siliceous rocks, which consist of a mixture of clay minerals in the actual sense (grain size <2 μm) and fine-grained non-clay minerals and weathering residues (sometimes >2 μm). The clay minerals are mainly kaolinite, illite and montmorillonite, while quartz, feldspars or sericite/hydrous mica are represented as weathering residues. In addition, various carbonates, sulphides, oxides and organic compounds can also be enriched in clays.

Due to the material complexity and also the diverse technical requirements, it is difficult to classify clay raw materials. Since the mineral content decisively determines the properties of the clays, the clay raw materials are dealt with in the following primarily on the basis of the usage criteria:

- Refractory clays
- Coarse-ceramic clays
- Special clays – kaolin/bentonite

First, basic aspects of the structure and classification of clay minerals or phyllosilicates are discussed.

3.3.1 Structure and Classification of Clay Minerals

Clay minerals belong to the group of phyllosilicates. The structure of phyllosilicates is built up from two basic building blocks, SiO_4 or AlO_4 tetrahedra and $Al(OH/O)_6$ or $Mg(OH/O)_6$ octahedra.

The base layer consists of SiO_4 tetrahedra, each with three tetrahedral corners connected by oxygen bridges (Fig. 3.15). For this layer, the Si:O ratio is 2:5, i.e.,

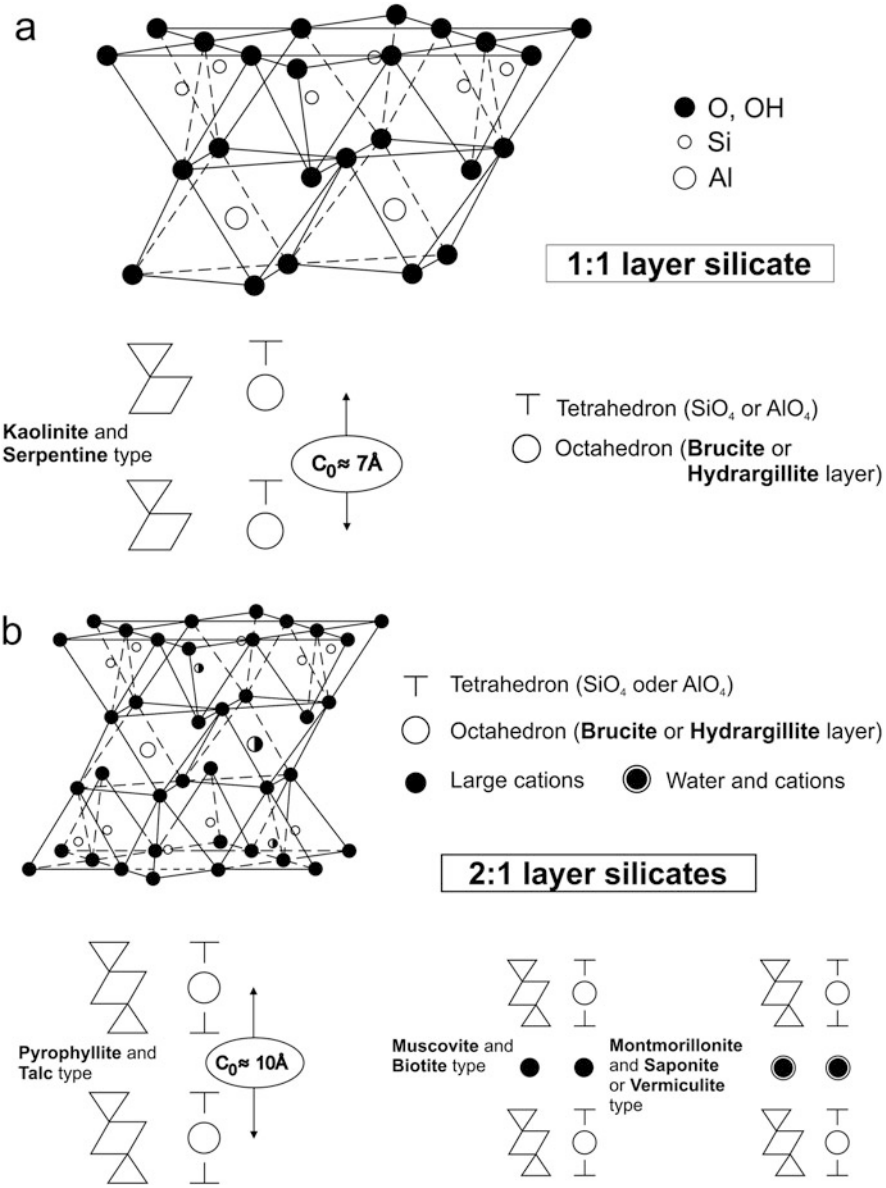


Fig. 3.15 Schematic representation of the basic structures of (**a**) 1:1 layer and (**b**) 2:1 layer silicates

$[Si_2O_5]^{2-}$. If the tetrahedra are occupied only by Si, pure silicates are formed, and if Si is partially substituted by Al, they are called aluminosilicates.

The second layer consists of aluminium or magnesium hydroxide octahedra, the triangular faces of which lie respectively on the tips of the tetrahedra. The oxygen atoms of two octahedral corners form oxygen bridges with the tetrahedra, and four

		not hydrated		hydrated	
	Octahedron layer Tetrahedron layer	dioctahedral	trioctahedral	dioctahedral	trioctahedral
1:1 layer	Silicate	**Kaolinite group** $Al_4[(OH)_8/Si_4O_{10}]$	**Serpentine group** $Mg_6[(OH)_8/Si_4O_{10}]$	**Hydrohalloysite** $Al_4[(OH)_8/Si_4O_{10}]\cdot(H_2O)_4$	-
	Alumosilicate	**Donbassite** $(Na,Ca,Mg)Al_4$ $[(OH)_8/AlSi_3O_{10}]$	**Berthierine group** $(Fe,Mg,Al)_6$ $[(OH)_8/AlSi_3O_{10}]$	-	-
2:1 layer	Silicate	**Pyrophyllite** $Al_2[(OH)_2/Si_4O_{10}$	**Talc** $Mg_3[OH)_2/Si_4O_{10}]$	**Montmorillonite group** $(Al,Mg)_2[(OH_2/Si_4O_{10}]$ $\cdot (Na,Ca)_x(H_2O)_n$	**Saponite group** $(Mg,Fe)_3[(OH)_2/Si_4O_{10}]$ $\cdot (Ca,Na)_x(H_2O)_n$
	Alumosilicate	**Muscovite group** $KAl_2[(OH)_2/AlSi_3O_{10}]$	**Biotite group** $K(Mg,Fe)_3$ $[(OH)_2/AlSi_3O_{10}]$	**Vermiculite series** $(Al,Fe,Mg)_2[(OH)_2/AlSi_3O_{10}]$ $\cdot (Mg,)Ca)_x(H_2O)_n$	$(Mg,Fe)_3[(OH)_2/AlSi_3O_{10}]$ $\cdot Mg_x(H_2O)_n$
2:2 layer	Silicate	-	-	-	-
	Alumosilicate	**Sudoite** $Al_2[(OH)_2/AlSi_3O_{10}]$ $\cdot Al_{2,33}(OH)_6$	**Chlorite group** $(Mg,Fe,Al)_3$ $[(OH)_2/(Si,Al)_4O_{10}]$ $\cdot (Mg,Fe)_3(OH)_6$	-	-

Fig. 3.16 Scheme of the most important phyllosilicates. (Modified after Rösler 1981)

corners are occupied by OH (Fig. 3.15). If the layer consists of $Mg(OH,O)_6$ octahedra, each octahedron is occupied by Mg (brucite layer). When occupied by Al (hydrargillite layer with $Al(OH,O)_6$ octahedra), every third octahedron is not occupied because of charge balance. Because of the difference in occupation, structures with divalent cations are called trioctahedral and those with trivalent cations are called dioctahedral.

The rhythmic succession of tetrahedral and octahedral layers results in the formation of different layer structures. If the basic structure consists of one tetrahedral and one octahedral layer, we speak of 1:1 layer minerals, which have an average spacing of 7 Å (Fig. 3.15). Examples include serpentine $Mg_3[(OH)_4/Si_2O_5]$ and kaolinite $Al_2[(OH)_4/Si_2O_5]$. 2:1 layered minerals with a second tetrahedral layer are talc $Mg_3[(OH)_2/Si_4O_{10}]$ and pyrophyllite $Al_2[(OH)_2/Si_4O_{10}]$ with mean spacings of 10 Å. The layer packages are only weakly connected to each other by means of Van der Waals forces.

If a partial substitution of Si^{4+} by Al^{3+} occurs in the tetrahedra, charge balancing occurs by cations incorporated between the layer packets (Fig. 3.15). Examples of these structures are the mica minerals such as muscovite $KAl_2[(OH)_2/AlSi_3O_{10}]$ or phlogopite $KMg_3[(OH)_2/AlSi_3O_{10}]$. Further cation substitutions and incorporation of water at the interlayer positions are noted in the montmorillonite-group. A scheme of the major phyllosilicates is compiled in Fig. 3.16.

3.3.2 Refractory Clays

Refractory clays ("fire clays") are clay raw materials used for the production of refractory products. These are materials that are stable at high temperatures. For refractory materials, 1500 °C is taken as the temperature limit, and highly refractory products can be used up to at least 1790 °C. Due to the stability requirements at high temperatures, the Al_2O_3 content (36–39 mass-%) is an important quality criterion for the clay raw materials used. The contents of alkali/alkaline earth oxides, Fe_2O_3 and loss on ignition should be very low for these raw materials.

Refractory clays are preferably used for the production of chamotte and as binding clays. Chamotte is a refractory ceramic product made of fired clay. In this process, the prepared clay raw material is fired at 1200–1500 °C in the kiln. The reactions of the clay minerals in the firing process result in the mineralogical composition of the chamotte, which essentially consists of mullite and glass. Such chamotte products make up about one third of the industrial refractory material. They are used either as a formatted product (Fig. 3.17) or as crushed material which is processed with binder clay.

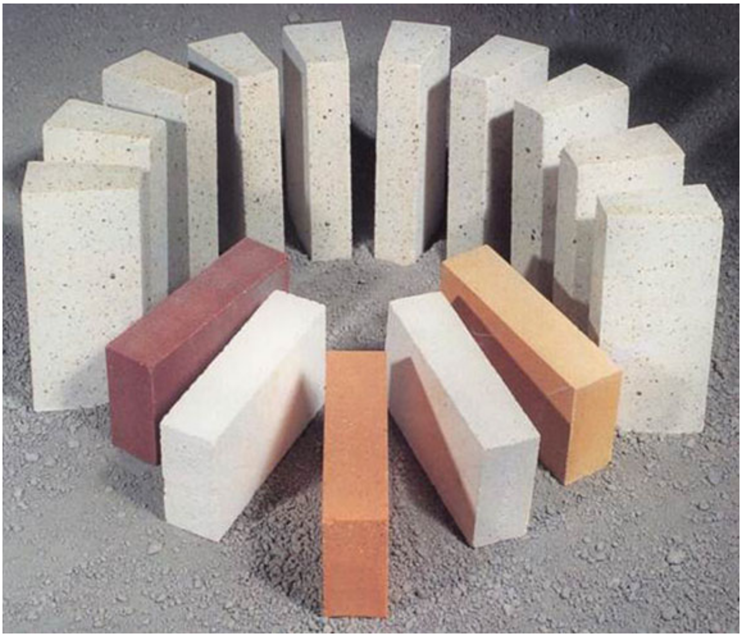


Fig. 3.17 Formatted fired clay bricks

3.3.3 Coarse Ceramic Clays

Coarse ceramic clays are used as raw materials for the production of various building products, such as bricks, roof tiles or vitrified clay pipes and fittings. Worldwide, several hundred million tons of brick clay and loam are processed annually. In Germany, mainly Tertiary and Quaternary clays and loams are used as coarse ceramic raw materials.

Important raw material parameters are physical-petrographic and technological parameters such as particle size distribution, mineralogical and chemical composition or compressive strength, flexural strength and water absorption. Harmful components such as stones, organic components, carbonates, sulphides or gypsum must be minimised by processing.

3.3.4 Special Clays: Kaolin

Kaolins (clay raw material with main mineral kaolinite) are among the highest quality and most important clay raw materials. They are the main raw material for fine ceramic products (porcelain), but are also needed for the production of white cement, as pigments and fillers in the paper and cosmetics industry or in the refractory industry. In foodstuffs, kaolin can be added as a separating and bleaching agent or as a carrier.

According to their formation, a distinction is made between residual kaolin (primary kaolin), secondary kaolin (kaolinite clays) and hydrothermal kaolins. Residual kaolins are formed in situ by exogenous weathering, usually have a large distribution area and often have a zoned composition to the bedrock (Fig. 3.18). Secondary kaolins are secondarily redeposited kaolins, which usually have thicknesses of only a few tens of metres. Hydrothermal kaolins usually represent small, tubular deposits, but are characterized by extreme purity and quality.

In Central Europe, many kaolin deposits were formed in the Upper Cretaceous and the Tertiary, as result of intensive chemical weathering during this geological period. The weathering of different source rocks led to kaolin deposits with different mineral compositions and properties. Kaolin deposits formed by the weathering of volcanic rocks (rhyolites and pitchstones) are characterized by high contents of illite-montmorillonite mixed-layer minerals. Deposits on weathered granites and granodiorites show the highest kaolinite contents, while weathered feldspathic sandstones (arkoses) may also contain significant proportions of illite-muscovite.

The different mineral composition of kaolins also determines their preferred industrial use. Kaolins with low iron contents and thus white firing colour are preferably suitable for porcelain production. Extremely high Al_2O_3 contents (high kaolinite content) and high whiteness are particularly favourable for the use of kaolin as a filler or coating kaolin in the paper industry. High Al_2O_3-content is also necessary for use in refractory products. On the other hand, high contents of illite-montmorillonite mixed-layer minerals result in high dry bending strength, which guarantees high stability in the unfired state even for complexely shaped green

Fig. 3.18 Kaolin deposit Caminau in Saxony, Germany. (With the kind permission of Quarzwerke GmbH, Frechen)

bodies. For this reason, these raw materials are preferred for the production of electroporcelain (e.g. insulators for high-voltage equipment).

For the production of high-quality kaolin, sometimes complex processing steps are necessary in order to meet the required quality criteria:

- Grinding
- Elutriation
- Fine screening in the hydrocyclone
- Sedimentation in the seddling basin
- Filter presses
- Drying

3.3.5 Special Clays: Bentonite

Bentonite is the name given to a clayey rock containing montmorillonite (usually $>50\%$ by mass) as the main mineral (cf. Fig. 3.16). The minerals of the montmorillonite group are also called smectites. Due to the exchangeability of ions in the interlayers (e.g. Ca, Na), smectites of different compositions occur.

Smectite is a group name for platy phyllosilicates of 2:1 layer and a layer charge of approximately 0.2–0.6 per formula unit. The d(001) spacing for natural samples is ca. 14.4–15.6 Å, which can vary due to water retention and interlayer occupancy (Guggenheim et al. 2006). The smectite group can be further divided into subgroups that are either dioctahedral (e.g. montmorillonite, beidellite, nontronite) or trioctahedral (e.g. saponite, hectorite, stevensite).

Smectite-rich clays are mainly formed during the weathering of basic rocks or the sedimentation of glass-rich, basic to intermediate tuffs in marine areas or in lakes. The sometimes highly variable quality and specific properties of bentonites place high demands on extraction and processing. The most important properties include:

- large specific and active surface
- high absorbency
- high binding capacity
- good swelling capacity
- easy dispersibility/suspendability
- high ion exchange capacity

Another characteristic property is thixotropy. At rest, a clay suspension of smectite is comparatively solid and metastable, whereas vibration and stirring result in abrupt liquefaction. This property makes bentonites strategic raw materials, as it is exploited, for example, when used as drilling mud (deep drilling, petroleum industry). On the other hand, increased contents of smectites can critically influence the stability of soils and landfills, as the encounter of water and mechanical vibrations can cause e.g. landslides.

However, the other properties of bentonites also result in a wide range of industrial applications. Other important applications include use as a binder in foundry sands or in ore pelletisation, as a sealing material in landfill construction, for cleaning foodstuffs (so-called bleaching earths) and in drinking water treatment, or for improving soils in landscaping and recultivation.

3.4 Quartz and SiO_2 Raw Materials

The natural SiO_2 raw materials represent a complex group of industrial minerals and usable rocks that are used extensively in industry and technology (Götze and Möckel 2012). The most important quartz raw material in terms of volume is high-quality industrial quartz sand with >98% SiO_2 (Sect. 3.2 “Sand and gravel”). In addition, very pure pegmatite quartz, hydrothermal gangue quartz, metamorphic quartzite and sedimentary quartzite (cement quartzite) are used.

Quartz is an enormously high-grade raw material with requirements in terms of purity and specific properties that are hardly placed on any other industrial mineral. Due to its application in telecommunications and optics, the semiconductor industry, electronics and the solar industry, quartz is gaining strategic interest as a high-quality raw material. At the same time, “synthetic” SiO_2 raw materials are also gaining in importance, but these are also produced from natural minerals – usually through a very complex purification process. In the following, the special problem of quartz raw materials will be dealt with in more detail.

3.4.1 The SiO_2 System

This system comprises 15 modifications of crystalline and amorphous silica (Table 3.2). Fibrous SiO_2 and keatite are only known as synthetic phases. Seifertite is a high-pressure modification that has only been detected in meteorites. Tridymite also occupies a certain special position. Tridymite does not occur as a pure SiO_2-phase and needs "impurities" of cations (e.g. Na, K) to stabilize the structure, which is given in many technical systems. The high-pressure phases stishovite and seifertite also represent a special feature, since, in contrast to the other SiO_2-phases, the structure is not built up of SiO_4-tetrahedra, but SiO_6-octahedra.

Looking at the stability ranges of selected SiO_2-modifications in the *p-T diagram* (Fig. 3.19), it is evident that most natural SiO_2-minerals occur at relatively low temperatures and different pressures, whereas in engineered systems it is mainly changing temperature conditions that cause the occurrence of different SiO_2-modifications.

In terms of natural occurrence and technical use, quartz (trigonal low-temperature quartz or α-quartz) represents the most important SiO_2 modification. The structure of α-quartz is composed of $[SiO_4]^{4-}$-tetrahedra, which form a three-dimensional

Table 3.2 The SiO_2 system. (According to Götze 2009)

Quartz-tridymite-cristobalite group (low/atmospheric pressure)	
Quartz	Trigonal
High-quartz	Hexagonal
Tridymite	Monoclinic
High- tridymite	Hexagonal
Cristobalite	Tetragonal
High-cristobalite	Cubic
Melanophlogite	Cubic
Fibrous SiO_2 (synthetic)	Orthorhombic
Moganite	Monoclinic
Keatite-Coesite-Stishovite group (high/ultra-high pressure)	
Keatite (synthetic)	Tetragonal
Coesit	Monoclinic
Stishovit	Tetragonal
Seifertite	Orthorhombic
Lechatelierite opal group (amorphous)	
Lechatelierite	Natural SiO_2 glass
Opal	Water-containing solid SiO_2 gel

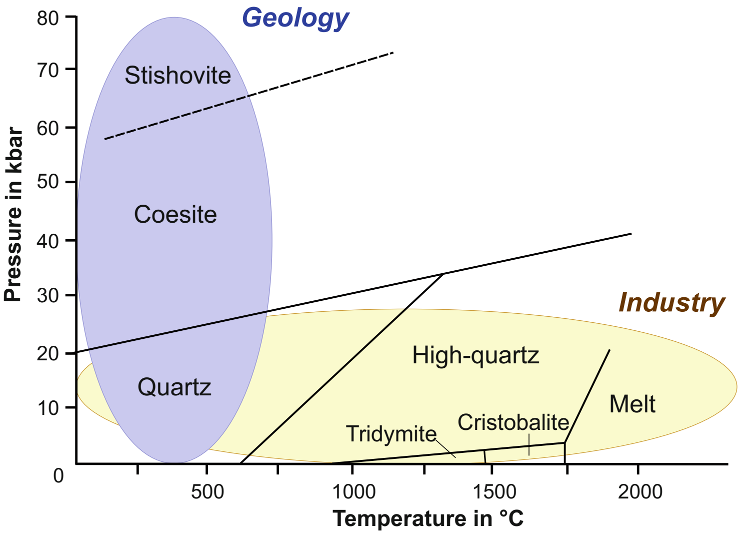


Fig. 3.19 Simplified pressure-temperature diagram of the SiO_2 system with the stability fields of selected SiO_2 modifications and their preferred occurrence in nature (blue) and industry (yellow)

network via oxygen bridges (Fig. 3.20). The c-axis in the trigonal quartz is identical to the optical axis, i.e., perpendicular to the circular section of the optical isotropy.

Morphologically, quartz can be distinguished into so-called left-handed quartz and right-handed quartz, which are caused by the different orientation of the tetrahedral chains along the *c-axis*. Macroscopically, the orientation can be identified by the position of the trapezohedron face *x* relative to the rhombohedron face *r* (Fig. 3.20). Various twinning, colour and shape varieties as well as growth phenomena such as macro-mosaic texture and lamellar structures (Friedländer or Bambauer quartz) are also frequently observed in quartz (Rykart 1995).

At a temperature of 573 °C, the trigonal low-quartz transforms into the hexagonal high-quartz, which is accompanied by a widening of the bond angles (Fig. 3.20). Since this transformation is reversible, it is called a displacive transformation. In contrast, irreversible reconstructive transformations with complete structural changes can also occur, such as the transition from high-quartz to cristobalite. The modification transitions caused by temperature changes are of great importance for the technical use of SiO_2 raw materials, since they are sometimes accompanied by enormous volume changes (Fig. 7.2), which can damage or destroy the materials.

3.4.2 Real Structure of Quartz

Quartz is by nature a very “pure” mineral, therefore even the smallest defects can have a decisive influence on its properties. According to their structure and size, a distinction is made between zero-dimensional point defects (foreign ions or intrinsic

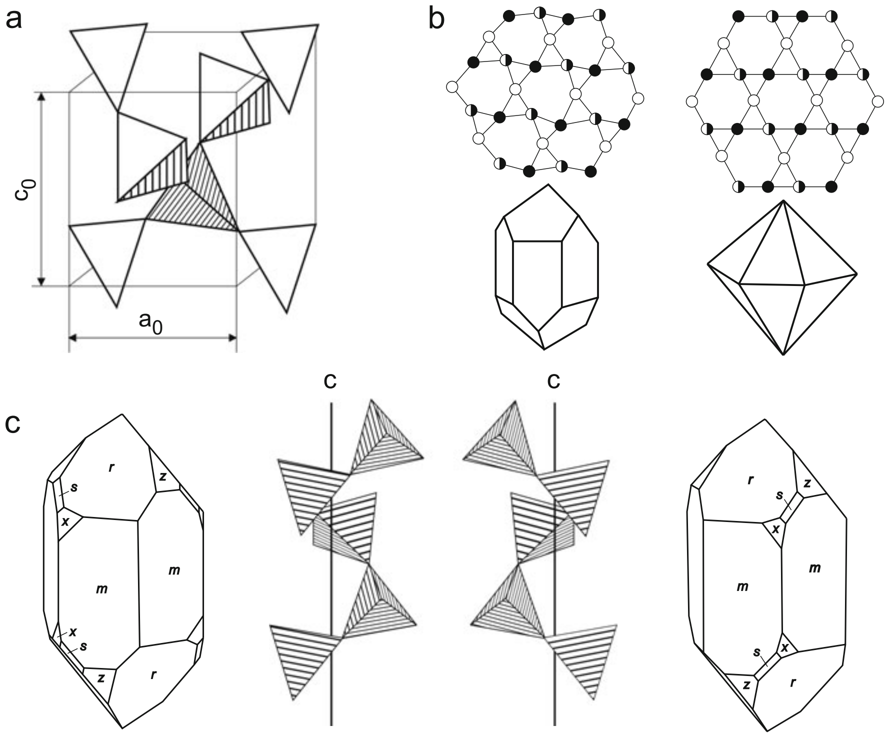


Fig. 3.20 Unit cell of trigonal low-quartz (**a**) and schematic structures and morphologies of low- and high-quartz (**b**); (**c**) arrangement of tetrahedral chains along the c-axis and typical morphology for left- and right-handed quartz. *m* prism; *r* positive rhombohedron; *z* negative rhombohedron; *x* trapezohedron; *s* dipyramid. (Modified after Blankenburg et al. 1994)

defects of the lattice such as vacancies), one-dimensional dislocations (screw and edge dislocations), two-dimensional defects (micrograin boundaries) and three-dimensional inclusions of gases, liquids and foreign minerals.

Even the occurrence of point defects can cause electrical instabilities in SiO_2 insulator layers and optical effects or negatively influence the oscillation behavior of piezoelectric crystals, which can have a decisive impact on their technical use. The different point defects are investigated by *electron paramagnetic resonance* (EPR) or by combination with other spectroscopic methods (luminescence, IR spectroscopy, absorption measurements).

The possibility of substitution of silicon on lattice sites is low due to the small ionic radius of Si^{4+} (0.42 Å) and high valence. So far, Al^{3+}, Ga^{3+}, B^{3+}, Fe^{3+}, Ge^{4+}, Ti^{4+} and P^{5+} are detected in quartz. Since charge balance is required for some of these ions, cations (e.g. Li^+, Na^+, H^+) are sometimes incorporated on interstitial sites in the structural channels parallel to the c-axis. Overall, as a result, the trace element contents in quartz are extremely low, showing contents of more than 1 ppm for only

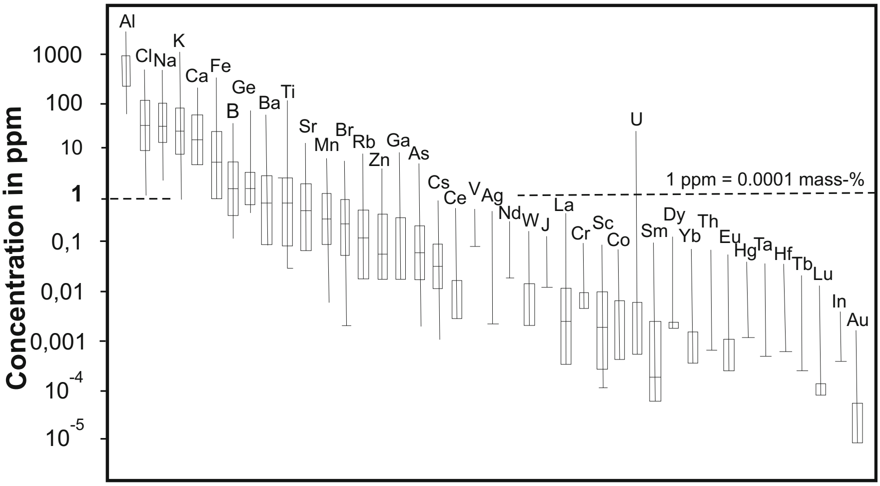


Fig. 3.21 Average contents and ranges of variation of trace elements in quartz. (Modified after Götze 2009)

a few elements (Fig. 3.21). Higher concentrations of impurities are usually concentrated along grain boundaries or bound to micro-inclusions in quartz.

The most important line defects are dislocations, i.e. boundary lines that separate the disturbed from the undisturbed crystal region. They can occur during crystal growth due to vacancy condensation or thermal and mechanical effects. The qualitative and quantitative detection of dislocations is carried out by etching methods or X-ray topography.

Inclusions of gases, liquids and foreign minerals are usually incorporated during crystallization of quartz. Although they constitute the bulk of the impurities, they can usually be removed by suitable preparation processes.

It is known from numerous studies that quartz forms very specific defects depending on the physicochemical conditions of formation. Thus, knowledge of this relationship is crucial for the selection of quartz raw materials for specific technical applications.

3.4.3 Geological Formation of Quartz Raw Materials

Quartz is one of the most important rock-forming minerals in the Earth's crust with 12.6% by mass. The majority of quartz, 93.6%, is concentrated in igneous rocks, while metamorphic and sedimentary rocks each contain 3.2% (Rösler 1981). Despite the enormous amount of magmatic quartz, rock quartz plays only a minor role as a raw material and only occasionally occurs as a by-product of the processing of other raw materials. The only exception is the extraction of so-called IOTA quartz by leaching an alaskite rock (alkali leucogranite). This produces an SiO_2 product of

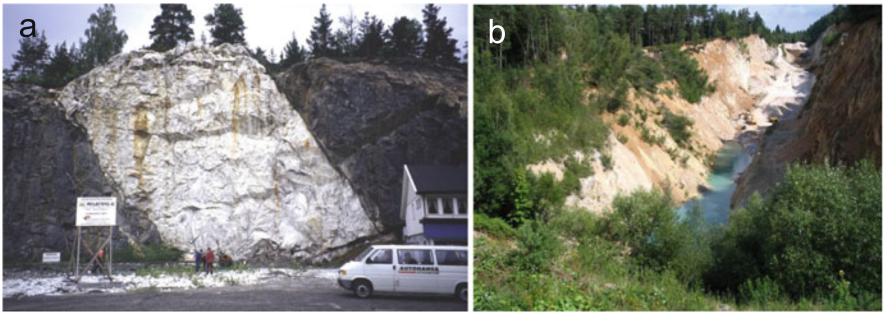


Fig. 3.22 Occurrence of pegmatite quartz in Evje-Iveland, Norway (**a**) and hydrothermal gangue quartz in the Bavarian “Pfahl”, Viechtach (**b**)

extreme purity (Al $<$ 10 ppm, Fe $<$ 1 ppm, Ti $<$ 2 ppm, Na $<$ 1 ppm, B $<$ 0.1 ppm, P $<$ 0.1 ppm).

Economically interesting quartz enrichments are found in pegmatites. Here, massive raw material bodies of high chemical purity are formed from magmatic residual solutions or during metamorphic processes. Important deposits can be found, for example, in Brazil, Angola, Russia or Scandinavia (Fig. 3.22).

Formations of nearly monomineralic vein fillings of hydrothermal quartz are very diverse in their appearance. The extent of such deposits can reach thicknesses of more than 100 m and extensions of more than 100 km (Fig. 3.22).

Similar to the igneous rocks, the metamorphic quartz-bearing rocks are relatively uninteresting for quartz extraction. Only almost monomineralic quartz rocks, such as metamorphic quartzites, are often used directly as raw material. However, due to pressure and temperature conditions during metamorphic processes, silica can be released, migrate over certain distances and crystallize in cavities. These vein- and lens-shaped quartz mobilisates are often characterised by high chemical purity and are therefore sought-after raw materials. These metamorphic formations also include so-called alpine fissures, which have been used for centuries to extract rock crystal. Extremely high-purity rock crystals from the Swiss Alps, the USA (Arkansas quartz) and Russia were used in the past, after appropriate processing steps, directly as piezo quartz or as raw materials for quartz single crystal synthesis and silica glass production.

The sedimentary environment is of extraordinary importance for the supply of quartz raw materials. Clastic sediments (sands and gravels) play the main role here (Sect. 3.2 “Sand and gravel”). High-purity industrial sands with appropriate grain-size distribution are used primarily in the glass and foundry industries. In addition, sedimentary quartzites, chert (flint) and diatomaceous earth are valuable raw materials for the industry.

3.4.4 Industrial Use

In the case of quartz raw materials, both the physical and chemical properties are used. While rock crystal and synthetic quartz are mainly used as single crystals (e. g. piezo quartz), other SiO_2 minerals and SiO_2 rocks are used as silicon ore, e. g. for the production of silicon alloys and metallic silicon. Since the raw material properties are significantly determined by the conditions of formation, specific quartz raw materials can be used in particular for certain industrial applications (Fig. 3.23).

One of the most important areas of application in terms of volume is the use of quartz sands for the manufacture of casting moulds in the foundry industry. For the production of moulds using various binder materials (bentonite, water glass, organic binders), the granulometric properties (grain-size distribution, grain shape, surface properties) of the sands are particularly important.

High-purity quartz sands are also the main raw materials in the production of silicate glasses. Up to 80% by mass of quartz is required in the raw material mix. In addition to the grain size (0.1–0.5 mm), the main characteristic for high-quality raw materials is in particular the chemical purity (low contents of Fe, Ti, Mn, Cr, etc.), in order to avoid disturbing colorations of the glasses.

For a number of applications in industry and technology (e.g. optics, piezo quartz), the requirements for perfection and purity of the raw materials cannot be met by natural quartz. In the 1950s, the hydrothermal synthesis of quartz single crystals at elevated temperatures (350–400 °C) and pressures (100–120 MPa) in

Magmatic / post-magmatic			
Quartz from Alaskite (“Iota quartz“)	chemical purity	→	high-purity synthetic SiO_2 products
Pegmatitic and hydrothermal Quartz	chemical purity perfect crystal structure	→	optical and piezo Quartz lascas for Quartz crystal growth solar silicon
Metamorphic			
Quartzite	SiO_2 > 98 wt.-%	→	refractory material
Metamorphogenic mobilisates	chemical purity	→	lascas for quartz crystal growth piezo quartz, silica glass
Sedimentary			
Quartz sand (Quartz gravel)	chemical purity granulometric properties	→	glass and foundry industry Si, SiC, Si alloys (FeSi) Cristobalite, quartz powder
Quartzite / Flint	cryptocrystalline SiO_2	→	refractory material
Diatomite	spezific surface	→	filler and carrier material

Fig. 3.23 Relationship between genesis, properties and industrial use of quartz raw materials

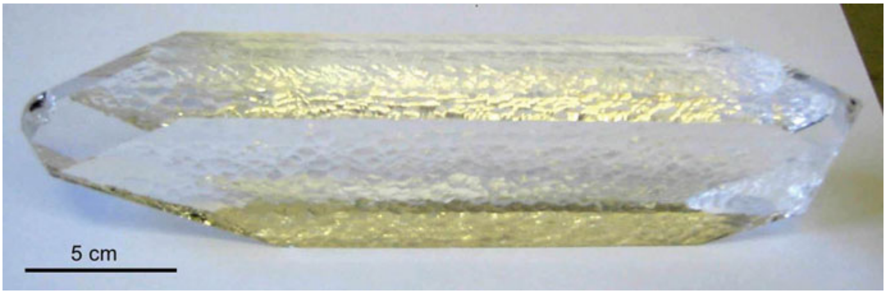


Fig. 3.24 Hydrothermally grown quartz single crystal

autoclaves was developed (Chap. 10 "Crystal Growing"), which provides high-purity crystals for these applications (Fig. 3.24). For this purpose, natural crystal fragments of extreme purity are used as starting material (so-called lascas), which are usually obtained from hydrothermal and pegmatitic deposits as well as metamorphic mobilisates. A complex preparation process involving manual selection, heating/quenching, acid treatment, etc. results in a ratio of starting material to finished raw material of 1:10,000–1:25,000.

There is a wide range of other industrial applications for quartz raw materials, which will only be listed here as examples. Quartz is used for:

- Preparation of SiO_2 gels
- Silicones
- Si alloys, Si metal, Si single crystal synthesis
- SiO_2 as an insulator in microelectronics
- Refractory materials (silica brick)
- Silicon carbide
- Quartz as a slag former in the production of phosphorus
- Quartz sands and gravels for filtering purposes
- Production of cristobalite and quartz powder

This compilation shows the enormous range of quartz raw materials, the use of which requires precise knowledge of the raw material properties and industrial requirements.

3.5 Feldspar

In terms of quantity, feldspar minerals represent the most common mineral group and are involved in the composition of the earth's crust with approx. 60% by mass. Regarding their geological formation, approx. 60% are found in igneous rocks, 30% in metamorphic rocks and 10% in sedimentary rocks.

3.5.1 Structure of Feldspar Minerals

Feldspars are monoclinic and triclinic tectosilicates (framework silicates) of the general formula:

$$\mathrm{A}_x^{+}\mathrm{A}_{1-x}^{2+}\left[\mathrm{T}_{2-x}^{3+}\mathrm{T}_{2+x}^{4+}\mathrm{O}_8\right]$$

with

$$\begin{aligned}&\text{mit} : 0 \le \mathrm{x} \le 1\\&\mathrm{T}^{4+} = \mathrm{Si}^{4+}\\&\mathrm{T}^{3+} = \mathrm{Al}^{3+}\\&\mathrm{A}^{+} = \mathrm{Na}^{+}, \mathrm{K}^{+}\\&\mathrm{A}^{2+} = \mathrm{Ca}^{2+}, \mathrm{Ba}^{2+}\end{aligned}$$

The structure consists of TO_4-tetrahedra connected by corner linkage to form a three-dimensional anion framework. The cations occupy irregular cavities in the tetrahedral framework (Fig. 3.25). In natural feldspars, these are preferentially K^+

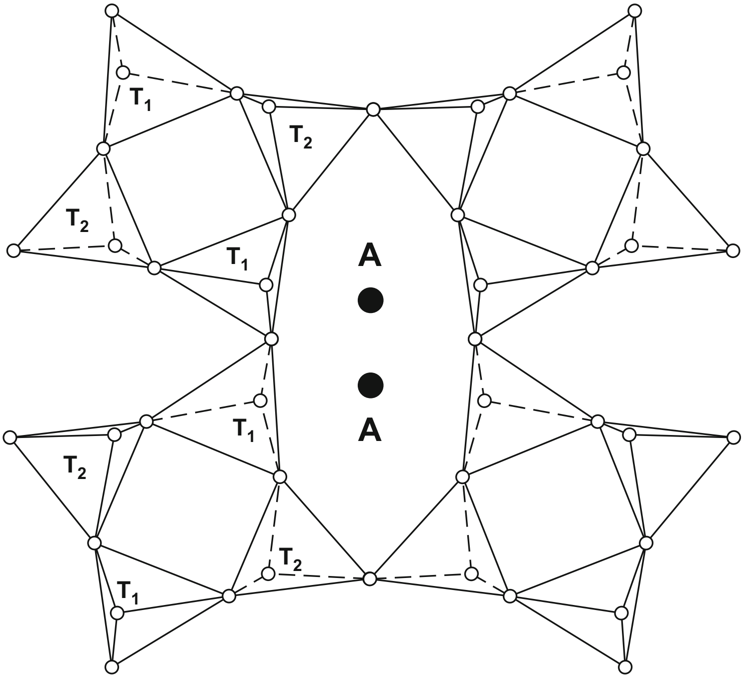


Fig. 3.25 Idealized feldspar structure showing a framework of TO_4-tetrahedra with alternating orientation and large cations (*A*) in structural cavities. (Modified after Götze et al. 2000)

Fig. 3.26 Successful feldspar syntheses (marked with a cross) with different cation and anion substitutions. (Data from Pentinghaus 1970)

M^+	T^{3+}				T^{4+}
	B	Al	Ga	Fe	
Na	x	x	x		Si_3
		x	x		Ge_3
		x			AlSiP
K	x	x	x	x	Si_3
	x	x	x	x	Ge_3
		x			AlSiP
Rb		x	x	x	Si_3
		x	x	x	Ge_3
NH_4		x			Si_3
M^{2+}	T_2^{3+}				T_2^{4+}
		Al_2	Ga_2		
Ca		x	x		Si_2
		x	x		Ge_2
Sr		x	x		Si_2
		x	x		Ge_2
Ba		x	x		Si_2
		x	x		Ge_2
Pb		x			Si_2

(K-feldspars – orthoclase, sanidine, microcline), Na^+ (Na-feldspar – albite), Ca^{2+} (Ca-feldspar – anorthite) and Ba^{2+} (Ba-feldspar – celsian).

Most feldspar minerals can be assigned to the K-Na-Ca system. However, K-Ba feldspars (hyalophane series), $NaBSi_3O_8$ (reedmergnerite) and $NH_4AlSi_3O_8$ (buddingtonite) also occur. Furthermore, extensive substitution occurs in natural feldspars at all structural positions, such as Fe, Ga, Ge, P at the tetrahedral sites and Rb, Li, Cs, Sr, Mn or REE at the cation position. A variety of substitution possibilities were also realized in synthesis experiments (Fig. 3.26).

The complex chemical composition of the feldspar minerals implies that the current symmetry is mainly determined by the T^{3+}:T^{4+} ratio of the respective end-members and the order/disorder of the tetrahedral occupations as well as the size of the A-cations. At equilibrium, disorder corresponds to a high temperature state and order to a low temperature state. Accordingly, at high temperatures Al-Si disorder (monoclinic) prevails and almost complete miscibility in the alkali feldspars and the plagioclases, whereas at low temperatures there are tendencies towards order (triclinic) and associated segregation (perthite – antiperthite) (Fig. 3.27).

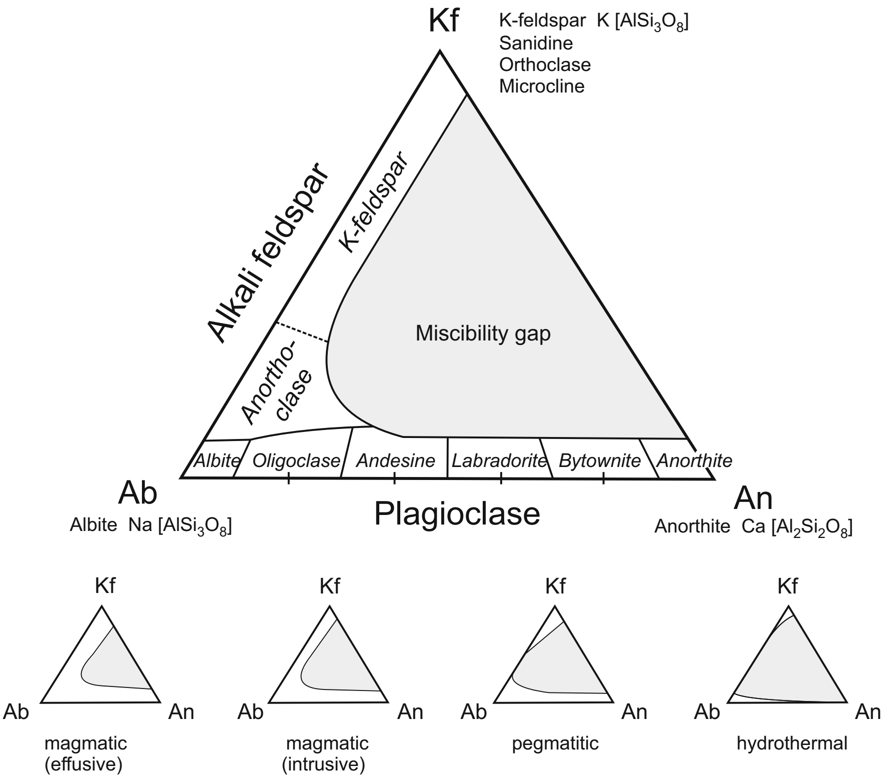


Fig. 3.27 Feldspars in the K-Na-Ca system and miscibilities at different temperatures (geological conditions of formation). (Modified after Rösler 1981)

3.5.2 Feldspar Raw Materials

Feldspars are important raw materials for the ceramic and glass industries. In the ceramic industry feldspar is used as a fluxing agent (property raw material), in the glass industry as supplier for Al (element raw material). In addition, feldspar is also required in other branches of industry, such as the electrical industry, the abrasives industry, the chemical industry and the iron and steel industry. Approximately 10 million tons of feldspar raw materials are mined worldwide every year.

An important application criterion for the use of feldspars in different industrial fields is the chemical composition, especially the K_2O:Na_2O ratio. Alkali feldspars are characterized by a wide temperature interval of softening and are therefore well suited for ceramic firing (porcelain) and enamel production. Plagioclases, on the other hand, have a narrow softening interval, which causes difficulties with regard to the stability of the ceramic raw body during the sintering process. Since albite also has a low melting point, plagioclases are mainly used as glaze feldspars or as raw materials in the glass industry (Al_2O_3-content).

The main customer for feldspar is the ceramic industry. In hard porcelain, the proportion of K-feldspar in the raw material mixture is 20–30% by mass (Chap. 4 "Ceramics"). In particular, potassium feldspar with a K_2O/Na_2O ratio ≥3 is used here. Criteria for the raw material quality are the chemical composition (K_2O, Na_2O, CaO, Fe_2O_3) and the phase characteristics. Chemical investigations and X-ray diffraction are used as analytical methods for this purpose.

3.5.3 Geological Conditions of Formation and Feldspar Deposits

Feldspar minerals are formed throughout the complete igneous range, during metamorphic processes, and in the pegmatitic to hydrothermal environment. In igneous rocks, feldspars show a clear increase in potassium feldspar contents in the trend from basic to acidic environments. Thus, the $K_2O:Na_2O$ ratio increases, which is important for the quality of the raw material. However, the extraction of monomineralic feldspar fractions from these mostly fine-grained igneous rocks is difficult. Therefore, in some cases, feldspar-rich rocks are used directly as raw materials. Examples are the use of nepheline syenites as Al raw material or the use of leucocratic granites, aplites and Fe-poor quartz rhyolites as raw materials for the glass industry.

The main feldspar raw materials worldwide are pegmatites. Here, feldspars with a very favourable chemical composition ($K_2O:Na_2O$ 2–5) occur in large areas, sometimes forming giant crystals as large monomineralic raw material bodies. As a result, a very high-quality product can be obtained in opencast mining by selective mining and hand selection (Fig. 3.28).

Sedimentary formation of feldspar sands (arkoses) can produce a natural high-quality feldspar raw material. Under surface conditions with predominantly arid climate and weak chemical weathering, the feldspar minerals are not completely converted into clay minerals. In result, selective enrichment of potassium feldspar occurs in the sediments due to the higher chemical stability compared to plagioclases. Such feldspar sands contain up to 30 mass-% potassium feldspar with extreme $K_2O:Na_2O$ ratios of up to >20 and, with low iron contents, are highly

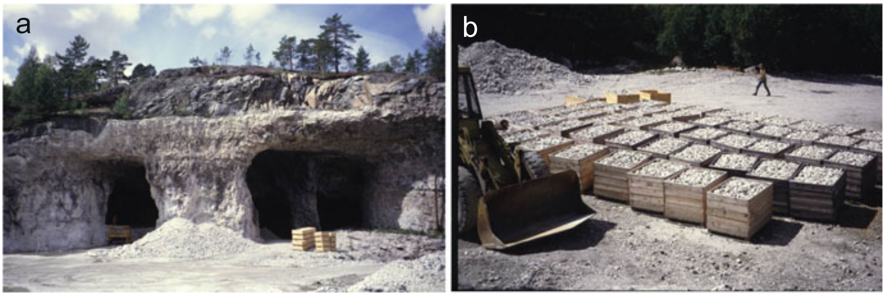


Fig. 3.28 Exploitation of feldspar in the pegmatite deposit Li (Evje-Iveland, Norway)

sought-after raw materials for the ceramic industry. Feldspar-rich river gravels with up to 75% feldspar content or feldspar-bearing clays (e.g. Hirschau-Schnaittenbach deposit in Germany) can also be used as valuable raw materials in the ceramic industry.

The formation of feldspar-rich rocks (e.g. gneisses) also occurs under metamorphic conditions. However, extraction and use is hardly possible due to the extreme fine-grained rock texture and the intergrowth of feldspar with other minerals. Due to geological processes within metamorphic rock complexes, however, metamorphogenic mobilisates with almost monomineralic feldspar composition can be formed. With sizes of several metres to hundreds of metres, they can be used as raw materials due to their chemical purity. For example, local deposits of such mobilisates in the Mulde valley near Dresden (Saxony) were historically used as raw materials for the famous Meissen Porcelain Manufactory.

3.6 Mica Minerals

The mica minerals belong to the class of phyllosilicates. Of the more than 30 minerals in this group, only muscovite and phlogopite play a role in industrial and technical applications (Table 3.3). The compilation of their properties illustrates why muscovite clearly predominates in industrial applications (Madhukar and Srivastava 1995).

The worldwide production amounts to a few hundred thousand tonnes per year, whereby a distinction is made between block mica, split mica (so-called splittings) and waste mica (powder) in terms of size, morphology and quality. The production of high quality block mica worldwide is only about 5000 t per year, of which more than 90% comes from India and Russia. The gentle mining process is difficult to mechanise and the processing and preparation costs are high.

The chemical composition of muscovite and phlogopite may vary within certain limits. A consequence of the variability in chemical composition is the fluctuation of

Table 3.3 Comparison of selected properties of muscovite and phlogopite

Property	Muscovite $KAl_2[(OH,F)_2/AlSi_3O_{10}]$	Phlogopite $KMg_3[(OH,F)_2/AlSi_3O_{10}]$
a_0 (in Å)	5.19	5.33
b_0	9.04	9.23
c_0	10.04	10.26
Density [g cm^{-3}]	2.7–2.9	2.4–2.9
Solubility in boiling HNO_3	Stable	Unstable
Vickers hardness (in N mm^{-2})	1549–2324	1177–1432
Compressive strength (in N mm^{-2})	$78–120 \cdot 10^3$	$29–59 \cdot 10^3$
Specific electrical resistance (in Ωcm)	$2.8 \cdot 10^{17}$	$9.4 \cdot 10^{15}$
Thermal conductivity (in cal (cm s grd)$^{-1}$)	$3.7–9.4 \cdot 10^{-4}$	$6.1–9.6 \cdot 10^{-4}$

properties. Structural disorder and macroscopic and microscopic inclusions also affect the physical and technical properties of muscovite and phlogopite. The main properties and industrial requirements that make mica (especially muscovite) a desirable raw material and material include:

- giant crystals
- perfect fissility
- very good punching and cutting properties
- high compressive strength
- low electrical conductivity
- low thermal conductivity and heat resistance
- high transparency and infrared transmission
- good welding and metallurgical properties

In the past, muscovite was used to a large extent in electrical engineering/electronics. Because of its good insulating effect and high dielectric constant, mica was incorporated into receiver tubes and capacitors to maintain distance. Due to the development of other materials in the modern electronics industry, these applications have declined considerably (Chap. 8 “Mineral Materials in Electrical Engineering/Electronics”).

Nevertheless, there are still numerous specific areas of application for block mica in technology where only few or no alternative materials exist. An overview of the relationship between properties and technical use is shown in Fig. 3.29.

Splittings and waste mica also have specific applications. Historically, splittings were glued to paper, silk or fabric with shellac (so-called micanites) in order to achieve larger dimensions and to use the material as an alternative to block mica. Today, mica insulating materials, foil mica and mica paper are manufactured on the basis of mica splittings. These materials are used to insulate rotating electrical machines (e.g. in generators) or as heating conductor supports and insulation for numerous resistance lines in electric heaters, irons, ovens, etc.

Due to the high technical requirements for mica, attempts have also been made to synthesize muscovite and phlogopite by hydrothermal processes and via melts of corresponding composition. The synthetic mica is thermally more stable, has lower dielectric losses and better transparency. However, it was only possible to produce large-format phlogopite slabs, whereas no economically viable size could be achieved for muscovite.

Attempts have also been and are still being made to substitute muscovite in particular with various alternative materials such as glass or plastic. However, mica is still used in many traditional applications due to its outstanding properties.

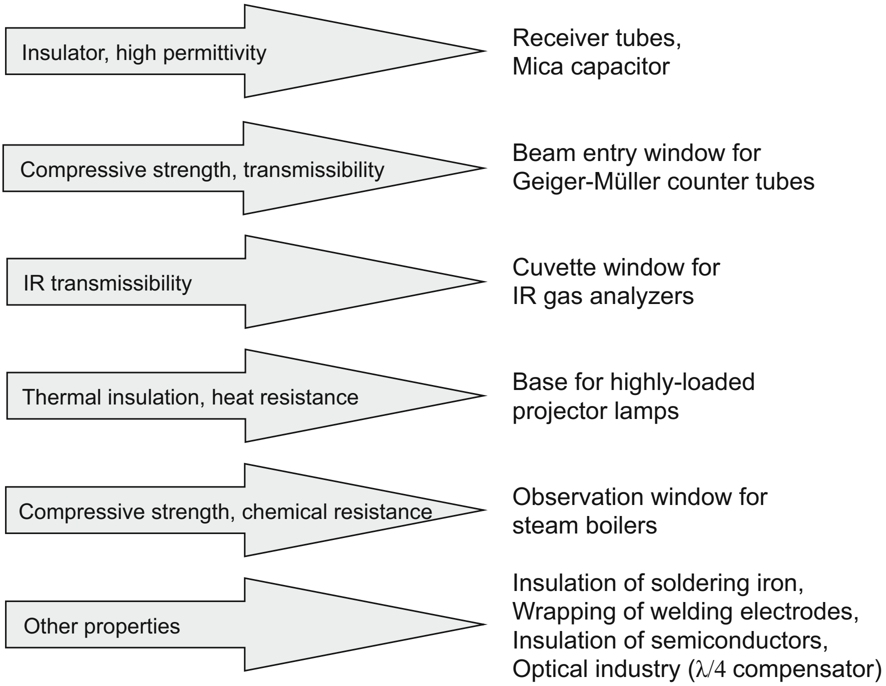


Fig. 3.29 Schematic representation of the relationship between properties and technical use of muscovite

3.7 Carbonates

Among the ca. 60 carbonates occurring in nature, only calcite ($CaCO_3$ – trigonal), aragonite ($CaCO_3$ – orthorhombic), dolomite ($CaMg(CO_3)_2$) and magnesite ($MgCO_3$) are important as rock-forming minerals. They occur in igneous, metamorphic and sedimentary rocks and can form during both inorganic and organic processes.

Carbonates are typical bulk raw materials, for which the transport costs usually significantly exceed the costs of extraction and processing. Depending on the physical and chemical properties, there are numerous industrial applications that can essentially be divided into four groups:

- unfired carbonate rocks
- burnt lime, sintered dolomite, sintered magnesite
- limestone for cement production
- optical calcite (Iceland spar)

While high-quality optical calcite with a production volume of a few hundred tonnes per year (USA, Australia) only plays a subordinate role in terms of quantity, several billion tonnes of carbonates are mined annually worldwide for different fields of application, with limestone (main mineral calcite) dominating in terms of quantity. In the following, the special requirements for carbonates in different areas of application will be discussed in more detail.

3.7.1 Unburnt Carbonate Rocks

Carbonate rocks are used directly in various industrial branches. Traditionally, limestone was and is used as building stone and decorative stone (Sect. 3.1 “Natural stone”). Large quantities are additionally used in the following sectors:

- Aggregates industry
- Pig iron production
- Glass industry
- Agriculture (fertilizer and feed lime)
- Fillers and carrier substances

Unfired carbonate rocks are important aggregates for various concrete products in building construction as well as cement- and bitumen-bound roadways in civil engineering. Due to the good compatibility with cement and mortar, high strengths are achieved in construction products, so that they are preferably used for construction elements with static loads. When used in road construction, on the other hand, the abrasion resistance of road surfaces with carbonate aggregate is significantly lower than with hard aggregate. Important quality requirements for carbonates used as aggregates are the absence of organic components, sulphur, chloride and nitrate compounds as well as low contents of clay minerals.

In pig iron production, carbonates (limestone, dolomite) are used as fluxes and slag formers (Chap. 14 “From Ore to Steel”). The addition of $CaCO_3$ lowers the melting temperature of pure Fe_2O_3 by approx. 400 °C. Besides, the addition of limestone in the blast furnace or in casting processes leads to the formation of an easily melting basic slag and to the binding of sulfur and other harmful components. The main requirements of carbonates for metallurgical processes are a high $CaCO_3$ content and low S content.

Ground limestone is an indispensable raw material in the glass industry as a CaO component in CNS glass (soda-lime silicate glass – Chap. 5 “Glass”). After grinding to the appropriate grain size (approx. 0.1–0.5 mm), the limestone is added to the glass batch (approx. 10 mass-% CaO). High demands on the chemical purity of the raw material are particularly necessary here, as various elements such as Fe, Cr or Mn can lead to undesirable colouring of the glass.

Carbonate rocks are also an important raw material in agriculture. Fertilizer lime or fertilizer marl ensure that the removal of the elements Ca and Mg, which are important for the plants, is compensated for by harvesting and leaching in the soil. At the same time, this neutralises the soil and improves the soil structure. High-quality ground limestone is also used as feed lime in animal breeding.

A special field of application is the use of $CaCO_3$ as a filler in the rubber and plastics industry and as a pigment and carrier in paints (Sect. 3.10 “Mineral fillers”). The high quality requirements, such as extremely fine grain sizes (98% < 10 μm), large specific surface area and high chemical purity, can only be met by special raw materials. For instance, so-called chalk is used here, a very fine-grained and mostly white limestone, which was mainly formed from organic remains.

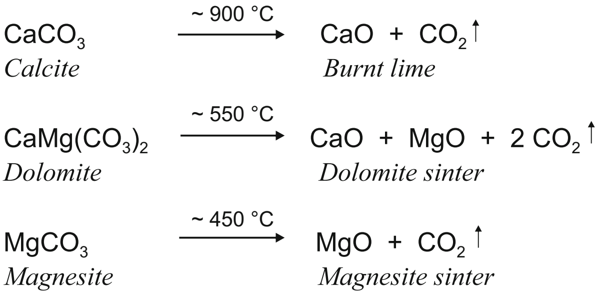
3.7.2 Burnt Lime, Sintered Dolomite and Sintered Magnesite

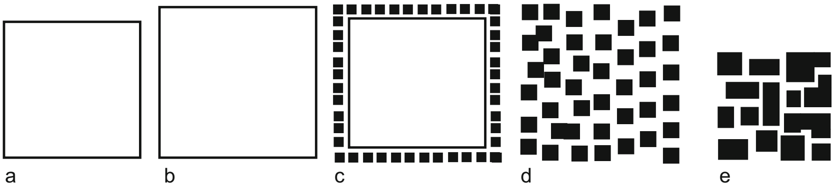
The term quicklime covers all carbonate raw materials that are thermally pretreated before use. In this process, lumpy raw material is burnt in a shaft kiln or rotary kiln, and the carbonates decompose at different temperatures to form oxides and CO_2 (Fig. 3.30).

As can be seen in Fig. 3.31, the firing process occurs in several stages, so a controlled firing regime is necessary for complete conversion. The type of firing unit, the strength and grain size of the raw material and non-carbonate impurities can influence the process.

Quicklime is used in various industries such as the chemical industry, metallurgy or the building industry. A high chemical purity (if possible 100 mass-% CaO) is

Fig. 3.30 Dissociation reactions of the carbonates during the burning process




a Limestone at room temperatur

b Thermal expansion before starting decalcination

c Surficial decalcination, increasing pore volume

d Final decomposition with growth of CaO crystals, max. pore volume (52%)

e Growth and sintering of CaO crystals, decrease in pore and sample volume

Fig. 3.31 Reaction stages in the thermal treatment of limestone required in the chemical industry, in metallurgy low contents of impurities such as S, SiO_2 or MgO are required.

Sintered dolomite is a high-grade product in the refractory industry (Chap. 7 “Refractory Materials”). It is used as a refractory lining for smelting and casting aggregates in metallurgy or kiln plants in the cement industry. Magnesite is mainly used in calcined (600–1000 °C – caustic magnesia) and dead-burned form (1700–2000 °C – sinter magnesia) in the refractory sector. Fused magnesia, which is produced at temperatures of 2800–3000 °C in an electric arc furnace, is a high-purity special product.

3.7.3 Limestone for Cement Production

Limestone is an indispensable raw material for the production of cement, as it represents the main raw material next to clay with approx. 85% by mass. The required amount of raw material can be estimated if one assumes that several billion tons of cement are produced worldwide every year. Due to the extreme quantities of raw materials, cement plants are usually stationed directly at the corresponding raw material deposits in order to minimize transport routes.

Limestone is fired together with clay in a rotary kiln where, at temperatures around 1500 °C, the clinker phases tricalcium silicate (C_3S – “alite”), β-dicalcium silicate (C_2S – “Belite”), tricalcium aluminate (C_3A) and tetracalcium aluminate ferrite (C_4AF – “Celite”) are formed (Chap. 6 “Building Materials and Binders”). For optimum cement production, the ratios of the main chemical components CaO, Al_2O_3, SiO_2 and Fe_2O_3 must be matched. A control is provided by specific raw material parameters (Fig. 3.32). For the reaction process, marly limestones are favorable because they have a reactive surface.

Lime standard $= \dfrac{100\ CaO}{2.8\ SiO_2 + 1.18\ Al_2O_3 + 0.65\ Fe_2O_3}$ **95 ... 100**

Silicate module $= \dfrac{SiO_2}{Al_2O_3 + Fe_2O_3}$ **1.8 ... 2.5**

Alumina module $= \dfrac{Al_2O_3}{Fe_2O_3}$ **1.5 ... 2.2**

Fig. 3.32 Chemical standards for the evaluation of the raw material mixture for cement

3.7.4 Deposits of Carbonate Rocks

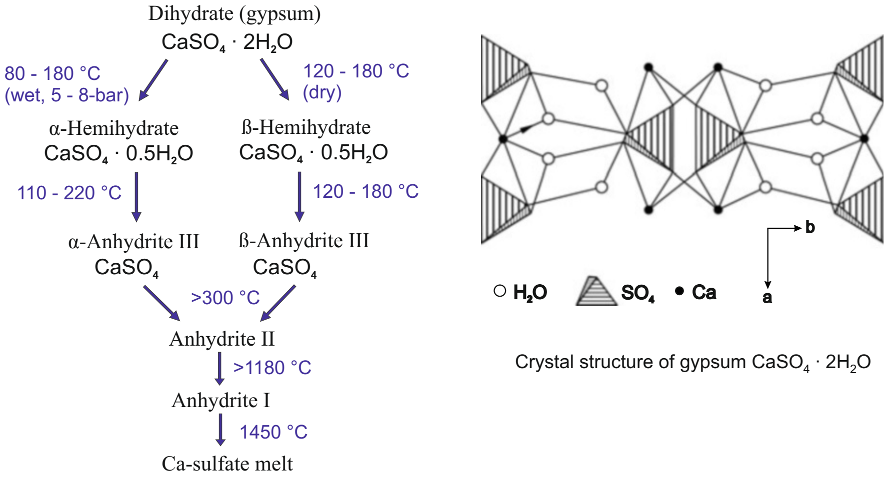
Raw materials for the industrial use of carbonate rocks are preferably obtained from near-surface deposits of sedimentary origin. In Germany and Central Europe, massive deposits of high-quality limestones and carbonates occur in particular in the Devonian (mass limestones), Triassic (Muschelkalk) and Jurassic geological periods. In the Upper Cretaceous there are deposits of the so-called chalk, which is used as a high-quality special raw material.

3.8 Sulphates

Calcium sulphates are the only group of industrially interesting sulphates and occupy a certain special position among the mineral raw materials. They belong to the easily soluble sedimentary rocks and possess the property of transforming into various anhydrous and hydrous compounds under different thermochemical conditions (Fig. 3.33). This property is the basis for their use as building materials.

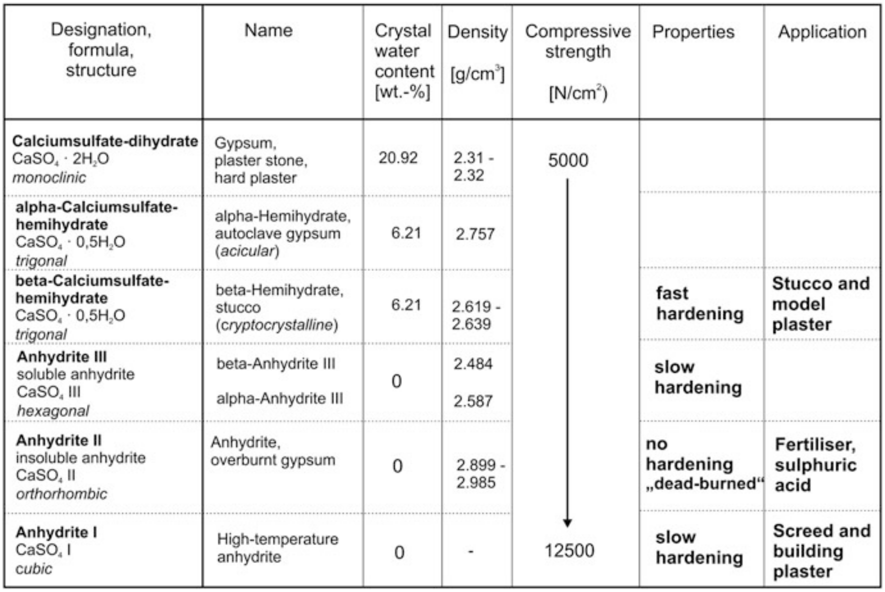
The $CaSO_4$-water system is characterized by five different compound types (Figs. 3.33 and 3.34), of which only gypsum ($CaSO_4 \cdot 2\,H_2O$) and anhydrite ($CaSO_4$) occur naturally. They can crystallize primarily from sulfate-saturated solutions or transform into each other by secondary processes. While anhydrite is mainly used for the production of fertilizers and sulfuric acid, gypsum has been used as a building material since ancient times and is of great importance in the binder industry (Langbein et al. 1982).

Hemihydrate and anhydrite III can occur as morphologically distinct α- and β-forms, with the formation of the α-forms being linked to the existence of a liquid



Crystal structure of gypsum $CaSO_4 \cdot 2H_2O$

Fig. 3.33 Main phases in the system $CaSO_4$-water with corresponding transformation temperatures. (Modified after Auras 2015)



Designation, formula, structure	Name	Crystal water content [wt.-%]	Density [g/cm^3]	Compressive strength [N/cm^2)	Properties	Application
Calciumsulfate-dihydrate $CaSO_4 \cdot 2H_2O$ *monoclinic*	Gypsum, plaster stone, hard plaster	20.92	2.31 - 2.32	5000		
alpha-Calciumsulfate-hemihydrate $CaSO_4 \cdot 0,5H_2O$ *trigonal*	alpha-Hemihydrate, autoclave gypsum (*acicular*)	6.21	2.757	↓		
beta-Calciumsulfate-hemihydrate $CaSO_4 \cdot 0,5H_2O$ *trigonal*	beta-Hemihydrate, stucco (*cryptocrystalline*)	6.21	2.619 - 2.639	↓	**fast hardening**	**Stucco and model plaster**
Anhydrite III soluble anhydrite $CaSO_4$ III *hexagonal*	beta-Anhydrite III alpha-Anhydrite III	0	2.484 2.587	↓	**slow hardening**	
Anhydrite II insoluble anhydrite $CaSO_4$ II *orthorhombic*	Anhydrite, overburnt gypsum	0	2.899 - 2.985	↓	**no hardening „dead-burned“**	**Fertiliser, sulphuric acid**
Anhydrite I $CaSO_4$ I *cubic*	High-temperature anhydrite	0	-	12500	**slow hardening**	**Screed and building plaster**

Fig. 3.34 Important properties of the phases in the system $CaSO_4$-water

phase. Anhydrite II is technically produced by burning anhydrite III, whereas anhydrite I is formed above 1180 °C under atmospheric conditions. In addition, $CaSO_4$ also exists as a melt.

During dehydration, water is partially or completely split off by temperature increase, resulting in higher density and higher compressive strength by recrystallization (Fig. 3.34). Complete dehydration results in higher chemical inertness.

According to the firing temperatures and the furnace aggregates used, each $CaSO_4$ phase has specific properties that are important for certain technical uses. For example, hemihydrate has fast-setting properties, while anhydrite I and III set more slowly. Stucco and model plasters therefore consist mainly of hemihydrate (subordinate anhydrite III), while anhydrite I is used as the main component of screed and building plaster. Anhydrite II (“dead-burned gypsum”) has no useful setting properties and is therefore undesirable in burnt gypsum. It is mainly used for the production of fertilizers or in the chemical industry for the production of sulfuric acid and ammonium sulfate.

From the facts presented, it can be seen that calcium sulphates can be used industrially in different forms. As an elemental raw material (ingredient raw material), gypsum and anhydrite have the same areas of application in the chemical industry, in fertilizer production and in the cement industry (setting regulation). Burnt gypsum, on the other hand, is a typical property raw material whose reactivity and setting behaviour are used. It is used in the construction industry, in arts and crafts, in the ceramics industry (moulds for slip casting porcelain) and in medicine.

Various industrial processes produce various Ca sulphates as by-products or waste products, which can be used as secondary raw materials. Examples of such processes are phosphoric and hydrofluoric acid production, residues from potassium salt extraction or sulphate residues from flue and exhaust gas desulphurisation (Chap. 11 "Mineralogical Aspects in Energy Technology"). Gypsum cullet from the ceramics and foundry industries can also be used as calcium sulphate secondary raw materials. Depending on their specific properties, the waste materials are used as burnt gypsum, as setting regulators in the cement industry or as raw materials for sulphuric acid production.

3.9 Zeolites

The name zeolite comes from the Greek and means something like "boiling stone" in reference to the swelling of the minerals when heated. The group of zeolites includes minerals with a complex chemical composition (Gottardi and Galli 1985). The empirical molecular formula is:

$$\left(\mathrm{M}_2^{+}, \mathrm{M}^{2+}\right)\mathrm{Al_2O_3}\, m\,\mathrm{SiO_2} \cdot n\,\mathrm{H_2O}$$

with

$$\mathrm{M}^{+} = \mathrm{Na}^{+}, \mathrm{K}^{+}$$
$$\mathrm{M}^{2+} = \mathrm{Ca}^{2+}, \mathrm{Mg}^{2+}$$

3.9.1 Structure

The basic building blocks of zeolites are $(\mathrm{Si,Al})\mathrm{O_4}$-tetrahedra, with several molecules connecting across the corners to form rings of four, six and eight. Charge balance is provided by monovalent and divalent cations, and zeolites also contain water (Fig. 3.35).

The group of zeolites consists of different types of structures, which are classified according to the different channel systems into:

- Zeolites with one-dimensional channels (fibrous zeolites, e.g. natrolite), which link one-dimensional chains of 4-membered rings in various combinations.
- Zeolites with two-dimensional channels (foliated zeolites, e.g. desmin), which form a two-dimensional structural system through a mixed combination of rings of 4, 6 and 8
- Zeolites with three-dimensional channel systems (cube zeolites, e.g. chabasite), consisting of a spatial structure system with a combination of 4, 6 and 8 rings.

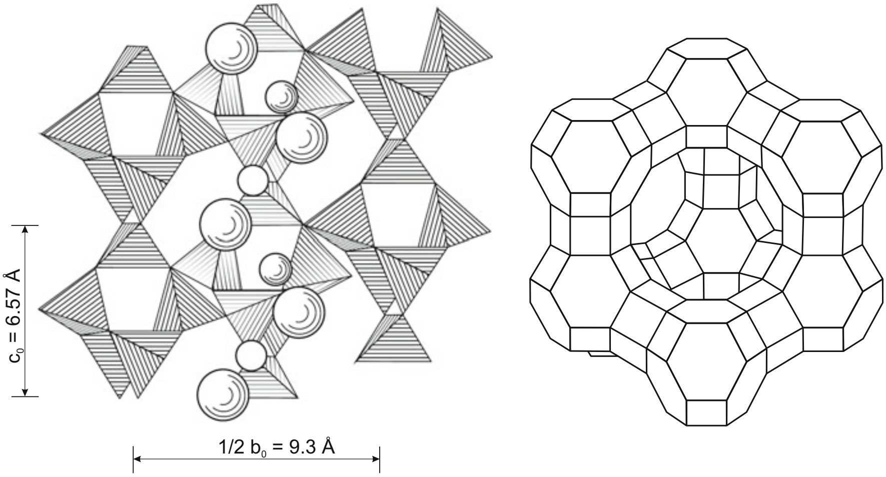


Fig. 3.35 Zeolite structure (ex. natrolite) in the direction of the a-axis with water molecules (large spheres) and cations (small spheres) in the channels perpendicular to the $(Si,Al)O_4$-tetrahedral chains; the right figure schematically shows the linkage to ring structures, with the tetrahedra reduced to points making up the corners of the ring structure for clarity. (Modified after Rösler 1981)

3.9.2 Properties and Applications

The zeolite structure represents a natural sieve with cavities in the order of 0.3–0.9 nm. This structure conditions the industrial use as molecular sieves and ion exchangers.

The effect as a molecular sieve enables, for example, the effective separation of components of different structure with overlapping boiling points or azeotropic mixtures. Impurities, e.g. from gas streams, can also be removed down to a few ppm.

The ion exchange capacity of zeolites is based on the weak binding of ions to the zeolite framework, which allows easy exchangeability with other ions. Due to the cavities, the specific surface area of zeolites is several 100 $m^2\ g^{-1}$ and is therefore suitable as a catalyst in material conversion processes (e.g. cracking/petroleum refining in petrochemistry), as a carrier or for drying and purifying gas streams. In the construction industry, tuffs rich in erionite are used as building materials or aggregates for pozzolanic cements.

3.9.3 Natural Occurrence and Synthesis

Natural zeolites are formed in various areas worldwide during the alteration of volcanic rocks (e.g. USA, Japan, Turkey, Fig. 3.36). They form when water reacts with volcanic glass, clays and feldspars under alkaline conditions (marine and/or

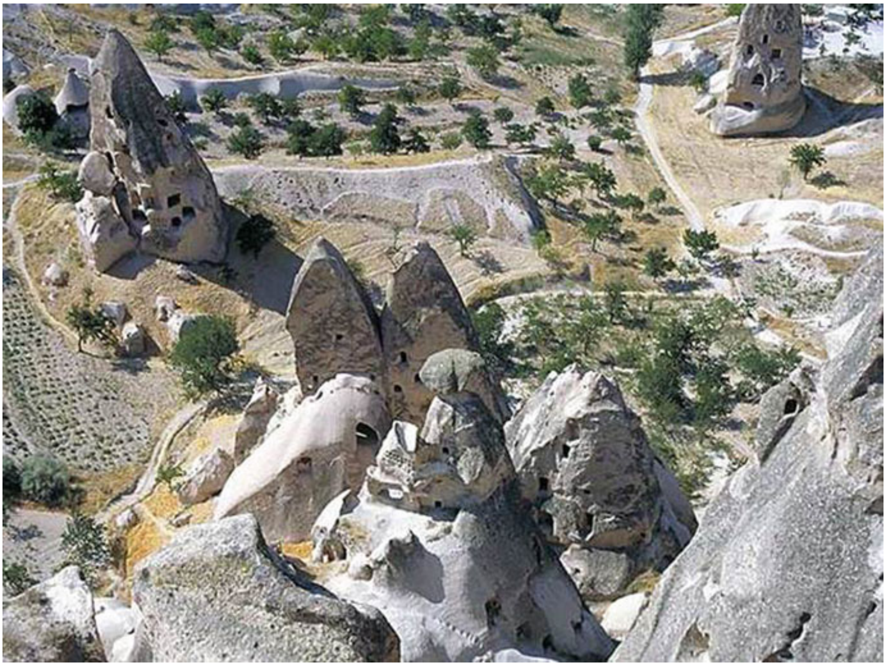


Fig. 3.36 Occurrence of erionite in volcanic tuffs of Cappadocia (Turkey)

hydrothermal alteration). World production of zeolites amounts to several million tonnes.

For constant material properties, high-quality zeolites are also synthesized. After mixing the reactants to form an amorphous gel, hydrothermal treatment takes place for several days in an autoclave at 100–220 °C under alkaline conditions.

3.10 Mineral Fillers

In many areas of industry, fine-grained mineral fillers and carrier substances are used which, due to their consistency, guarantee or improve essential quality properties of the corresponding materials and at the same time reduce the costs of these products. The proportion in various industrial products can be more than 90%.

By definition, fillers are solid, fine-grained, natural and synthetic, inorganic or organic substances which are insoluble in the base material and which are added in varying proportions to a mostly organic base material in order to reduce the quantity of the base material used and/or to adapt its properties specifically to the process of use.

The special function of carriers is to bind an active substance to them by sorption and to release it again under certain conditions. Dyes, on the other hand, should have

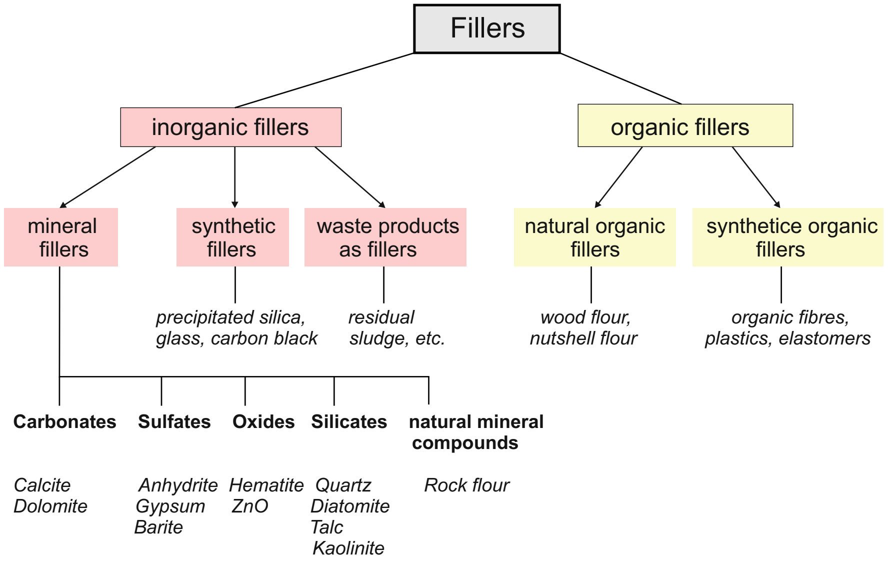


Fig. 3.37 Overview of important fillers

a relative refractive index >1 compared to their coating material and have a color-providing or color-covering function.

For industrial use, a whole range of properties is necessary to meet the above requirements:

- fine-grained mineral powder (<1 μm)
- granulometric properties (grain-size distribution, shape, surface)
- tight binding capacity
- dispersion behaviour
- hardness, density
- refraction, colour (whiteness)
- solubility in water, alkalis, acids
- thermal behaviour
- chemical composition, purity

From this compilation it can be seen that the requirements for fine-grained fillers are extremely complex and therefore only a few minerals and substances fulfil these conditions. Figure 3.37 shows a list of some important fillers.

Depending on the application, the corresponding fillers can be used untreated or surface-treated. Filler mixtures and combinations are also possible for property optimization.

From the group of inorganic mineral raw materials, the most important are calcite ($CaCO_3$), barite ($BaSO_4$), talc ($Mg_3[(OH)_2/Si_4O_{10}]$) and kaolinite ($Al_2[(OH)_4/Si_2O_5]$) as important fillers. Calcite is preferred in the plastics and elast industries due to its good polymer compatibility. In addition, it is also suitable as a carrier for pesticides. Calcite, barite and talc are widely used in the paint and varnish industry. In the paper industry, kaolinite, calcite, barite and, for special papers, TiO_2 (anatase) and zeolites are mainly used. The range of mineral fillers and carriers used in pharmaceuticals and cosmetics includes the phyllosilicates talc and kaolinite as well as palygorskite and silica (SiO_2).

3.11 Gemstones

Gemstones have been sought-after minerals since ancient times. The specific properties that make a mineral a gemstone are primarily high hardness and special optical properties and effects – but rarity is also an important criterion (Baumgärtel et al. 1989). Although the world production of gemstones is only about 10–12 tons annually, the gemstone market adds enormous value. A high-quality diamond alone can fetch a price of over $5000 per carat (0.2 g). For this reason, gemstones represent important mineral raw materials, especially in terms of value, which are to be presented here as well. However, various gemstones also possess excellent physical and technical properties that are indispensable for certain branches of industry (Chap. 9 "Natural and Synthetic Hard Materials").

3.11.1 Classification and Formation of Precious Stones

Only about 100 minerals of the appropriate size and formation are considered to be gemstones. The diamond dominates the entire gemstone market with approx. 95% (Fig. 3.38). The red and blue color varieties of corundum (Al_2O_3), ruby, and sapphire, as well as the emerald (green beryl – $Be_3Al_2[Si_6O_{18}]$) occupy another ca. 5%, while the rest of the gemstone market of <1% is accounted for by the remaining hundred minerals.

Gemstones can be divided into natural substances and artificial products:

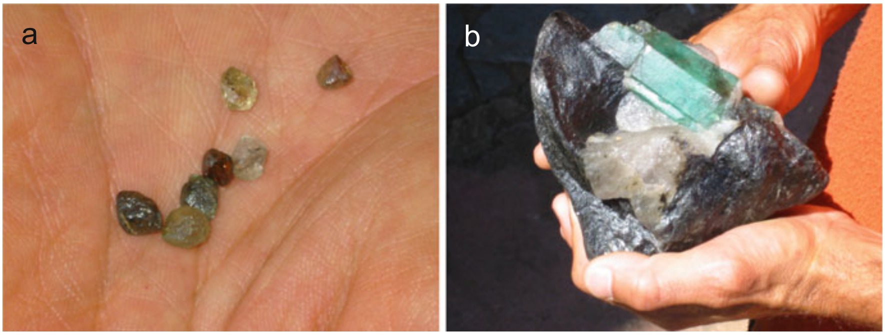


Fig. 3.38 Rough diamonds from Diamantina, Brazil (**a**) and emerald from Belmont, Brazil (**b**)

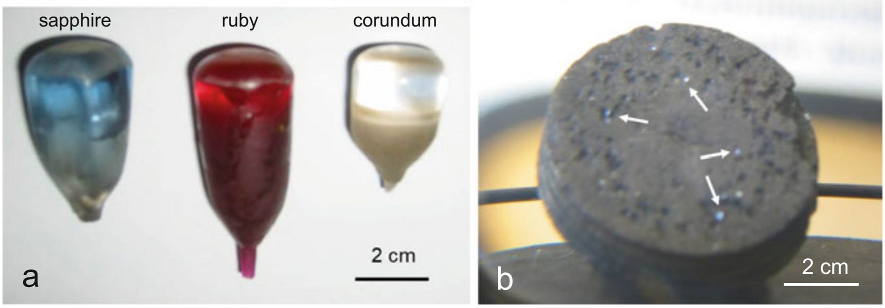


Fig. 3.39 Pear-shaped crystals of sapphire, ruby and precious corundum from Verneuil synthesis (**a**) and small diamond crystals (*arrows*) in graphite matrix from the belt press (**b**)

- natural substances
- artificial products
  - synthetic stones
  - composite stones
  - imitations
  - reconstituted stones

Taking gemstone prices into account, it is understandable that gemstone treatments to achieve better quality/colour (e.g. heat treatment, irradiation) and artificial products (especially imitations) play and have always played a major role in the gemstone sector. Imitations have traditionally been dominated by glass, since virtually any color can be produced. More recently, other modern materials have also been used as imitations, especially for diamond. Specific names such as "Arizona Ruby" for red garnet (pyrope), "Bohemian Diamond" for rock crystal or "Brazilian Emerald" for green tourmaline are also used to increase the value of the minerals. Gemstone syntheses are mainly carried out by the Verneuil process from the melt (e.g. corundum, spinel, Fig. 3.39), by flux-growth (emerald) and in a high-pressure, high-temperature belt press (diamond, Chap. 10 "Crystal Growing").

Natural minerals with gemstone quality can be formed in all geological environments. Of course, early crystallization under high pressures and temperatures (diamond), pegmatites (beryl) and contact metamorphism (corundum, emerald) are of particular interest, as the most important gemstones are formed here. For gemstone mining, however, gemstone placer deposits in marine and fluviatile sediments play the most important role, since here high-quality minerals have been enriched by natural processing and can be mined relatively easily.

Nevertheless, the extraction and processing of gemstone deposits has certain peculiarities:

- extremely low content of gemstone material
- separation from the host-rock without destroying the gemstones

- high digging output required
- determination of gemstone content not possible by chemical analysis

In addition, many deposits are located in poorly developed areas with a lack of infrastructure, making mechanization difficult. Processes with manual preparation are therefore frequently encountered.

3.11.2 Gemstone Properties and Methods of Determination

The determination of diagnostic properties for gemstone identification is usually subject to certain limitations, since destruction of the minerals should/must be largely avoided. Also, already framed jewellery and polished stones do not allow many conventional examination methods, so that only specific methods are used for the analysis of gemstones for characterization. A modern analytical method is e.g. Raman spectroscopy, which enables the non-destructive phase determination of gemstones by vibrational spectroscopy. As a rule, characteristic properties of the minerals are used for diagnosis or differentiation.

Of the mechanical properties, hardness and density play a major role, while cleavability and fracture are particularly important for gemstone cutting and grinding. Gemstones usually have a high hardness (scratch hardness ≥7). For gemstone classification, the normal Mohs scale of hardness is therefore extended in the upper range by some intermediate grades, so that a more precise use is possible:

Mohs hardness	Gemstone
6.5	Nephrite
6.5–7	Olivin
7–7.5	Pyrope
7.5	Beryl
8.5	Chrysoberyl
9.5	SiC

The non-destructive determination of density is also possible for very small mineral aggregates. The hydrostatic scale, the Mohr-Westphal scale or various gravity solutions are used here. The latter are also suitable for separating certain gemstone species based on their different densities. Since imitation gemstones generally have lower hardnesses and densities than genuine stones, they are relatively easy to identify in most cases.

The most important optical property of gemstones is the refraction index. This can be determined with sufficient accuracy using immersion fluids or refractometers (Fig. 3.40). Above all, it is also possible to analyse stones that have already been framed and polished without any problems.

The *colour* is not always applicable as a diagnostic property, since different minerals can occur with the same or similar colours and quite a few minerals can have different colours. In addition, the colours can be decisively changed by

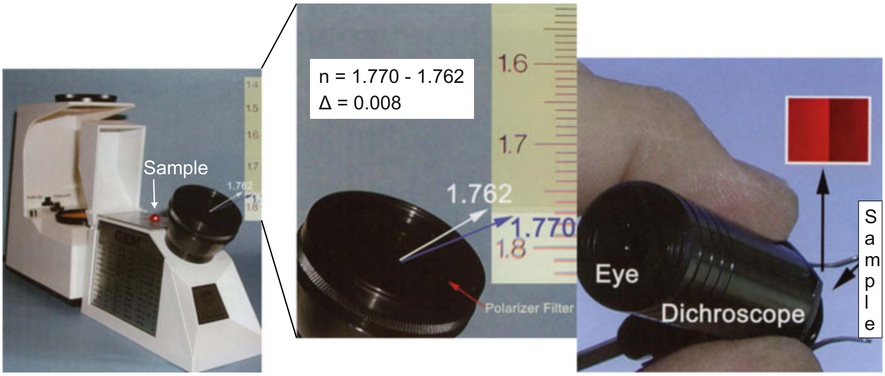


Fig. 3.40 Determination of light refraction *n*, birefringence Δ and pleochroism using a gem refractometer (**a**) and dichroscope ocular (**b**) respectively

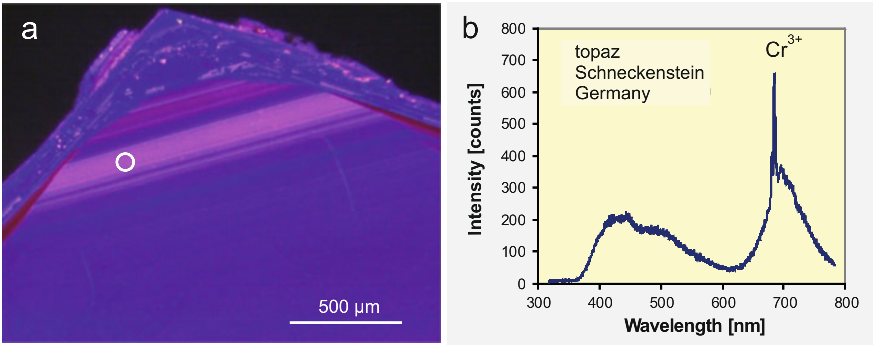


Fig. 3.41 Cathodoluminescence microphoto of a topaz crystal from Schneckenstein (Saxony, Germany) and associated emission spectrum with evidence of trace Cr^{3+} content (the white circle in (**a**) marks the analytical spot)

subsequent heat treatment and/or irradiation. For this reason, attempts are made, for example, to distinguish gemstones of the same colour by means of colour filters (e.g. dichromatic Chelsea filter with transmission at 570 and 690 nm). A more detailed analysis is also possible by evaluating absorption spectra, which in combination with other analytical methods also allows a more precise identification of possible colour centres. As a number of gemstones also exhibit pleochroism, this property is investigated with the aid of a dichroscope ocular, which can also detect very slight colour differences (Fig. 3.40).

Imaging and spectral studies of the luminescence of minerals are also used to diagnose gemstones. Characteristic luminescence properties not only allow different minerals to be distinguished, but can sometimes also provide clues to specific localities or be used to differentiate between natural and synthetic gemstones (Fig. 3.41).

Very important, especially for the use of gemstones in the jewelry industry, is the formation of various special light effects:

- Chatoians (Cat's Eye Effect)
- Asterism
- Silk gloss
- Adularize
- Aventurize
- Labradorize
- Iridescence
- Opalescence

The knowledge and targeted use of these properties makes it possible to achieve striking optical effects that have a significant influence on the value of the jewellery.

3.11.3 Gemstone Processing

Gemstone processing is the most important process in the value chain. Here, the value of the gemstone can be increased many times over through suitable processing. Essentially, the processing of the stones comprises three process steps:

1. Removal of excess material and shaping (ebauching or pre-grinding)
2. Creation of the shape (smooth grinding) or the surfaces (facet grinding)
3. Smoothing the surfaces (polishing) and achieving optical effects

The shape of the cut determines the basic habitus of the stone (e.g. olive, trapezoid, sphere, hexagon), while the type of cut determines the concrete formation (e.g. stair cut, star cut, cross cut). Pure cuts, multiple cuts and also mixed cuts are possible. Taking into account the dominant role of the diamond, the most important type of cut is the brilliant cut. The principle of the shape and, related to this, the course of the rays of light is very similar in the various types of the brilliant cut. The most common shape is that of the fine-cut brilliant (Fig. 3.42).

This cut contains 32 facets on the front and 24 facets on the back and was developed by the Venetian Peruzzi. Due to the exact position and angular relationship of the facets, a maximum light yield (73% of the incident light) is achieved, light refraction and dispersion provide the typical brilliance.

In general, different gemstones are often processed with specific cuts in order to achieve optimal light effects and thus maximum value. Last but not least, the cuts used also depend on the current understanding of fashion.

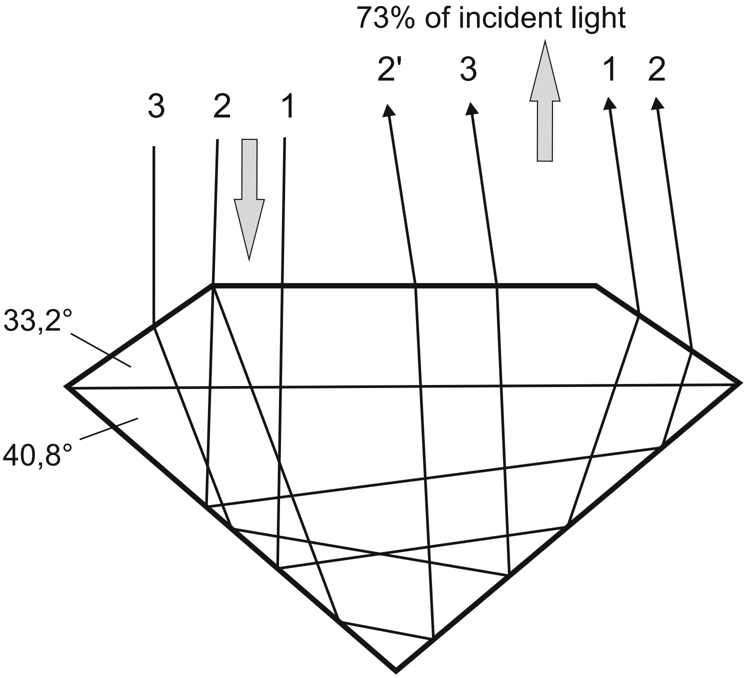


Fig. 3.42 Schematic trajectory of light in the diamond fine-cut brilliant with 32 facets on the front side and 24 facets on the back side

3.12 Evaporites

Occurrences and deposits of evaporites (potash and rock salts, borates, nitrates) can develop wherever evaporation is greater than rainfall. In recent times, these are mainly areas in equatorial high plateaus, desert areas, rain shadow areas of mountains or continental regions (e.g. Andes, Central Asia). In the geological past, very large Phanerozoic deposits were formed, which are suppliers of potash and rock salt worldwide:

- Devonian: western N America, Belarus
- Carboniferous: Paradox Basin, Utah (USA)
- Carboniferous/Permian: Russia (Kama Basin, Ural Mountains), New Mexico/ Texas (USA)
- Zechstein: NW Europe (e.g. Germany, Poland)
- Paleogene/Neogene: Italy, Spain

Through the successive natural evaporation of the saline solutions according to the solubility product, characteristic sequences of Ca-carbonate, Ca-sulphate, halite and

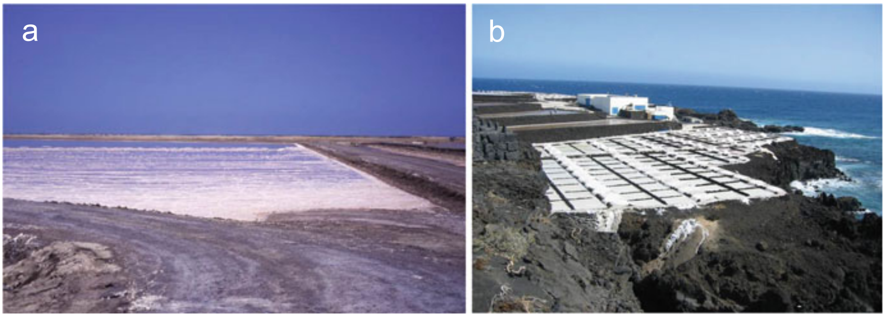


Fig. 3.43 Sea salt extraction on the Atlantic coast near Panther Bacon, Namibia (**a**) and in evaporation basins near Fuencaliente, La Palma Island (**b**)

K-Mg salts are formed in the salt deposits. Today, the natural processes of salt formation are also used for the extraction of sea salt (*solar evaporation)* by evaporation in separated salt water basins by sun and wind (Fig. 3.43).

The salt minerals are used for different industrial applications depending on their chemical composition. Approx. 50–60% of the world production of rock salt (halite, NaCl) is used in the chemical industry. Further applications are found in the food industry, freeze leaching and the oil industry. K-Mg salts (e.g. carnallite $KMgCl_3 \cdot 6\ H_2O$, kainite $KMg[Cl|SO_4] \cdot 3\ H_2O$, kieserite $MgSO_4 \cdot H_2O$), on the other hand, are used almost exclusively for fertilizers. The main producers of potash and rock salt worldwide are the USA, Canada, Germany, Russia and China.

In addition to the traditional salt minerals, borates and nitrates can also be formed by evaporation and form deposits of industrial interest. Borates are formed especially in lakes and playas of desert areas, where they are mined as raw materials for boron extraction. The most important mineral here is borax ($Na_2B_4O_7 \cdot 10\ H_2O$). It is used in insulator materials, textile fiber glass, borosilicate glass, and pharmaceuticals.

The use of nitrates as mineral raw materials is relatively insignificant. Only a fraction of the world's nitrogen consumption is covered by mineral sources. Since 1830, Na and K nitrates (saltpetre) have been mined in the Atacama Desert in Chile.

3.13 Other Industrial Minerals

In the following, a few more industrial minerals will be briefly listed which, although they have comparatively low production values (<1 million to several million t a^{-1}), are nevertheless indispensable raw materials and materials in various branches of industry.

3.13.1 Fluorite

Fluorite (CaF_2) has an extremely wide range of formation as a mineral. Usable deposits are found in hydrothermal-sedimentary formations (*Mississippi Valley type*), in hydrothermal veins, in magmatic alkali complexes, carbonatites and other types of deposits. Depending on the quality, different fields of application are distinguished (Leeder 1978).

The optical industry places extreme demands on the purity and perfection of optical fluorspar for lenses. Therefore, only synthetic fluorite can be used here, which is mainly produced from the melt in the Bridgeman process (Chap. 10 "Crystal Growth"). The best grade of natural fluorites (*acid grade*, >97% CaF_2) is used in the chemical industry for hydrofluoric acid production and for the synthesis of cryolite (Na_3AlF_6) and other fluorides. Cryolite is used as a flux in aluminum production. *Ceramic grade* fluorite (80–96% CaF_2) is starting material for production of special ceramics, enamels, glasses, glass fibers, etc. The lowest grade (*metallurgical grade*, 60% CaF_2) is mainly used as a flux in metallurgy (iron and steel production). Here, however, an extremely low S content is important, which severely restricts the use of hydrothermal fluorite with sulphidic or sulphatic parageneses.

3.13.2 Barite

Barite ($BaSO_4$) is formed mainly in hydrothermal processes, whereby vein-shaped deposits dominate. Various properties of barite are used technically. When barite is used as a gravity agent in drilling suspensions, its high density is exploited. In the plastics, paper and paint industries, barite is used as a filler and for surface finishing. The high degree of whiteness is particularly sought after. In analytical devices for measuring the whiteness of materials and raw materials (leucometre), barite powder is set as standard 100. Barium sulfate is also used as an elemental raw material in the chemical industry.

3.13.3 Graphite

Graphite, the hexagonal carbon modification, is predominantly formed metamorphically from carbon-rich source rocks. Occasionally, however, graphite can also form directly from fluids in hydrothermal deposits. Graphite possesses a whole range of special metallic and non-metallic properties. These include good electrical and thermal conductivity, thermal and chemical resistance and very good sliding properties. This leads to a wide range of technical applications as a refractory material, in the foundry and steel industries, as a lubricant, as an electrode material and in batteries. Traditional is the use in pencils.

3.13.4 Wollastonite

Wollastonite ($Ca_3[Si_3O_9]$) is an interesting mineral, of which no production was recorded until 1930. The increasing interest as an industrial mineral is due to its possible use as an asbestos substitute and to the use of long-fiber wollastonites in plastic composites and ceramics. A further increase in consumption in the coming years is forecast. Wollastonite is mainly extracted from contact metamorphic limestones (calc-silicate rocks).

3.13.5 Zircon/Baddeleyite

The chemical element zirconium is essentially derived from two minerals: Zircon $Zr[SiO_4]$ and baddeleyite ZrO_2. These two minerals are also extreme property raw materials. Zirconium oxide is one of the most resistant refractory materials and is used in various high-temperature materials such as crucibles, chemically resistant furnace bricks, refractory moulding materials or high-temperature cements. It is also used as an abrasive material.

Zirconium is also an alloying constituent of high-speed and hard-cutting steels and armour steels. Special Zr-Sn/Zr-Nb alloys (zircalloy) are used in nuclear technology as cladding material in nuclear fuel rods (Chap. 11 “Mineralogical Aspects in Energy Technology”). Special ceramics based on ZrO_2 are also used as biomaterials or ion conductors. Last but not least, suitable qualities of zircon and baddeleyite crystals can also be processed as jewellery.

The main quantity of zirconium minerals is extracted from sedimentary beach placers. Subordinate extraction also takes place from magmatic deposits such as alkali rocks or carbonatites.

The chemical element hafnium (Hf) behaves geochemically analogous to zirconium and is therefore contained in Zr minerals from which it is extracted. Hafnium is an important component of special materials in nuclear technology, in superalloys and in high-temperature ceramics.

3.13.6 Garnet Group

Minerals of the garnet group are representatives of the nesosilicates and form predominantly during regional or contact metamorphism. They form solid solutions of the general formula:

$$A_3^{2+}B_2^{3+}[SiO_4]_3$$

with

$$A^{2+} = Mg^{2+}, Fe^{2+}, Mn^{2+}, Ca^{2+}$$
$$B^{3+} = Al^{3+}, Fe^{3+}, Cr^{3+}$$

Garnet has been mined for abrasives since the Middle Ages, and even today its main use is as an abrasive (sandblasting agent, polishing agent, waterjet cutting) (Chap. 9 "Natural and Synthetic Hard Materials"). Industrially used garnets are mostly almandine-bearing mixed crystals $\left(Fe_3^{2+}Al_2^{3+}[SiO_4]_3\right)$. Garnets of suitable quality (especially pyrope $Mg_3Al_2[SiO_4]_3$) are also used as gemstones.

3.13.7 Olivine

Olivine $(Mg,Fe)_2[SiO_4]$ is an important mineral constituent of peridotites, the only monomineralic olivine rock is dunite. Olivine used in industry usually has about 50% MgO content. Although a number of deposits exist worldwide, the bulk of the several million tons of world production occurs in the Åheim district in Norway, which has almost unlimited resources (about 30 km^3). The industrial applications of olivine are as a slag former in the iron and steel industry, as foundry sand with high refractoriness, as a component of refractory bricks and as an abrasive material.

3.13.8 Apatite

Apatite $Ca_5[(F,OH)/(PO_4)_3]$, together with frankolite (carbonate-bearing apatite containing about 2% CO_3), is the only mineral source of phosphorus. In most rocks, phosphorus occurs only in concentrations of a few ppm, but phosphates can contain up to 40 mass-% P_2O_5. The main occurrences of apatite occur in magmatic alkali complexes (e.g. Khibine/Kola Peninsula, Phalaborwa/South Africa) and as phosphorite in the marine-sedimentary zone (*upwelling zones* on the continental margin). In addition, there may be local accumulations of bird excrements (so-called guano) that are worth mining (e.g. Christmas Islands, Pacific). A total of several hundred million tonnes are extracted annually worldwide.

Phosphorus is a fundamental element of life, which is why the main use of apatite and phosphorite is in fertilizer production. In this process, the raw materials are decomposed with sulfuric acid to form soluble phosphates that are available to plants. For use in the chemical industry, elemental phosphorus is extracted from apatite in an electrothermal process using quartz as a slag former. Other uses are in the detergent, food and metal industries, in matches, poisons and in the dental industry. Uranium, which can occur in elevated concentrations in apatite, is sometimes extracted as a by-product from certain phosphate deposits.

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Ceramic Materials

4

Ceramic materials comprise a versatile group of materials that have become indispensable in modern industry and technology (Kingery et al. 1960). In addition to silicate ceramic materials, which already have a long tradition and have been used in people's daily lives for many hundreds of years, oxide and non-oxide ceramics are playing an increasing role as modern materials (Fig. 4.1).

According to a proposal by Hennicke (1967), ceramic materials are inorganic, non-metallic, sparingly soluble in water and at least 30% crystalline. As a rule, they are formed from a raw mass at room temperature and obtain their typical material properties by a firing treatment above 800 °C.

Completely new compounds with extreme material properties are being developed in the field of special ceramics (Fig. 4.2). The group of these high-performance ceramics includes, on the one hand, so-called structural ceramics, which are mainly used for components with high mechanical loads (e.g. Al_2O_3, ZrO_2, Sialone; Chap. 9 "Hard Materials"). On the other hand, this also includes so-called functional ceramics in which microstructural effects are exploited, such as ionic conduction, pyro-, piezo- and ferroelectricity or biocompatibility (e.g. $BaTiO_3$, $SrTiO_3$, hydroxyapatite, Chap. 8 "Materials in Electronics" and Chap. 13 "Biomaterials").

The focus in this chapter will be on silicate ceramic materials. These are ceramic materials that are preferably manufactured from silicate raw materials. Differences in grain size, porosity or colour can not only be used as classification criteria for the various materials (Fig. 4.3), they also result in a range of varying physical and chemical properties that are crucial for practical use (Salmang and Scholze 1982). Despite these differences, significant commonalities can be found in the raw materials, rheological behaviour and shaping, as well as the firing process. In the following, some representatives of fine ceramic (porcelain, earthenware) and coarse ceramic materials (bricks, clinker) will be presented.

J. Götze, M. Göbbels, *Introduction to Applied Mineralogy*,
https://doi.org/10.1007/978-3-662-64867-4_4

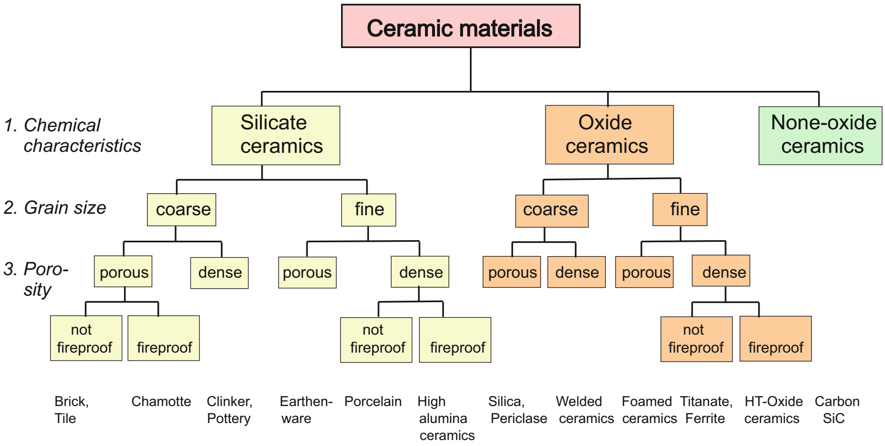


Fig. 4.1 Classification of ceramic materials. (According to Petzold 1991)

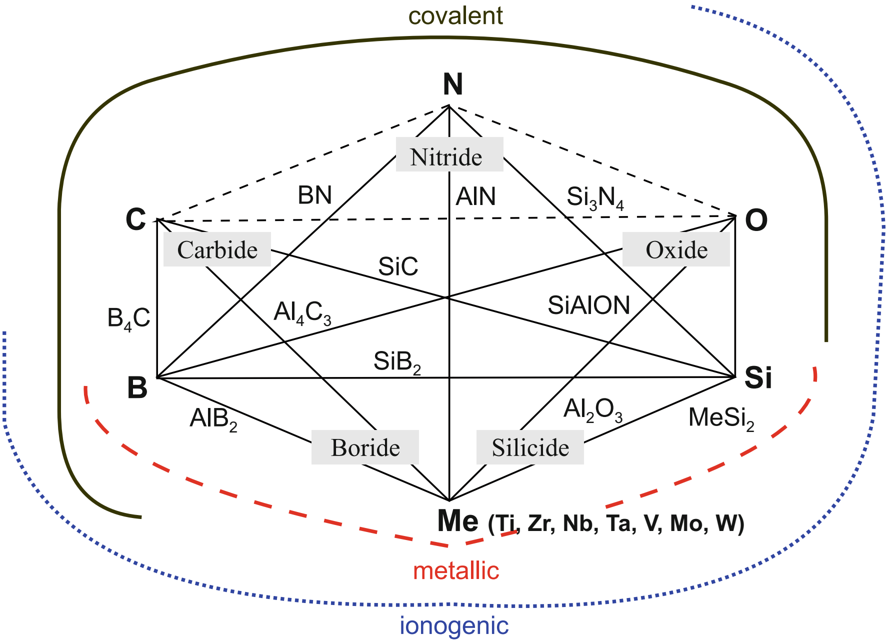


Fig. 4.2 Relationships and bond type of special ceramics in the system C-N-O-Si-B-Me-(Al). (Modified after Michalowsky 1994)

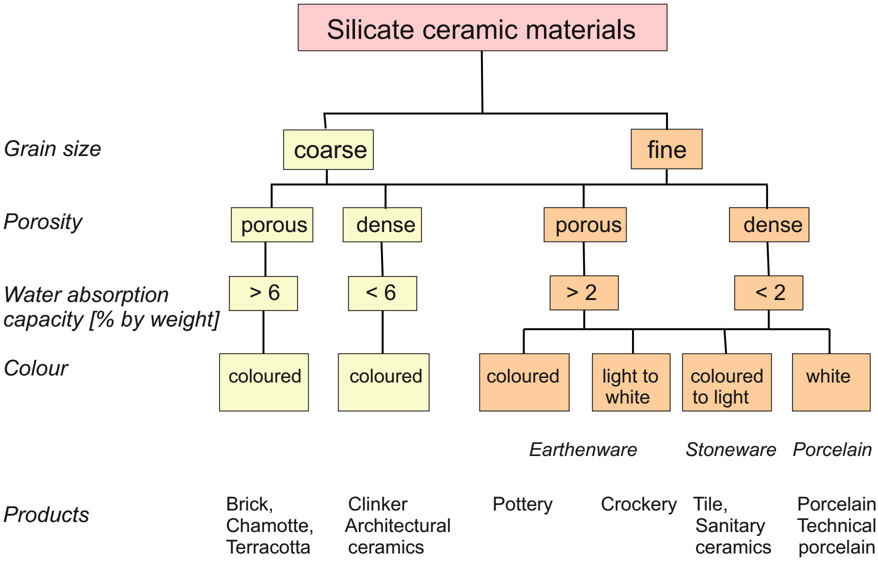


Fig. 4.3 Classification of silicate ceramic materials. (According to Petzold 1991)

4.1 Fine Ceramic Silicate Materials

4.1.1 Raw Materials for Silicate Fine Ceramics

Fine ceramic silicate materials are produced from silicate raw materials (kaolin/clay, quartz, feldspar) after wet grinding/solid processing by sintering. The materials can be porous or dense; in the first case they are earthenware (or stoneware), in the second porcelain (or stoneware) (Fig. 4.3).

A distinction is made between plastic and non-plastic raw materials:

- plastic raw materials
  - Clay minerals (e.g., kaolinite $Al_2[(OH)_4/Si_2O_5]$).
- non-plastic raw materials
  - Lean agent = quartz (SiO_2)
  - Flux = K/Na feldspars ($(K,Na)[AlSi_3O_8]$)

The plastic raw materials (clay minerals) are responsible for the plastic behaviour of the raw material mixture, which is essential for the shaping process of the ceramic bodies. Plasticity refers on the one hand to the mineral raw materials directly (crystal plasticity) and on the other hand also to clay-water mixtures, which exhibit plastic (mouldable) properties as a raw material mixture (clay plasticity). In technical terms, this is also referred to as plasticity. The quartz as a leaning agent “dilutes” the plastic matrix and provides the mechanical stability. The flux lowers the sintering temperature during the firing process of the ceramic, whereby the alkalis ensure that part of the ceramic matrix solidifies glassy. Raw material batches with high clay contents are called “fat”, and those with significantly lower clay contents are called “lean”.

An average porcelain set consists of approx. 50 mass-% kaolinite, 25% quartz and 25% K-feldspar. Due to the high proportion of clay minerals in the backfill, the main representatives of the fine ceramic silicate materials (porcelain, stoneware) are often also referred to as clay-ceramic materials.

4.1.2 Rheological Behaviour of Clay-Water Mixtures

Ceramic masses take on properties through the addition of water, which are technically used for shaping processes (turning, pressing, rolling, casting, etc.). The corresponding properties are described by rheology, in particular the rheological properties of clay minerals. Clay minerals exhibit colloidal chemical behaviour, as they have a very small particle size, an anisometric shape and a negative surface charge (Fig. 4.4).

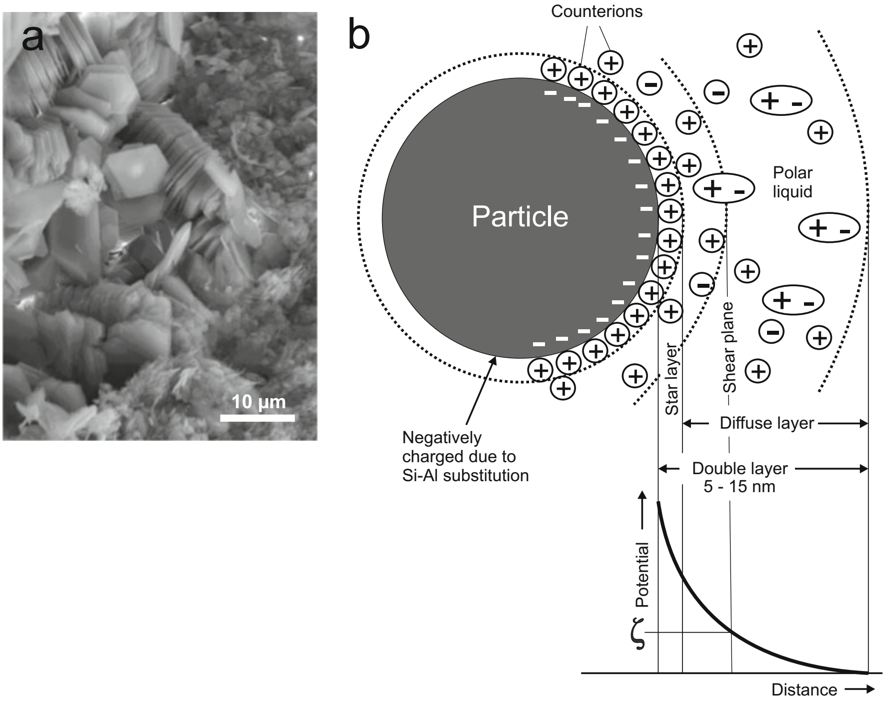


Fig. 4.4 (**a**) Clay minerals (kaolinite) in the scanning electron microscope image, (**b**) Model of the electrical double layer with potential curve around a particle in water (hydrate shell)

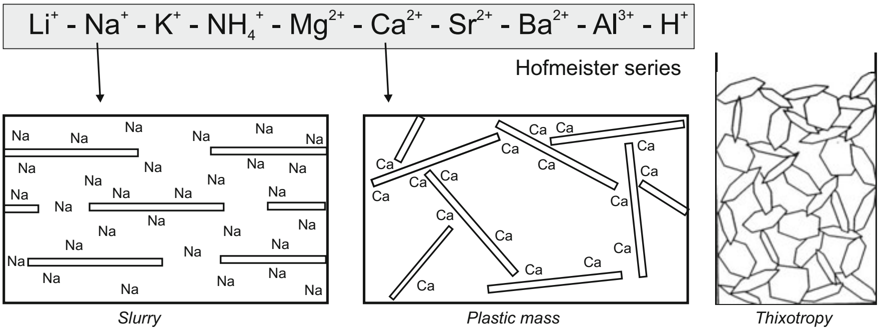


Fig. 4.5 Hofmeister series with increasing tendency to cation exchange and resulting rheological behaviour of clay-water mixtures

The general negative surface charge of the clay minerals (in particular 2:1 sheet silicates) results from a substitution of ions in the tetrahedron and octahedron layers which is not in accordance with the law and can rather be described as a misplacement. Compensation for this negative surface charge is achieved by the addition of hydrated cations and the alignment of the dipoles of water in the surrounding hydrate shell. As a result, a 5–15 nm thick electrical double layer forms around the individual clay mineral particles (Fig. 4.4). This double layer consists of an inner shell of relatively tightly bound cations and a second layer that becomes more diffuse with increasing distance. The thickness of the layer is determined by the amount and type of cations. The electric potential that builds up in the double layer is called the ζ-potential (zeta potential).

If water is added to a clay in excess, the clay is liquefied to suspension and a so-called slurry (structurally viscous liquid) is formed. The flow behavior of slurries is altered in the presence of soluble electrolytes by cation exchange and can be characterized by the ζ-potential. Natural kaolins and clays have predominantly Ca^{2+}- and Mg^{2+}-ions in exchange positions, in acidic environments also H_3O^+-ions. The propensity for cation exchange results in a ranking, the so-called Hofmeister series (Fig. 4.5). A Hofmeister series also exists for anions, but it is not important here.

Cations positioned further to the left are more easily exchanged by ions positioned to the right than vice versa. This order is an expression of the increase in the energies of attraction and the decrease in the thickness of the diffuse electrical double layer around the clay particles. Na-occupied clay minerals consequently possess a relatively thick electrical double layer, whereas Ca occupation results in a thin double layer (Fig. 4.5). This can lead to the formation of metastable structures in the form of pasty masses which liquefy again when subjected to mechanical stress (shear forces, e.g. shaking). This phenomenon is known as thixotropy (Fig. 4.5). Thixotropic solid-liquid mixtures, e.g. bentonite-water mixtures, are used, for example, to stabilise boreholes when changing drill heads. When at rest, the suspension is able to withstand the earth's pressure; when it is moved, e.g. when the new drill pipe is introduced, the suspension liquefies again and can be flushed out.

In principle, it is therefore possible to influence the thickness of the electrical double layer, and thus the rheological behaviour of clay-water mixtures, by adding ions with hydrate shells of different sizes. The cation exchange capacity (CEC) varies structurally for different clay minerals.

4.1.3 Shaping of Ceramic Bodies

Depending on the amount of water added and the physicochemical properties of the raw materials, there are transitions in ceramic masses between crumbly powders, pasty, viscous bodies and viscous suspensions, the slurries. Plastic bodies are required for plastic shaping (pottery, pressing, rolling, turning, etc.), while aqueous suspensions are used for slip casting using hollow casting or core casting techniques (Fig. 4.6).

Divisible gypsum moulds are preferred for slip casting, as they have a favourable suction coefficient. The suction effect removes water from the suspension, resulting in the formation of a stable solid (green body). This is particularly important in hollow casting, as a stable, thin layer of the green body can form on the inner wall of the plaster mould. After a suitable time, when the desired layer thickness of the green body has been reached, the rest of the liquid slip is poured out of the mould. After opening the mould, the dried green body can then be exposed.

An important step in the manufacture of ceramic products is the drying process. In this process, up to 30% by mass of water is removed from the green body without damaging the microstructure. As a rule, the drying process comprises three phases (Fig. 4.7):

1. Drying by leakage of moisture, where the volume shrinkage corresponds to the water leakage.

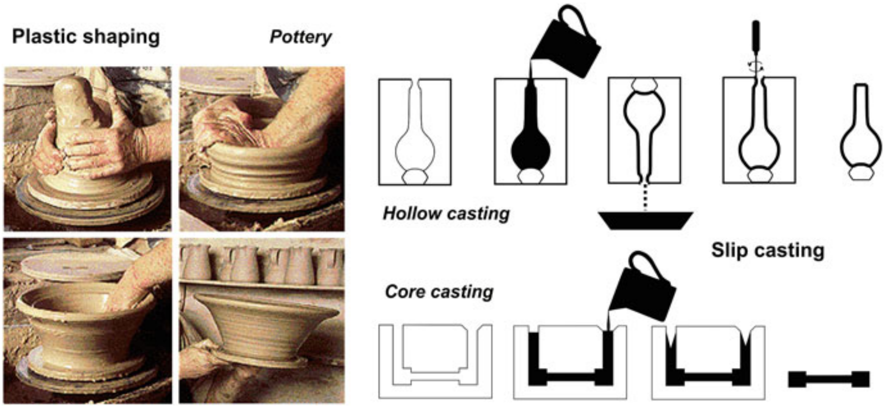


Fig. 4.6 Schematic representation of the shaping of plastic ceramic masses (plastic shaping) or aqueous suspensions (slip casting)

Fig. 4.7 Schematic representation of the drying process of a ceramic mass, for explanations see text. (Modified after Salmang and Scholze 1983)

2. Drying combined with volume reduction, whereby shrinkage due to the formation of air voids is smaller than the volume of evaporated water.
3. Drying without volume reduction (shrinkage), as the space of the escaping water is filled with air.

It is important for further processing that the green body remains mechanically stable before and during the firing process and does not deform. This breaking strength is usually measured as bending strength and is referred to as dry bending strength. The dry bending strength depends on various factors:

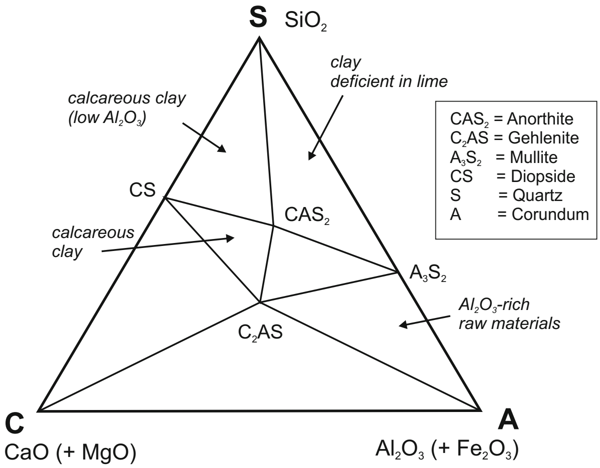
- the bulk density of the green body (density of the particle packing)
- the particle size
- the cation exchange capacity
- the drying temperature
- the drying speed

4.1.4 The Ceramic Firing Process

Ceramics only acquire their typical material properties when the raw material mixture is fired at high temperatures. During sintering (heating), water is released, the volume decreases and the pores are reduced. In addition, significant phase reactions of the starting minerals take place, which lead to the formation of a microstructure in the ceramic. The phase formation during the firing process is determined by the reactions of the main phases.

The dried green body has only a low strength. The application of a glaze would be too complicated to handle. Therefore, a so-called glow firing (also biscuit firing) is carried out before the main firing, which strengthens the ceramic mass, initiates the first decomposition reactions of the clay minerals and strengthens the body, which can now already be described as a ceramic body. In this state, glaze slips or paintings can be applied without any problems.

Fig. 4.8 Ceramic triangle (ternary system CaO – Al_2O_3 – SiO_2) with cotectic triangles of the main phases, designation of the phases analogous to the abbreviated oxide notation (C = CaO, A = Al_2O_3, S = SiO_2)



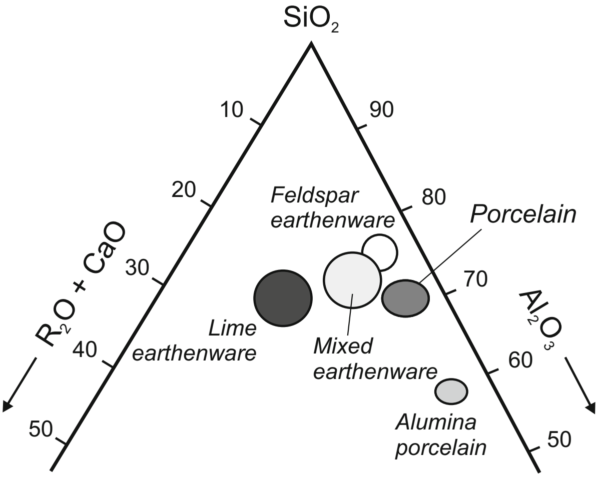
In principle, phase diagrams can be used to predict the reactions of the main phase formation and the resulting reaction products (Fig. 4.8). Within the phase systems, the stable phases form so-called cotectic triangles, which delimit fields for common phase formations. The vertices of the field, in whose area the chemical composition of the raw material mixture falls, thus define the respective phases, which are formed primarily from a homogeneous melt. However, the problem with phase formation in the ceramic firing process is that a heterogeneous mixture is assumed, which is sintered when the temperature is increased (no homogeneous melt), and thus there is no thermodynamic equilibrium.

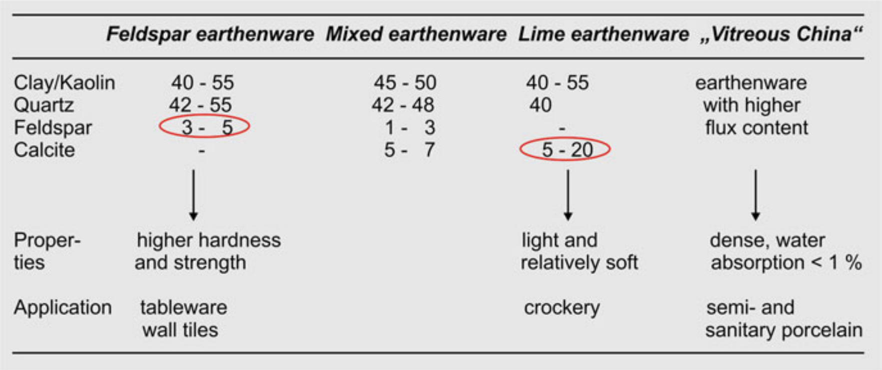
In addition to the raw material mixture, the firing temperature also has an important influence on the formation of melt phases. With the same raw material composition, a higher firing temperature can produce a higher proportion of melt phase and thus a higher proportion of glass in the ceramic. Since the glass phase (melt phase) usually accumulates in the interstitial spaces between the mineral phases and thus reduces the porosity, a general relationship can be derived: *Increasing the firing temperature increases the proportion of glass phase in the ceramic and thus decreases its porosity. A* typical example of this are the coarse ceramic materials *clinker* and *brick,* which are produced from analogous raw materials. Whereas bricks have a high porosity due to relatively low firing temperatures (approx. 900 °C), clinkers are densely fired at higher firing temperatures of approx. 1300 °C. The porosity of clinker is reduced by an increase in the flux content. An increase in the flux content results in an analogous effect.

4.1.5 Fine Ceramic Silicate Materials

Fine ceramic silicate materials (earthenware, stoneware, porcelain, Fig. 4.3) are produced from analogous raw materials and therefore have a similar chemical

Fig. 4.9 Position of fine ceramic materials in the system ((R_2O + CaO) − Al_2O_3 − SiO_2 in mass-%)





	Feldspar earthenware	*Mixed earthenware*	*Lime earthenware*	*„Vitreous China“*
Clay/Kaolin	40 - 55	45 - 50	40 - 55	earthenware with higher flux content
Quartz	42 - 55	42 - 48	40	
Feldspar	3 - 5	1 - 3	-	
Calcite	-	5 - 7	5 - 20	
Proper-ties	higher hardness and strength		light and relatively soft	dense, water absorption < 1 %
Application	tableware wall tiles		crockery	semi- and sanitary porcelain

Fig. 4.10 Different earthenware materials with raw material offsets (in mass-%), properties and applications (the red marking shows the essential difference between feldspar and lime earthenware)

composition (Fig. 4.9). The differences are in the colour and above all in the porosity. Higher firing temperatures result in dense materials (stoneware, porcelain), while porous ceramics (earthenware,) are fired at lower temperatures.

Earthenware is a fine ceramic silicate material that has not been densely sintered during ceramic firing. It has a white body and a uniform, fine-grained structure. Relatively low firing temperatures (1150–1250 °C) and a low flux content result in a porous body with mullite as the main phase and low glass content. Due to the high porosity, the body is usually coated with a dense glaze before use.

In general, a distinction is made between different types of earthenware and vitreous china (Fig. 4.10). The subdivision results from the type and quantity of flux in the raw material backfill.

A higher feldspar content in the raw material leads to higher strength, while the addition of lime produces a light and relatively soft ceramic. Increasing the flux

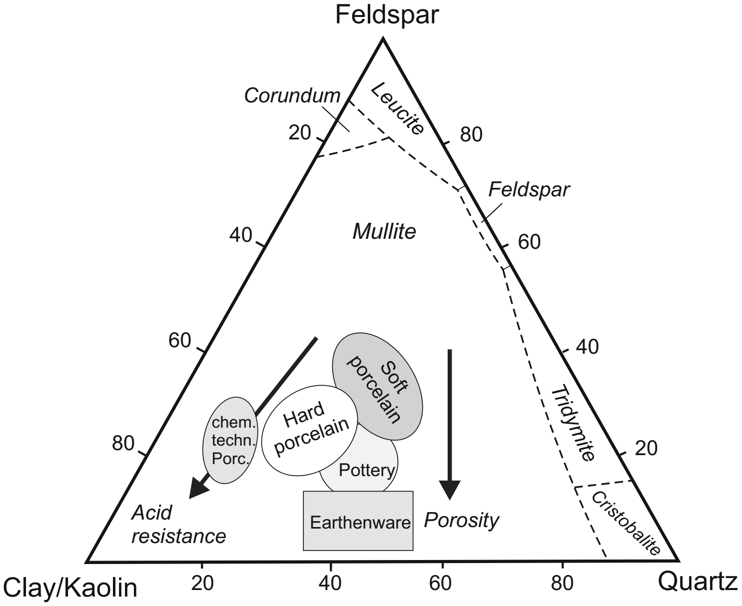


Fig. 4.11 Raw material composition and properties of various fine ceramic materials

content in "Vitreous China" results in higher glass contents and thus a dense body. This ceramic is therefore particularly suitable as sanitary porcelain. It should be noted that the addition of lime to the raw material never results in the formation of CaO, but only shifts the phase equilibria towards higher contents of the CaO component.

Porcelain is a densely fired, white ceramic (aluminosilicate) material with a transparent vitrified body. Porcelain is made from a raw material mixture of kaolin, feldspar and quartz and can therefore be chemically represented in the ternary system K_2O-Al_2O_3-SiO_2. A classic porcelain raw material mixture contains 50% kaolinite, 25% K-feldspar and 25% quartz and is fired at 1400 °C. This ceramic is also called hard porcelain.

The historically first porcelain, which was developed in China in the seventh century, is richer in feldspar and less kaolinitic (40% kaolinite, 35% feldspar, 25% quartz) and is also fired at lower temperatures of approx. 1200–1300 °C. Due to its lower strength, this ceramic material is called soft porcelain. A consequence of the variation of the raw material mixture are also changed properties of the ceramic products (Fig. 4.11).

Reducing the quartz content results in improved thermal properties, and this porcelain is therefore used as high-voltage porcelain (better thermal shock resistance). Increasing the quartz content, on the other hand, results in better mechanical properties, such as those required for chemical-technical hard porcelain. More feldspar improves transparency and is used for the production of transparent soft porcelain.

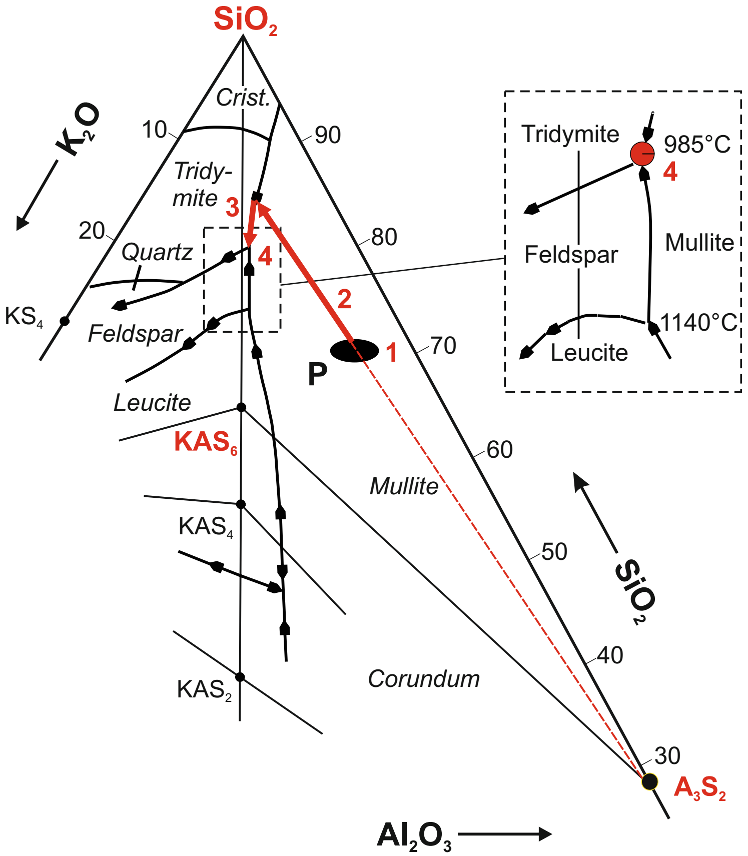


Fig. 4.12 Phase formation in the system ($K_2O - Al_2O_3 - SiO_2$ with abbreviations A – Al_2O_3, S – SiO_2, K – K_2O, in mass-%)

The theoretical porcelain composition can be deduced from the phase relationships in the ternary system $K_2O - Al_2O_3 - SiO_2$ (Fig. 4.12). The chemical composition of the porcelain raw materials with a mixture of 50% kaolinite, 25% potassium feldspar, 25% quartz (point P) falls within the cotectic triangle S – A_3S_2 – KAS_6 (with abbreviations A – Al_2O_3, S – SiO_2, K – K_2O) and thus yields tridymite, mullite and potassium feldspar as possible mineral phases.

The ternary diagram also allows the reconstruction of the crystallization sequence from a theoretically assumed homogeneous melt. Since point P (representative of the composition of the raw material mixture) is located in the stability field of mullite, mullite would initially crystallize at temperatures below 1400 °C (point 1). This progressively depletes the Al_2O_3 content of the melt and the composition of the melt moves along line 2 with further formation of mullite. Upon encountering the mullite/tridymite field boundary (point 3), joint crystallization of mullite and tridymite occurs below 1280 °C. Withdrawal of SiO_2 from the melt due to the simultaneous

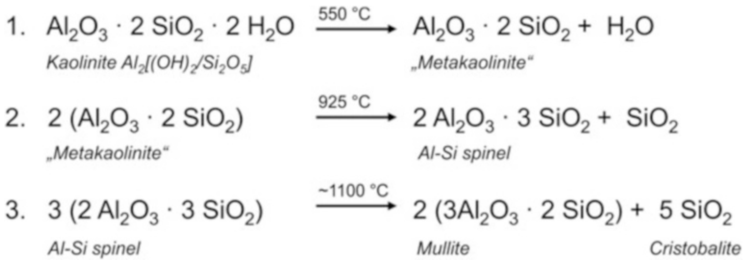


Fig. 4.13 Main reactions of kaolinite during ceramic firing with corresponding temperatures

precipitation of mullite and tridymite now moves the melt composition along the field boundary to point 4, the ternary eutectic mullite-tridymite-potassium feldspar. At this point, below the eutectic temperature of 985 °C, these three mineral phases crystallize equally from the residual melt. The theoretical phase composition after complete crystallization would then be 29.7% mullite, 26.6% potassium feldspar and 43.7% tridymite. In practice, however, feldspar and SiO_2 solidify as glass, so that the practical composition of porcelain is close to 29.7% mullite and 70.3% glass (with some residual quartz and tridymite/cristobalite).

With such a high melt fraction, one would expect in the first approach that the firing products would melt together and lose their partly detailed shape. However, since the melt has very high SiO_2 contents, it is highly viscous and extremely dimensionally stable.

The practical reaction sequence also differs in that no crystallization takes place from a homogeneous melt, but that the raw material mixture is gradually heated in the firing process. With regard to the main phase kaolinite, a multi-stage reaction sequence can be observed (Fig. 4.13).

At approx. 550 °C, kaolinite is transformed into metastable metakaolinite by the expulsion of the hydroxyl groups. Above 900 °C the structure collapses completely and a highly disordered vacancy spinel (defect spinel) $Si_8Al_{10\ 2/3}\square_{5\ 1/3}O_{32}$ is formed. Finally, above about 1100 °C, a rearrangement of the structure occurs with the formation of mullite. The morphology of the mullite is initially finely scaly (primary scaly mullite) and changes to acicular crystals (secondary needle mullite) when crystallized from the melt (Fig. 4.14).

The reactions occurring during ceramic firing can also be detected by thermoanalysis (Fig. 4.15).

The differential thermoanalysis (DTA) curve of kaolinite shows three peaks which can be assigned to corresponding reactions. Between 550 and 600 °C an endothermic reaction takes place during the dehydration of kaolinite (1). Two exothermic reactions below and above 1000 °C are the result of the formation of the defect spinel (2) and the crystallization of mullite (3), respectively. All three reactions can be detected in the dilatometer curve after initial thermal expansion due to volume reductions. Finally, the thermogravimetric curve shows the quantitative water loss during dehydroxylation of kaolinite (formation of metakaolinite).

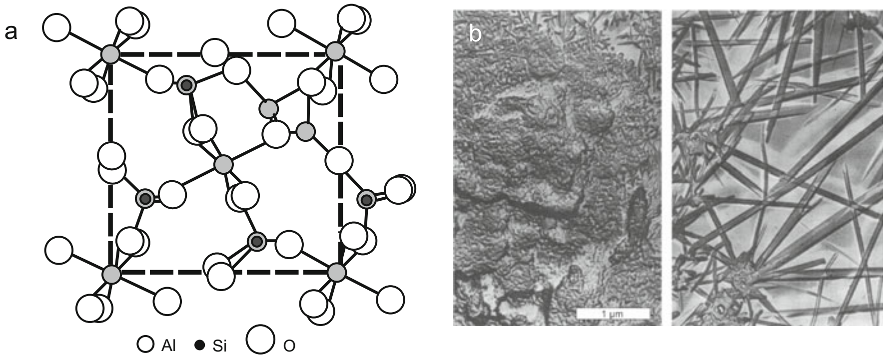


Fig. 4.14 Unit cell of mullite with (AlO_6) chains and (Si, Al)O_4 tetrahedra (**a**) and morphological formation of primary “scaly mullite” and secondary “needle mullite” (**b**). (Modified after Petzold 1991)

The entire ceramic firing process with corresponding temperatures and phase formations is summarized schematically in Fig. 4.16.

Ceramic firing takes place either in chamber kilns, bogie hearth kilns or in tunnel kilns. The choice of kiln type is determined by the quantity of products. Small quantities are fired in chamber kilns, larger quantities on bogies with the help of sintering aids (shelf constructions made of SiC) stacked in large chamber kilns, the so-called bogie hearth kilns. The products to be fired are placed in the cold furnace. The kiln runs through the appropriate temperature program of heating up, maximum firing and cooling down until the finished products are taken out of the kiln, which has meanwhile become cold again. These are discontinuous processes. These kilns are usually heated electrically.

Tunnel kilns of 30–150 m length are used for large quantities. In this case, the long, gas-heated kiln is in constant operation with unchanging stable temperature distribution. From the entrance, the temperature increases continuously up to the maximum temperature, which is constant over a suitable length of the tunnel kiln in accordance with the movement of the firing products. Then the temperature decreases again continuously until the exit, where the products finally have temperatures of 60–40 °C. This entire temperature distribution in the kiln length is exactly matched to the product and the passage speed. The fired products move either on rotatable corundum tubes arranged one after the other (roller belt principle) or by means of carriages running on rails. The firing products are stacked on the carriages in suitably arranged “shelves”, so-called sintering aids made of SiC. However, the axles and wheels of the carriages must be suitably shielded from the high temperatures in the upper tunnel kiln (up to 1450 °C). Such a furnace journey can take several days.

It is practically impossible to use absolutely iron-free raw materials, especially for stoneware or porcelain, where the highest purity in the white shade is important. Even iron impurities in the ppm range are critical. In oxidizing firing (excess air), Fe^{3+} forms, which gives the stoneware or porcelain a slight beige color. Such

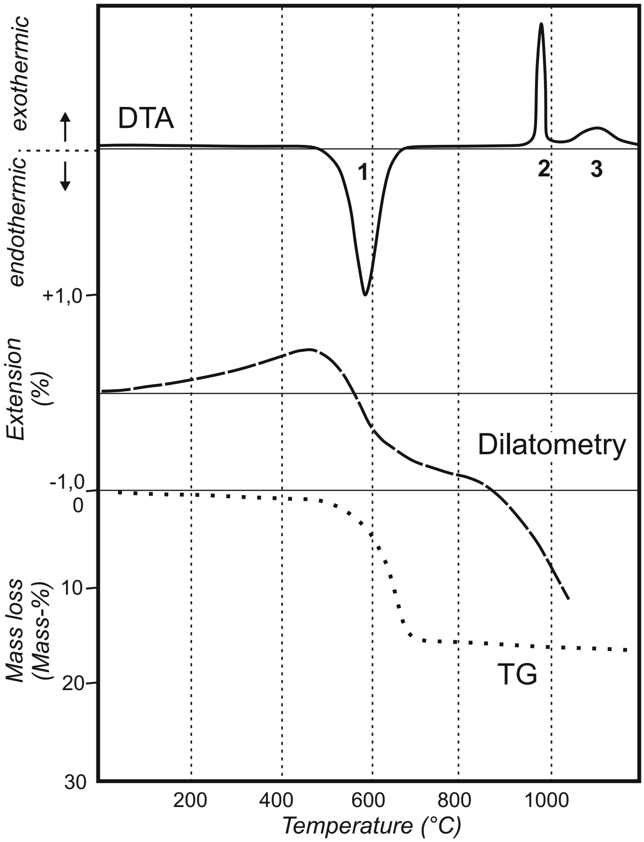


Fig. 4.15 Differential themoanalysis (DTA), dilatometry and thermogravimetry (TG) curves during thermal treatment of kaolinite. *1* Dehydration, *2* Formation of defect spinel, *3* Formation of mullite

coloured products have a rather deterrent effect. Reducing firing (underfiring with air) forms Fe^{2+}, which gives a light blue-green coloration. This has a cold effect and comes much closer to our impression of white, pure and noble.

From the raw materials and during the production of the green body and cullet during the annealing firing, it may happen that organic components, oils and fats adhere to the firing products. If such carbon-contaminated products were now fired in a reducing manner, the carbon would be converted to graphite and the product would show grey haze or even black spots. The solution is targeted atmospheric control. In the front area of the tunnel kiln or in the heating cycle of the chamber kilns, the atmosphere is set oxidizing, the carbon burns, and the iron becomes Fe^{3+}. In the rear area of the tunnel kiln or in the cooling cycle of the chamber kiln, the atmosphere is set reducing and the iron is reduced to Fe^{2+}.

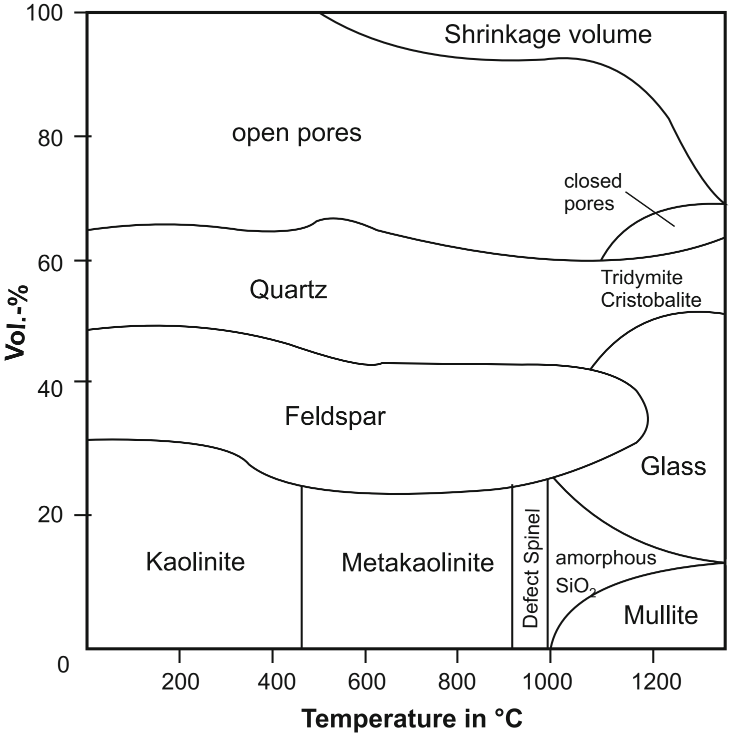


Fig. 4.16 Development of the phase composition of a porcelain raw material mixture of kaolinite, quartz and feldspar during ceramic firing as a function of temperature

4.2 Coarse-Ceramic Silicate Materials

Depending on the firing temperature and the resulting content of glass phase, coarse-ceramic materials can be porous (bricks) or dense (clinker). The sintering temperature for brick firing is approx. 900 °C, while clinker is fired at approx. 1300 °C. Clays relatively low in Al_2O_3 are used as raw materials for bricks and clinkers (Fig. 4.17). Refractory clays with higher Al_2O_3-contents are used for the production of fireclay (Chap. 7 "Refractory Materials"). An important criterion for the selection of raw materials is the grain size distribution, on the basis of which raw materials for various coarse ceramic products are classified (Fig. 4.17).

The phase composition of the coarse-ceramics again develops as a function of the raw material composition (Fig. 4.8). In the case of low-calcium raw materials, mullite, a glass phase and residual quartz form, analogous to porcelain. Lime-rich raw materials lead to the crystallization of additional Ca-containing phases such as gehlenite ($Ca_2Al[(Si, Al)_2O_7]$), diopside ($CaMg[Si_2O_6]$) and/or wollastonite ($Ca_3[Si_3O_9]$).

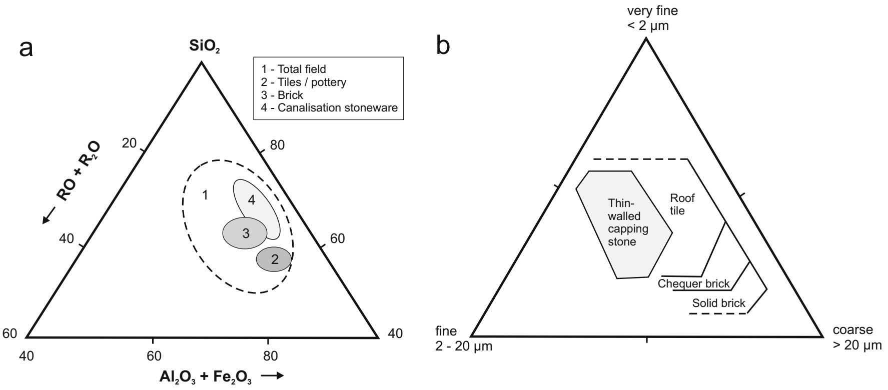
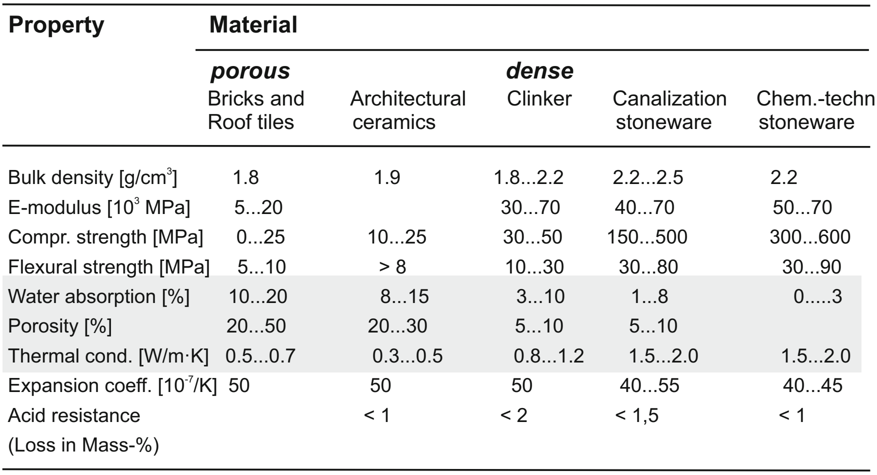


Fig. 4.17 (**a**) Position of the coarse-ceramic materials in the system (RO + R_2O = alkali/alkaline earth oxides) – (Al_2O_3 + Fe_2O_3) – SiO_2 (in mass-%), (**b**) Classification of raw materials based on grain size (Winkler diagram). (Modified after Salmang and Scholze 1983)



Property	Material				
	porous		*dense*		
	Bricks and Roof tiles	Architectural ceramics	Clinker	Canalization stoneware	Chem.-techn. stoneware
Bulk density [g/cm^3]	1.8	1.9	1.8...2.2	2.2...2.5	2.2
E-modulus [10^3 MPa]	5...20		30...70	40...70	50...70
Compr. strength [MPa]	0...25	10...25	30...50	150...500	300...600
Flexural strength [MPa]	5...10	> 8	10...30	30...80	30...90
Water absorption [%]	10...20	8...15	3...10	1...8	0.....3
Porosity [%]	20...50	20...30	5...10	5...10	
Thermal cond. [W/m·K]	0.5...0.7	0.3...0.5	0.8...1.2	1.5...2.0	1.5...2.0
Expansion coeff. [10^{-7}/K]	50	50	50	40...55	40...45
Acid resistance (Loss in Mass-%)		< 1	< 2	< 1,5	< 1

Fig. 4.18 Selected properties of non-refractory heavy clay materials

Figure 4.18 summarises some selected properties of non-refractory ceramic materials. In addition to mechanical strength and chemical resistance, thermal insulation and properties that influence frost resistance (porosity, water absorption) are particularly important for the characterisation of building materials used outdoors. Here, clear differences between porous and dense materials can be seen. While bricks guarantee better thermal insulation, clinker bricks are characterized above all by low water absorption.

The frost resistance, which is important for outdoor use, is influenced by the total porosity and the pore-size distribution. The measure for this is the saturation coefficient S, the ratio of voluntary to maximum water absorption (Sect. 3.1 "Natural stone”). Structural ceramics are described as frost-resistant if S < 0.8; at 0.8 < S < 0.9 the material is frost-endangered and at S > 0.9 it is not frost-resistant. For the experimental determination of the frost resistance of masonry bricks, a 25-fold freeze-thaw test is often used.

Salt efflorescence (salt blasting) caused by soluble salts, especially alkali and alkaline earth sulphates, can also have a damaging effect on the building fabric. These substances can originate from the raw material, the firing process, the soil moisture, the mortar or even from the air.

4.3 Glazes

The ceramic base body is referred to as the “body”. After the annealing firing, a glaze is applied as a slip. The thin glaze layer must melt completely during the firing process, in contrast to the body, which forms a maximum of 70% melt at the maximum temperature. However, this thin glaze coating must not mix with the melt of the body during the main firing. Furthermore, the glaze must have a colouring effect in desired areas, but this should not overlie the adjacent colourless or differently coloured areas in order to ensure a sharp motif image.

During the cooling process, the glaze must solidify glassy, it must not crystallize. During this process, the firing product undergoes a shrinkage process (negative thermal expansion). The volume and mass majority is represented by the body. Glasses withstand compressive stress well, tensile stress poorly. In order to prevent cracking of the glaze, the thermal shrinkage of the glaze must be lower than that of the body, so that pressure is exerted on the glaze during the shrinkage process while cooling. However, if this pressure is too high due to large differences in shrinkage, the glaze will flake off. The matching of body and glaze with regard to melting behaviour, expansion and shrinkage behaviour is highly complex and requires exact knowledge of the raw materials and their properties in adjustment with each other. The colouring of the glaze follows similar considerations like those for the colouring of glasses.

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Glass

5

Glass is a material with a very long tradition in humans life. Glasses were already being manufactured in Babylonia about 5000 years ago. It is also interesting to note that ancient Egyptian glass (sodium silicate glass) already had a similar chemical composition to modern window glass (CNS glass = soda-lime silicate glass). In modern technology, however, there is a wide range of glass materials, which are systematized primarily according to their chemical composition:

- single and multi-component oxide glasses: silica glass, borate glass, phosphate glass
- silicate glasses: alkali alkaline earth silicate glass, borosilicate glass, lead silicate glass
- non-oxide and non-silicate glasses: halide, sulphide, selenide, telluride glasses
- metallic and carbonaceous glasses

In terms of quantity, silicate glasses dominate in industrial use, although some of the other material groups have very interesting properties.

However, glasses can also occur in the natural geological environment, especially during the rapid cooling of volcanic melts. Basic melts (45–50% SiO_2) form sideromelane, acidic melts (>65% SiO_2) form perlite or obsidian. Natural glasses of other genesis also occur during impact events (meteorite impact), where they form impact glasses in the area of the impact craters (e.g. Ries crater, Bavaria, Germany) or form glassy tektites as supercooled melt droplets. The melting of sandy sediments during lightning (fulgurites = glassy lightning tubes) or of rocks during tectonic processes (frictionites) also lead to the formation of natural glasses.

The following chapters provide an overview about the structure, properties and applications of glass.

J. Götze, M. Göbbels, *Introduction to Applied Mineralogy*,
https://doi.org/10.1007/978-3-662-64867-4_5

5.1 The Glass State

The vitreous-amorphous state differs from the crystalline state by its disordered structure and the random arrangement of the building blocks (Fig. 5.1). Due to the lack of symmetry and periodicity, the typical features of a crystalline structure are lacking and isotropy prevails.

The glass state also represents a thermodynamically metastable state that has a higher internal energy than the crystalline state. One condition that can lead to this is the freezing of disordered structures by rapid cooling. Accordingly, glass formation is a largely kinetically controlled process. Following a suggestion by Scholze (1988), only non-crystalline bodies with intermediate internal energy produced from the melt are called glasses. This provides a distinction from other amorphous non-crystalline bodies (Fig. 5.2). According to this conception, glass is therefore an inorganic melt product which gradually solidifies without crystallizing when it cools.

The glassy state is characterized by a continuous change of the physical and chemical properties during the transition from one state to another,. In Fig. 5.3 this fact is illustrated by the temperature-enthalpy relationship in comparison with a crystalline solid.

A crystallizing melt ideally transitions to the crystalline state below the melting temperature T_S accompanied by an abrupt change of properties (and enthalpy). Upon further cooling, the properties of the crystal continue to change, but with a slower gradient than the crystal melt.

The glass melt (red in Fig. 5.3) initially changes its properties with decreasing temperature, comparable to the crystal melt. However, due to the lack of a melting point, there is no drastic change of properties in this temperature range. The slope of the change in properties oscillates slowly and then follows that of a crystalline solid

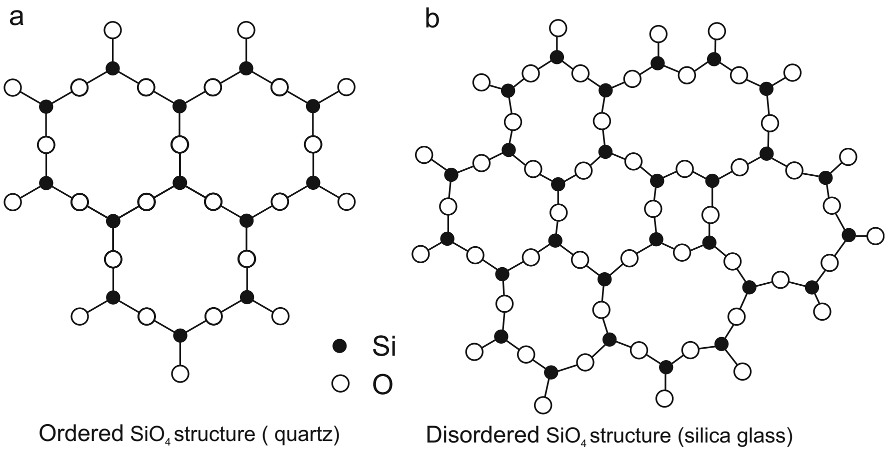


Fig. 5.1 Schematic representation of the structures of the SiO_2 compounds quartz (**a**) and silica glass (**b**); quartz has a short- and long-range order, while silica glass has only a short-range order without long-range order

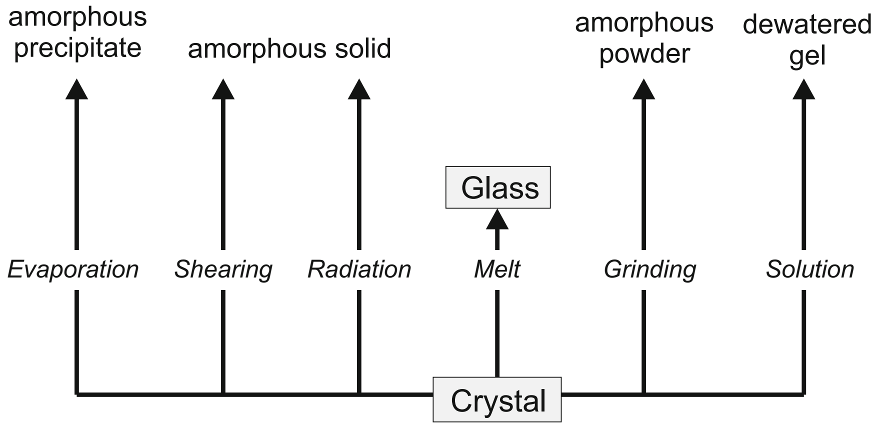


Fig. 5.2 Schematic classification of non-crystalline (glassy and amorphous) solids. (Modified after Scholze 1988)

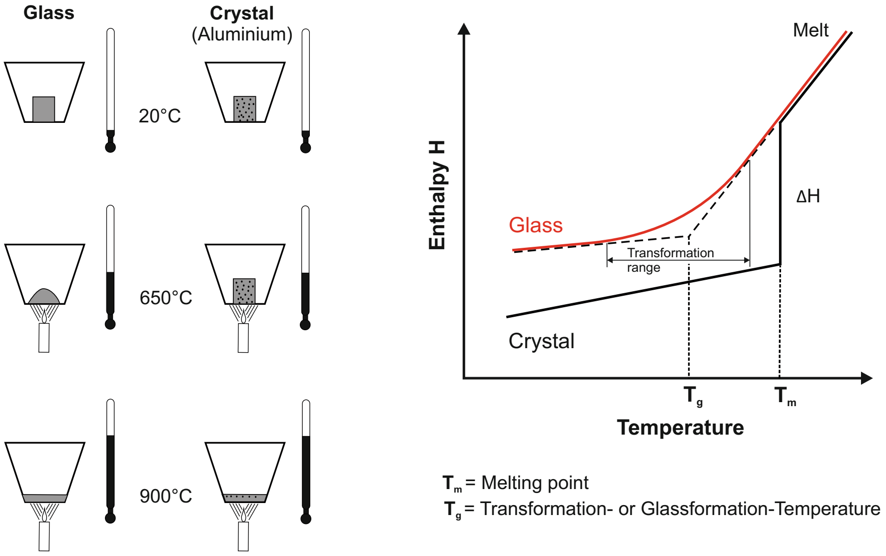


Fig. 5.3 State ranges of glasses and crystals in the temperature-enthalpy diagram

at lower temperatures. The glass melt is first supercooled and then frozen when crystallization fails (or is suppressed). This glass formation process is reversible. Consequently, glass is a frozen, supercooled melt/liquid in the physicochemical sense.

The temperature range in which the change of properties of the glass melt is not longer comparable to that of a crystal melt is called the transformation range. Thus a glass does not have a melting point, but a transformation range, and is not subject to

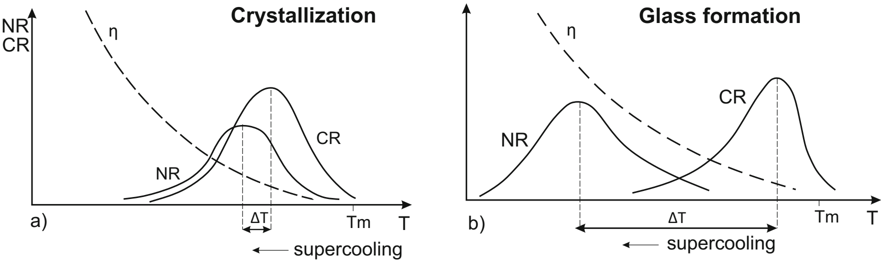


Fig. 5.4 Nucleation (NR) and crystallization rate (CR) for crystallizing (**a**) and glassy solidifying (**b**) silicate melts (η = viscosity; Tm = theoretical melting temperature)

the conditions of thermodynamic phase equilibria. If one now puts a tangent to the linear slope of the property change curve at high and at low temperatures (black dashed line in Fig. 5.3), the intersection of the tangents gives the transformation point T_G of this glass (transformation or glass formation temperature T_g – generally about 2/3 T_m). Mathematically, this point can also be described as the inflection point in the first derivation.

Since glass formation is primarily a kinetically controlled process, it mainly occurs during extremely rapid cooling. Glass formation is essentially controlled by two factors: Factor 1 is the number of crystallization centers or nuclei forming per volume and time unit (nucleation rate NR), factor 2 is the linear crystallization rate (CR). Depending on the chemical composition of the melt, temperature-dependent maxima exist for these two factors (Fig. 5.4). Glass formation can be expected if the two maxima of NR and CR are far apart. If the two maxima overlap, the melt will crystallize on cooling. The crystallization of a glassy solidified melt can be promoted by heating it up again to the temperature of the maximum crystallization rate or by adding nuclei (heterogeneous nucleation). This is used technically, for example, in glass-ceramic materials (vitroceramics).

Glass formation is also influenced by the type and number of cations present in the melt, their ionic radii (coordination) and bonding types. In multicomponent systems, preferential glass formation is observed in the range of eutectics, while crystallization dominates in the range of stable compounds. Low melting temperatures can also promote glass formation.

5.2 Structure of Glasses

Although glasses do not build symmetric crystal structures, the arrangement of the building blocks follows certain regularities. For the formation of oxide glasses there are the following conditions:

1. The coordination number of the cation must be small (KZ = 3 or 4). The formation of distinct coordination polyhedral is determined by the ratios of the ionic radii of the cations and anions involved (Fig. 5.5).

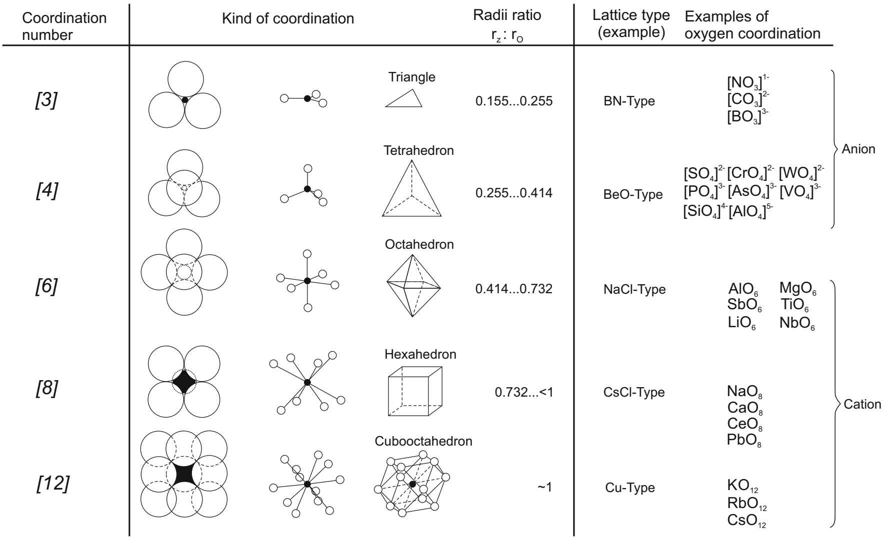


Fig. 5.5 Relationships between ionic radii and coordination polyhedra of selected ions. (Modified after Rösler 1981)

2. An oxygen ion may not have more than two cations as partners.
3. Oxygen polyhedra may have only common corners, but no common edges or faces.

These conditions are fulfilled by oxides of the type:

- R_2O_3: B_2O_3, As_2O_3
- RO_2: SiO_2, GeO_2
- R_2O_5: P_2O_5, As_2O_5

Another special feature of glass structures is the occurrence of mixed bonds. This results in the coexistence of directed and non-directed forms of bonding, e.g. the combination of covalent and ionic bonding in oxide glasses (so-called resonance structures).

For technical glass systems the structure of silicate glasses is most interesting. The ratio of the ionic radii of Si^{4+} in tetrahedral coordination ($r_{Si^{4+}} = 0,41\mathring{A}$) and O^{2-} ($r_{O^{2-}} = 1,32\mathring{A}$) is 0.3, resulting in a tetrahedron as a cation-anion polyhedron (Fig. 5.5). Pure silica glass (SiO_2) can consequently be described as an irregular, three-dimensional network of SiO_4-tetrahedra (Fig. 5.1).

According to Zachariasen and Warren (Zachariasen 1932) and Warren, the structure of glasses can be described as a spatial, random, asymmetrical network of a glass former. This network can be broken up (transformed) by so-called network modifiers (Fig. 5.6). Consequently, glass has no long-range order.

According to this theory, network formers are ions for which glass formation is possible without other components (coordination number 3 or 4). This applies to the

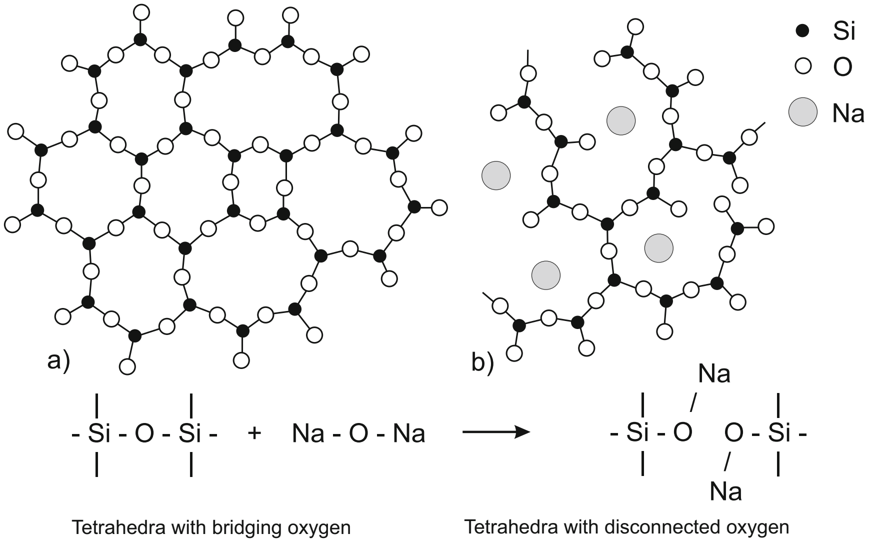


Fig. 5.6 Schematic representation of the build-up of glass structures by network formers (e.g. Si) and network modifiers (e.g. Na)

elements Si, B, P, Ge, As, Be. Network modifiers, on the other hand, are cations with a relatively large ionic radius, such as Na, K, Ca or Ba (coordination number > 6), which break these chains. In general, the maximum content of network formers in glass formation is 50 mol%. At higher contents, sufficient three-dimensional cross-linking is no longer possible. An exception are so-called inverted glasses, in which strong multivalent cations participate in the cohesion of the structure.

A third group comprises so-called intermediate oxides (coordination number 4–6), which can act both as network formers or as network modifiers. However, they cannot act alone as network formers. Representatives of this group are, for example, Al, Mg, Zn, Pb. The role of intermediate oxides can be explained using the example of aluminium. The larger ionic radius in tetrahedral coordination ($r_{\mathrm{Al}^{3+}} = 0,51 \mathring{A}$) results in a possible tetrahedral or octahedral coordination for Al in combination with oxygen, as it is also realized in silicate minerals. Therefore, Al can also substitute Si as a network former or act as a network modifier, but no pure Al_2O_3 glasses exist.

A further development of the network theory was made with the introduction of the field strength F:

$$F = Z_{\mathrm{K}} \; / \; a^2$$

with:

F	Field strength
Z_K	Valence of the cation
a	$r_{Cation} + r_{Anion}$

Network formers have field strengths of $F = 1.4–2.0$, network modifiers of 0.1–0.4, and intermediate oxides of 0.5–1.0.

Important insights can also be gained from phenomena of microphase separation in supercooled silicate melts:

1. Glass melts which consist of only one component (e.g. SiO_2, P_2O_5, or B_2O_3), i.e. only of so-called network formers, solidify homogeneously glassy during supercooling.
2. Glass melts which correspond to the composition of a defined stable chemical compound, i.e. which contain only one type of component, also solidify homogeneously glassy on rapid supercooling; however, they crystallize easily (e.g. Li-silicates).
3. All glass melts which, according to their composition, lie between two stable chemical compounds, tend to segregate.
4. Depending on the total volume, each phase can appear as droplets or as a matrix. At the segregation maximum, interpenetrations are observed.
5. Depending on the supercooling, an additional component of low concentration is enriched almost 100% in the microphase, which offers the best coordination possibilities.

These observations can be used to explain and predict segregation phenomena in glasses. For example, sodium borosilicate glasses have a slight tendency to microphase separation. A particularly strong segregation tendency occurs in the Na_2O-B_2O_3-SiO_2 system along the so called anomaly line (ratio $Na_2O:B_2O_3 = 16:84$; so-called boric acid anomaly). This phenomenon is used technically to produce special glasses with microphase separation.

5.3 Glass Materials and Glass Production

As already mentioned at the beginning, the systematisation of glass materials is essentially based on their chemical composition. Since silicate glasses account for the majority of industrial production, this group will be discussed in more detail. Figure 5.7 shows how different glasses with different properties can be produced by using different components. The starting point is SiO_2, which is the main component in silicate glasses with 50–80% by mass.

The diagram shows which main components and thus, which glass raw materials are used in the production of silicate glasses (Lange 1993):

- Network former
  - SiO_2 quartz sand (SiO_2)
  - B_2O_3 borax ($Na_2[B_4O_5(OH)_{4]} \cdot 8H_2O$), boric acid ($H_3BO_3$)
  - P_2O_5 various phosphates

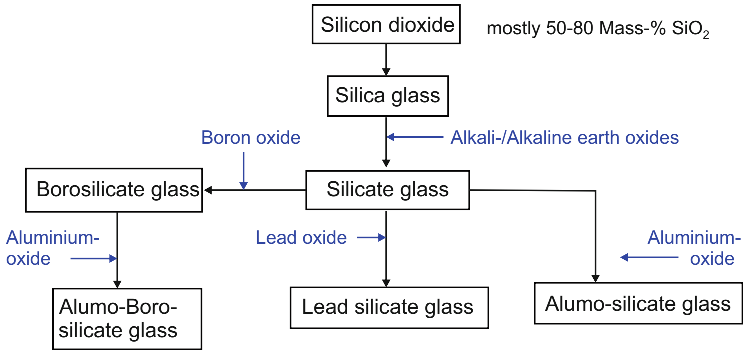


Fig. 5.7 Chemical variation of silicate glasses

- Network modifier
  - Na_2O soda (Na_2CO_3)
  - K_2O potash (K_2CO_3)
  - CaO limestone ($CaCO_3$), dolomite ($CaMg[CO_3]_2$).
  - BaO witherite ($BaCO_3$)
- Intermediate Oxides
  - Al_2O_3 potassium feldspar ($K[AlSi_3O_8]$).
  - PbO red lead (Pb_3O_4)
  - ZnO zinc oxide (ZnO)

In addition, there is a wide range of raw materials added as refining raw materials (e.g. As_2O_3), melting accelerators (e.g. shards, fluorides), coloring oxides (various metal oxides), decolorizing raw materials (e.g., saltpeter), or opacifiers to lower transparency (e.g., fluorite, cryolite). Figure 5.8 schematically shows the raw material composition for different glass types.

The process of glass production starts with the mixing of the raw materials. Since quartz sand is the main component of the raw material mixture, the grain size of the other raw materials is adapted to that of the sand (approx. 0.1–0.5 mm). These raw materials are melted into "broken glass" of the same quality as the glass to be produced and mixed together by the differences in density and surface tension of the as yet non-homogeneous melt droplets. An additional homogenizing effect is created by introducing Ar gas via a bubble stone at the bottom of the melting tank. Heterogeneities and bubbles are additionally removed by the addition of so-called refining substances. Most of the "broken glass" is melted in previous melting processes especially for this melting procedure of the raw materials.

The melting process usually takes place in continuously operating glass furnaces at temperatures ranging from 1400 to 1800 °C, depending on the glass batch. For special glasses, glass pots are sometimes used for one-off or periodic melting processes.

The actual forming process then takes place at temperatures of 1200–900 °C by pulling, rolling, pressing or hollow forming. A special process is the so-called float

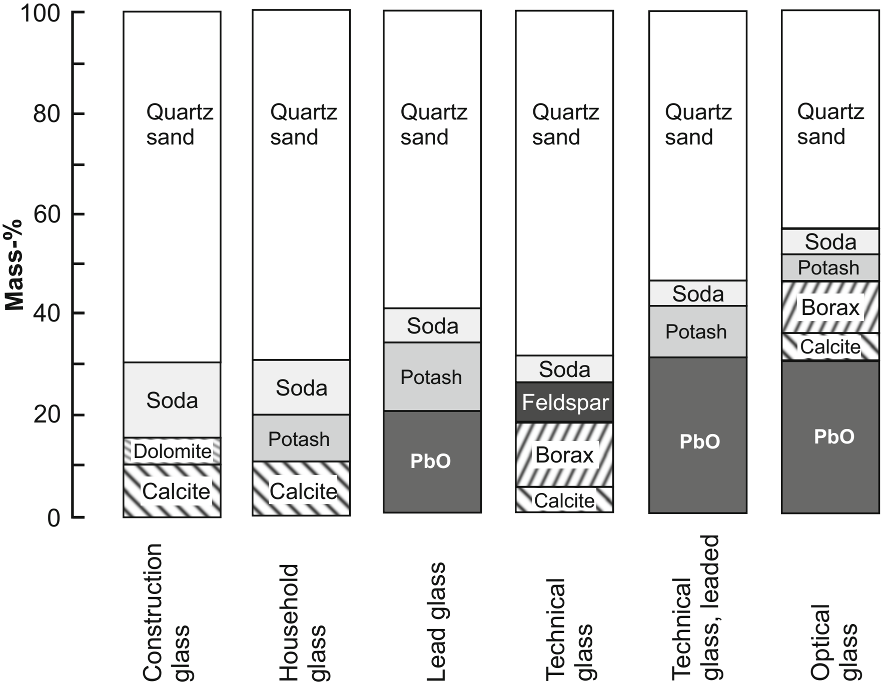


Fig. 5.8 Variation of raw material mixtures for different glasses

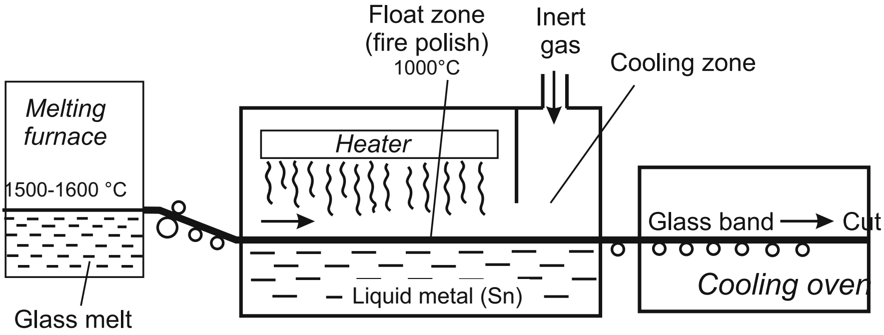


Fig. 5.9 Scheme of the float glass process

glass process (Fig. 5.9), in which the molten glass is moved over a metal bath (Sn) to produce flat glass (e.g. window glass) with very good surface properties.

The float glass process uses the effect that an absolutely flat interface is formed between two liquids of different density. The pulling speed controls the thickness of the glass layer. The furnace zone in which the float glass process takes place must be absolutely free of oxygen, i.e. requires reducing atmospheric conditions. In addition, there is a temperature gradient in the furnace which must be above T_G at the entrance so that the plane boundary layer between the glass and the liquid tin can form, and below T_G at the end so that the solidified glass can be lifted off the molten tin and led out of the furnace.

The end products are formatted and cooled if necessary. Due to the stresses often present as a result of non-uniform cooling, many glass products must be subsequently tempered at 500–600 °C.

Impurities affecting the quality of the glass can be caused by various factors. They can result from the raw material (e.g. non-melting mineral particles), be produced by technological problems (e.g. incorrect temperature regime) or be caused by reactions with the refractory tank material. In principle, a distinction is made between:

- gaseous inhomogeneities (CO_n, O_2, N_2)
- glassy heterogeneities (streaks with deviating composition)
- crystalline inclusions (impurity phases or crystallized melt relics)

Crystallized melt relics can be identified by their composition, which is close to the melt composition in the phase diagram (Fig. 5.10).

5.4 Glass Properties

The properties of crystalline solids are influenced by two essential components: the chemical composition and the structure. The structural component can have a very strong influence on the properties, which is best illustrated by polymorphic compounds (e.g. graphite and diamond).

In glasses, the structural component is omitted, so that the chemical composition has a dominant influence on the physical and chemical properties. Due to this direct interrelation, it is possible to adjust certain glass properties via the chemical composition (raw material mixture). Conversely, the estimation of specific properties from the chemistry of the glasses is feasible (Vogel 1992). This relationship is expressed by the following formula:

$$y = \sum f_i \cdot C_i$$

with:

y certain property
f_i Property factor (Fig. 5.11)
c_i Concentration measure of the property component i

The derivation of property parameters from the chemical composition of glasses is applicable for:

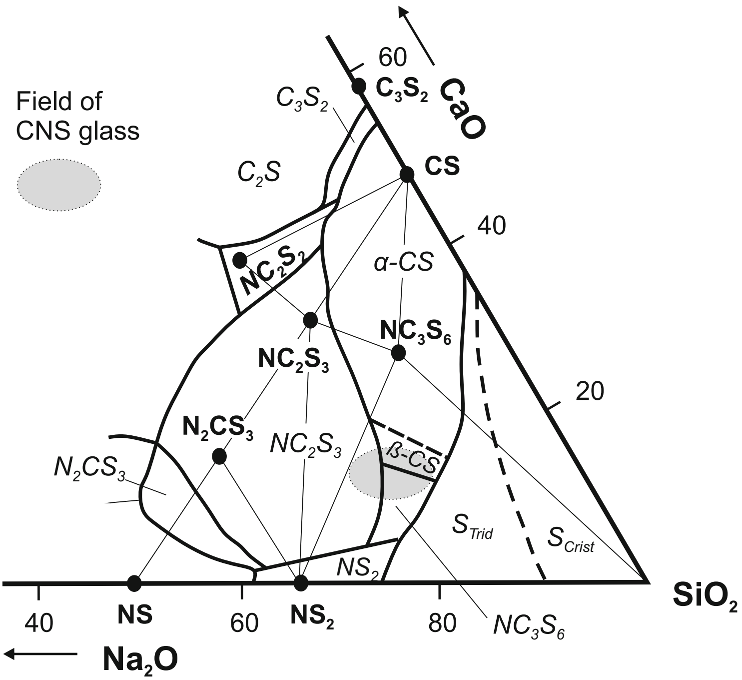
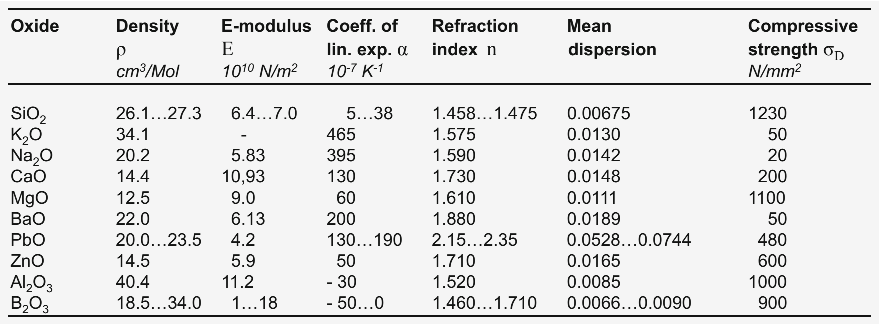


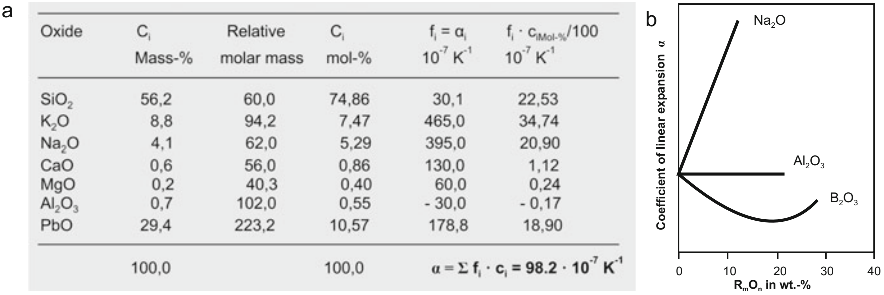
Fig. 5.10 Phase relationships (cotectic triangles and stability fields) in soda-lime silicate glasses (CNS glasses) with possible devitrification crystals



Oxide	**Density** ρ *cm³/Mol*	**E-modulus** E *10¹⁰ N/m²*	**Coeff. of lin. exp.** α *10⁻⁷ K⁻¹*	**Refraction index** n	**Mean dispersion**	**Compressive strength** σ_D *N/mm²*
SiO_2	26.1…27.3	6.4…7.0	5…38	1.458…1.475	0.00675	1230
K_2O	34.1	-	465	1.575	0.0130	50
Na_2O	20.2	5.83	395	1.590	0.0142	20
CaO	14.4	10,93	130	1.730	0.0148	200
MgO	12.5	9.0	60	1.610	0.0111	1100
BaO	22.0	6.13	200	1.880	0.0189	50
PbO	20.0…23.5	4.2	130…190	2.15…2.35	0.0528…0.0744	480
ZnO	14.5	5.9	50	1.710	0.0165	600
Al_2O_3	40.4	11.2	- 30	1.520	0.0085	1000
B_2O_3	18.5…34.0	1…18	- 50…0	1.460…1.710	0.0066…0.0090	900

Fig. 5.11 Property factors of selected oxides for estimating the effect in glass

- Strength
- Density
- Surface tension
- Specific heat
- Thermal conduction/thermal expansion
- Modulus of elasticity



Oxide	C_i Mass-%	Relative molar mass	C_i mol-%	$f_i = \alpha_i$ 10^{-7} K^{-1}	$f_i \cdot c_{iMol\text{-}\%}/100$ 10^{-7} K^{-1}
SiO_2	56,2	60,0	74,86	30,1	22,53
K_2O	8,8	94,2	7,47	465,0	34,74
Na_2O	4,1	62,0	5,29	395,0	20,90
CaO	0,6	56,0	0,86	130,0	1,12
MgO	0,2	40,3	0,40	60,0	0,24
Al_2O_3	0,7	102,0	0,55	- 30,0	- 0,17
PbO	29,4	223,2	10,57	178,8	18,90
	100,0		100,0	$\alpha = \Sigma f_i \cdot c_i = 98.2 \cdot 10^{-7}$ K^{-1}	

Fig. 5.12 (**a**) Calculation of the linear expansion coefficient α for a lead silicate glass, (**b**) Influence of different oxides on the thermal expansion upon substitution of SiO_2 in silica glass

- Dielectric constant
- Refraction index

However, there are also properties for which this direct dependence does not exist, such as for viscosity, crystallization strength, electrical conductivity or chemical resistance.

Figure 5.12 uses the example of a lead silicate glass to demonstrate how the linear coefficient of thermal expansion α can be derived from the chemical composition. From the known property factors, it is now possible to modify the property specifically by changing the chemical composition (Fig. 5.12b).

The average coefficient of thermal expansion of glasses also has a direct influence on their thermal shock resistance. Glasses with a low coefficient of expansion (silica glass, borosilicate glasses) have the highest thermal shock resistance and are therefore suitable for use in the case of large temperature fluctuations.

For many applications, the optical properties of glasses (e.g. refraction index, dispersion, transmission, color) are very important. Here, too, the chemical composition plays a dominant role, resulting in the strong variation of the refraction index for glasses of different compositions:

Refraction index (n_D at 589 nm)

Silica glass	1.45843
Window glass	1.52
Spectacle crown glass	1.5230
High lead flint glass	1.75–1.90

The refraction index can be increased in particular by the addition of heavy metals (e.g. PbO, BaO, La_2O_3, Ta_2O_3, TiO_2, ThO_2).

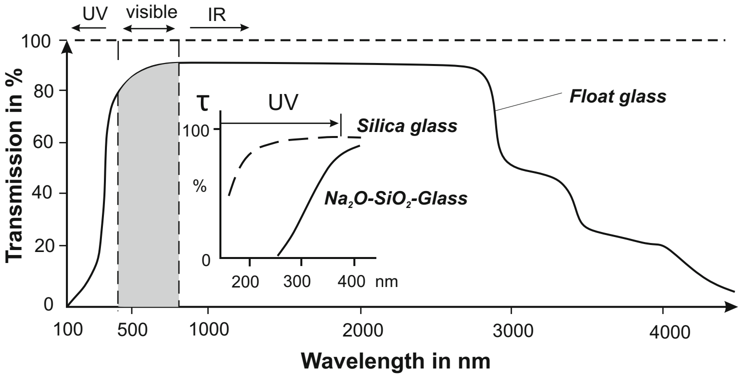


Fig. 5.13 Spectral transmittances of flat glass as well as silica glass and sodium silicate glass (inset). (Modified after Blankenburg et al. 1994)

Dispersion (light scattering) and spectral transmittance (transmission) also have a major influence on various optical effects. The Abbe number ν_e (= reciprocal dispersion) is used as a parameter to characterize the dispersion:

$\nu_e > 55$	Crown glasses
$\nu_e < 50$	Flint glasses
ν_e 50–55	Crown flint

Glasses with a high Abbe's number (low dispersion) are used, for example, in optics or for eyeglasses, while a strong light dispersion in lead glass is responsible for striking effects of sparkling.

The spectral transmittance (transmission) varies greatly for glasses of different compositions (Fig. 5.13). Common window glass (flat glass) shows a sharp drop in the transmission curve in the ultraviolet spectral range (<380 nm), so that a large proportion of the UV radiation is absorbed. Silica glass, on the other hand, has a high spectral transmittance for the UV range and can therefore be used, for example, for lenses and optical components in analytical instruments.

The coloring of glass plays an important role not only for objects of art. Even in ancient times, attempts were made to achieve certain colours by using admixtures. By adding various oxides, silicate glasses of almost any colour can be produced by different ions (Table 5.1).

One last property that should be briefly addressed here is viscosity. The temperature-dependent viscosity is very important, especially for the glass moulding process. While a sudden change in viscosity occurs at the melting point during the crystallization of solids, the viscosity of glass melts changes continuously (Fig. 5.14). The viscosity curve of a glass has its inflection point near the transformation point T_g, which is between 400 and 850 °C depending on the chemical composition. Qualitatively, oxides that promote network formation (SiO_2, B_2O_3) increase viscosity, while network-modifiers (Na_2O, K_2O) lower viscosity.

Table 5.1 Selected oxides (ions) for glass staining

Oxide	Ion	Color
Fe_2O_3	Fe^{3+}	Yellowish brown
Fe_2O_3 + FeO	Fe^{2+}/Fe^{3+}	Green
FeO	Fe^{2+}	Blue-green
Mn_2O_3	Mn^{3+}	Purple
UO_3	U^{6+}	Yellow
V_2O_5	V^{5+}	Green
Cu_2O	Cu^{4+}	Red
CuO	Cu^{2+}	Blue
CoO	Co^{2+}	Blue
Nd_2O_3	Nd^{3+}	Purple
TiO_2	Ti^{4+}	Enhances coloration of other ions

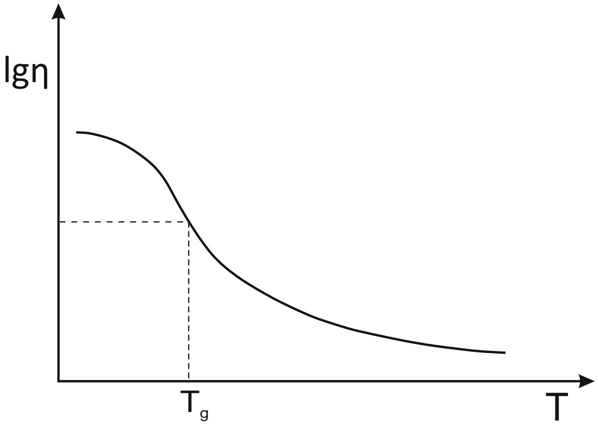


Fig. 5.14 Schematic viscosity-temperature curve for glass

5.5 Glass Ceramics

Glass ceramic or vitroceramic is a special ceramic product made from a glass by controlled crystallization.

The term glass ceramic is actually a contradiction in terms: glass is an amorphous solid, whereas ceramics consists of a framework of predominantly crystalline components. A glass ceramic consists of both – glassy solidified amorphous parts and crystallites. In principle, the ratio of the respective proportions is arbitrary, but crystals are mostly found in a glassy amorphous matrix.

For the production of glass ceramics, bulk raw materials even with low impurity contents cannot be used. Thus, high purity chemicals are required.

Whereas nucleating components are to be avoided in common glass production, they must be introduced into the glass ceramic in a controlled and targeted manner. Certain ions have a nucleating effect, such as Ti^{4+}, Sn^{2+}, Zr^{4+}, Ba^{2+}, but also

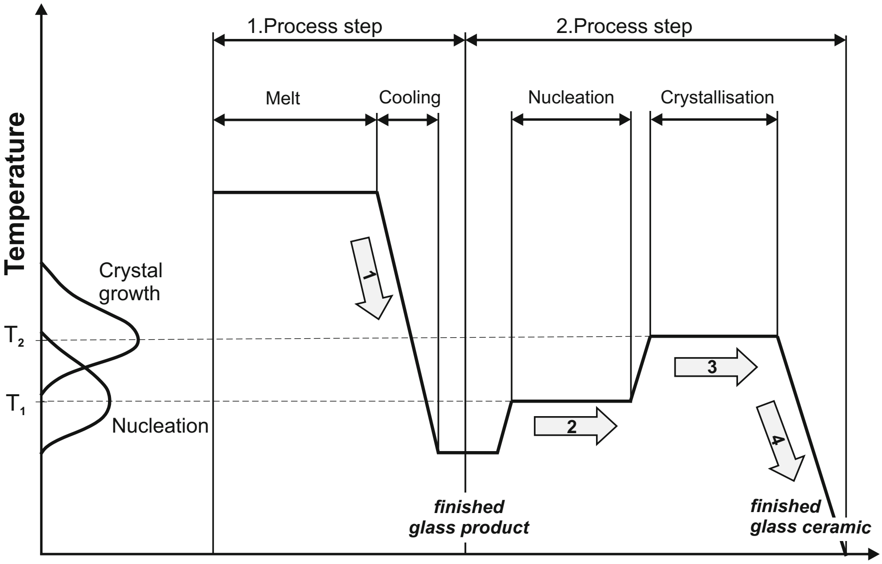


Fig. 5.15 Schematic of the pyroceram process for the production of glass ceramics (vitroceramics)

fluorides and phosphates. Using a high nucleation rate, crystallites of uniform grain size and very small crystal dimensions (micrometer range) are produced.

Although glass as an amorphous phase differs from crystalline solids, some properties of the melt are valid in both cases. This also applies to the Ostwald-Miers range. At low supercooling below the melting point or significant superheating above the transformation point, nucleation is inhibited, but nuclei present can grow. In the case of stronger supercooling below the melting point or slight superheating above the transformation point, nucleation is accelerated and nuclei can form rapidly.

The technological sequence for the production of vitroceramics is shown schematically in Fig. 5.15. In a first step (1), a glass melt is cooled and a glassy product is produced. The following two-stage annealing above T_G first results in a maximum nucleation in the temperature range T_1, where the number of crystallites is determined by time (2). Subsequent annealing at T_2 with maximum crystallization defines the size of the crystallites again by residence time (3). After cooling (4), the final vitroceramic is completed.

The advantage of this process is that a manufacture of complicated shapes (e.g. hollow shapes) is possible. Crystallization at constant shape and dimension generates specific properties, such as high strength, high impermeability to gases, acid resistance or insulation.

Another very important possibility is the production of materials with extremely low thermal expansion. Such vitroceramics are produced in particular in the systems $MgO\text{-}Al_2O_3\text{-}SiO_2$ (MAS ceramics with main phase cordierite $Mg_2Al_3[AlSi_5O_{18}]$) and $Li_2O\text{-}Al_2O_3\text{-}SiO_2$ (LAS ceramics with main phase eucryptite $LiAl[SiO_4]$).

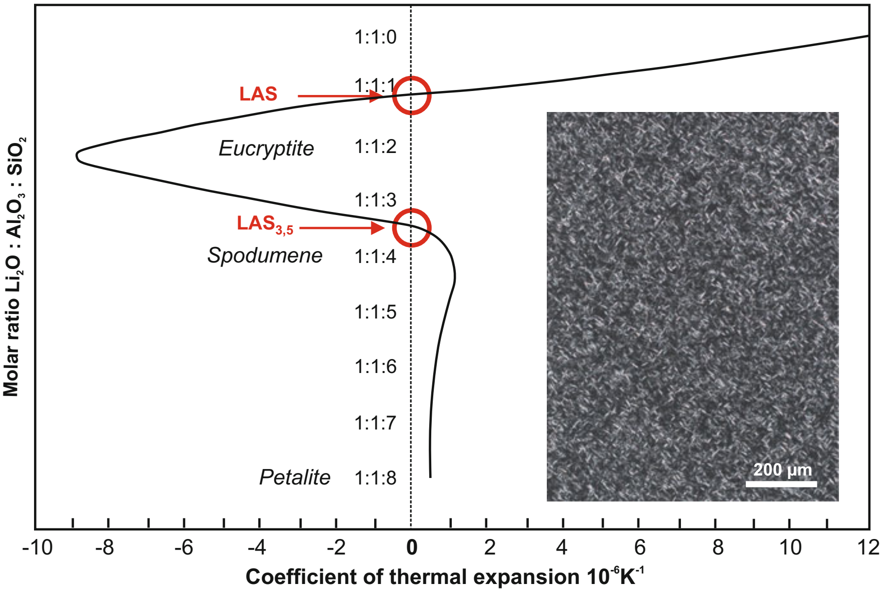


Fig. 5.16 Thermal expansion of various LAS ceramics and microphoto (polarized light) of the microstructure of a vitroceramic (Inset)

Several phases with different coefficients of thermal expansion exist in the LAS system, with the LAS and $LAS_{3.5}$ compositions having a coefficient of 0 (Fig. 5.16).

Such materials are predestined for use under extreme temperature variations. Well-known examples are the use of vitroceramics in ceramic stove tops or as catalyst carriers in motor vehicles.

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Building Materials and Binders

6

Binders and building materials have occupied mankind since the path to clay, brick and natural stone buildings was taken. The first approaches to more solid shelters can be found starting from wood with loam as a building material and clay bricks as a construction material. Here, clay is found with organic materials such as manure, slurry, egg white or blood as "binders" and straw or brushwood as a three-dimensional network mesh. Clay alone lacks the binding and cross-linking properties. Half-timbered houses, which we still find today in our latitudes, prove that these materials between the wooden framework also represent a functioning building material in non-arid regions.

6.1 Building Materials

The first building materials used by man to make dwellings were wood, clay and later natural stones. The choice of natural stones was primarily subject to spatial and civilizational conditions such as local occurrence and the state of the craft (Sect. 3.1). Later, bricks, clinker, concrete blocks, etc. were added. In order to increase the stability and "cohesion" of structures, especially in the case of smaller stones, binders were then required to consolidate the stone bond more permanently.

6.2 Binders

Gypsum, lime and cement are the basis of the most important inorganic binders. These will be examined in more detail below. Binders that set under water are called "hydraulic". Aggregates that react hydraulically only by basic excitation are called "latent hydraulic". These include brick chippings, volcanic ashes, trass, fly ash, granulated blast furnace slag, etc. In terms of chemical composition, the various binders can differ extremely in some cases (Fig. 6.1).

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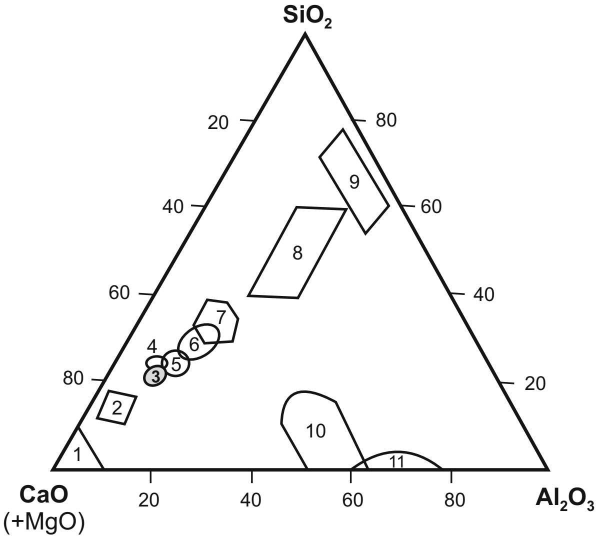

Fig. 6.1 Location of binders and hydraulic additives in the CaO-Al_2O_3-SiO_2 system (data in mass-%). 1 White lime; 2 Water lime; 3 Portland cement; 4 Hydraulic lime; 5 Iron Portland cement; 6 Blast furnace cement; 7 Blast furnace slag; 8 Hard coal filter ash; 9 Trass; 10 Alumina cement; 11 High alumina cement. (Modified after Petzold 1991)

6.2.1 Gypsum-Based Binders

The raw materials used are gypsum, anhydrite or FGD gypsum (flue gas desulphurisation plant gypsum) (Sect. 3.8). If gypsum is subjected to a thermal process at a pressure of 1 bar, i.e. burnt, the following simplified dehydration reactions take place:

$$\underset{\text{“Di-Hydrate”}}{\mathbf{CaSO_4 \cdot 2H_2O}} \xrightarrow[\text{ca. } 70-350\,^\circ\text{C}]{} \underset{\text{“Hemi-Hydrate”}}{\mathbf{CaSO_4 \cdot {}^1\!/\!_2H_2O}} + 1{}^1\!/\!_2H_2O \xrightarrow[>350\,^\circ\text{C}]{}$$

$$\mathbf{CaSO_4} + \underset{\text{Anhydrite}}{{}^1\!/\!_2H_2O} + 1{}^1\!/\!_2H_2O$$

Strictly scientifically, different modifications of hemihydrate and anhydrite exist. The transformations run in each case over temperature ranges and are dependent on the degree of grinding up etc.. Therefore, only rough temperature ranges can be given here for the simplified consideration.

Anhydrite and hemihydrate are used as binders, whereby the hemihydrate has a higher reactivity. The hemihydrate is also called stucco gypsum. The setting process then simply takes place with the addition of water:

$$\underset{\text{“Hemi-Hydrate”}}{\mathbf{CaSO_4 \cdot {}^1\!/\!_2H_2O}} + 1{}^1\!/\!_2H_2O \xrightarrow[\text{room temperature}]{} \underset{\text{“Di-Hydrate”}}{\mathbf{CaSO_4 \cdot 2H_2O}}$$

This binder is excellent to work with, reacts quite quickly and the excess water evaporates. However, it shows a big disadvantage: gypsum is water-soluble, does not set under water and has a fairly low hardness. Therefore, it is only suitable for dry indoor areas.

6.2.2 Limestone-Based Binders

Burnt lime and cement are the two main binders produced on the basis of limestone (calcite, $CaCO_3$). Dolomite, magnesite or marble are not used as raw materials in the binder sector (Sect. 3.7).

Burnt Lime

If pure lime is subjected to a thermal process, the following decalcination reaction takes place:

$$\underset{\text{Limestone}}{\mathbf{CaCO_3}} \xrightarrow[\text{ca.}850\,^\circ\mathrm{C}]{} \underset{\text{Burnt Lime}}{\mathbf{CaO}} + CO_2$$

If water is added, this is also called "slaking", portlandite is formed:

$$\underset{\text{Burnt Lime}}{\mathbf{CaO} + H_2O} \xrightarrow[\text{room temperature}]{} \underset{\text{Slaked Lime/Portlandite}}{\mathbf{Ca(OH)_2}}$$

This reaction is quite violent and exothermic. The slaked lime can now be used together with aggregates. Over time, the binder hardens with the absorption of CO_2 from the air and accompanied by the evaporation of the released water:

$$\underset{\text{Slaked Lime}}{\mathbf{Ca(OH)_2}} + CO_2 \xrightarrow[\text{room temperature}]{} \underset{\text{Limestone}}{\mathbf{CaCO_3}} + H_2O$$

This binder can be processed quite well, has a slightly higher hardness than gypsum building materials and is less soluble in water. It is suitable for outdoor use to a limited extent. However, it requires carbon dioxide from the air to set. It is not "hydraulic".

Cement

Cement is a binder which, historically, can be traced back to a development by the Romans who, under the term *opus caementicium,* produced a mixture of volcanic ash, lime and water with the addition of gravel or brick chippings. This material opened up for the first time the possibility of building large, freely supporting arches and domes without the use of supporting columns (e.g. Pantheon in Rome, 114–118 AD). After this development fell into oblivion in the Middle Ages, it was rediscovered in England in the eighteenth/nineteenth century.

Today, it is impossible to imagine the modern construction industry without cement. Above all, the high strength, low raw material costs and the relatively low energy consumption in cement production compared to other materials (e.g. glass, plastics, steel, aluminium) have led to cement becoming a genuine mass material with an annual global consumption of more than 4 billion tonnes.

The term cement refers to binders that harden in air and under water and are water-resistant after hardening, consisting essentially of compounds of CaO with SiO_2, Al_2O_3 and Fe_2O_3.

Cement is usually produced from a mixture of limestone and clay, whereby the hydraulic clinker minerals or cement clinkers (mainly calcium silicates/aluminates) are formed from the raw materials by a burning process at approx. 1500 °C. The hydration and solidification of the binder is achieved by adding water to form calcium silicate hydrates, portlandite ($Ca(OH)_2$) and calcium sulpho aluminate hydrates. When sand/gravel is added as aggregate, concrete is formed (Gani 1997).

In modern construction, cements of various constitutions can be used for different applications and requirements, with Portland cement being the most commonly used. The average chemical composition of Portland cement (in mass-%) is:

CaO	60–67
SiO_2	17–25
Al_2O_3	3–8
Fe_2O_3	0.5–6
MgO	0.1–4
SO_3	1–3
$Na_2O + K_2O$	0.5–1.3

From the chemical composition it can be deduced that the main raw materials for cement are limestone (approx. 85% by mass) and clay. Limestones in nature are rarely pure. Significant impurities of clay minerals, Fe oxides, dolomite, marl lime etc. are often found. Higher dolomite contents are not desirable for the production of cement. Clay minerals, on the other hand, are necessary and SiO_2 proportions are essential, which are introduced in the raw material (lime marl) via the clay minerals or quartz.

An important aspect of cement production is the adjustment of the suitable chemical composition of the raw meal, which is determined from the raw material analyses by means of the formula of the “lime standard”.

In practice, limestone with a suitable amount of clays is mined, crushed, ground up, chemically analyzed and often fed to a blending bed. On the way to the burning process, this raw meal is then optimized according to the desired target composition by adding corrective components.

Figure 6.2 shows the phase diagram of the system $CaO\text{-}Al_2O_3\text{-}SiO_2$. Fe_2O_3 has been neglected for clarity. The chemical components are often used in abbreviated notation: $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $H = H_2O$.

The conversion of the cement raw materials into the cement clinker phases takes place in a high-temperature process in the rotary kiln. The principle of the corresponding drying and burning process is shown in Fig. 6.3.

The firing process runs according to the countercurrent principle. The rotary kiln consists of a hollow steel cylinder (length 70 m, diameter 4 m) lined with refractory bricks. The ground and chemically adjusted raw meal is fed into the rotary kiln via a preheater and calciner and then directed towards the burner. This countercurrent

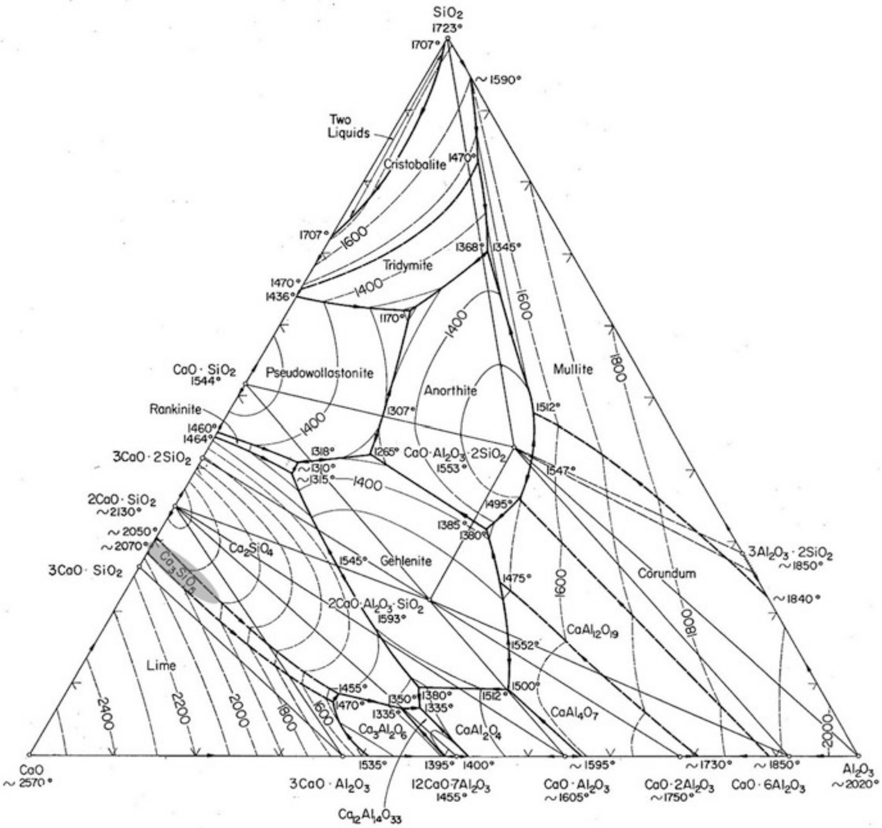

Fig. 6.2 The CaO-Al_2O_3-SiO_2 ternary system with entry (gray box) of chemical composition for modern Portland cement. (Modified from American Ceramic Society: Phase diagrams for ceramists, Vol. I, Fig. 630, reprinted with permission of the American Ceramic Society (1964))

principle makes it possible to use the thermal energy of the exhaust gas for drying and decalcining the raw meal, thus optimizing the energy input. Decalcination is largely completed at the inlet to the rotary kiln (Locher 2000).

In addition to fossil fuels, many secondary fuels and also, for example, motor vehicle tyres can be used in the rotary kiln. The degrees of substitution are over 50% in Germany. Due to the high temperatures in the rotary kiln, no dioxins are produced, and the SiO_2 or the steel inserts of the car tyres are taken into account when adjusting the chemical composition of the cement.

In the rotary kiln, the material to be fired is granulated (1–10 cm). Due to the inclination and rotation of the kiln, the material is transported towards the burner. The burner is located at the lower end of the rotary kiln. The filling of the rotary kiln with granules is selected so that the residence time in the kiln is sufficient for the conversion of the material. At the end of the rotary kiln, the material falls into a cooler to force rapid cooling. The cooled granules are called cement clinker.

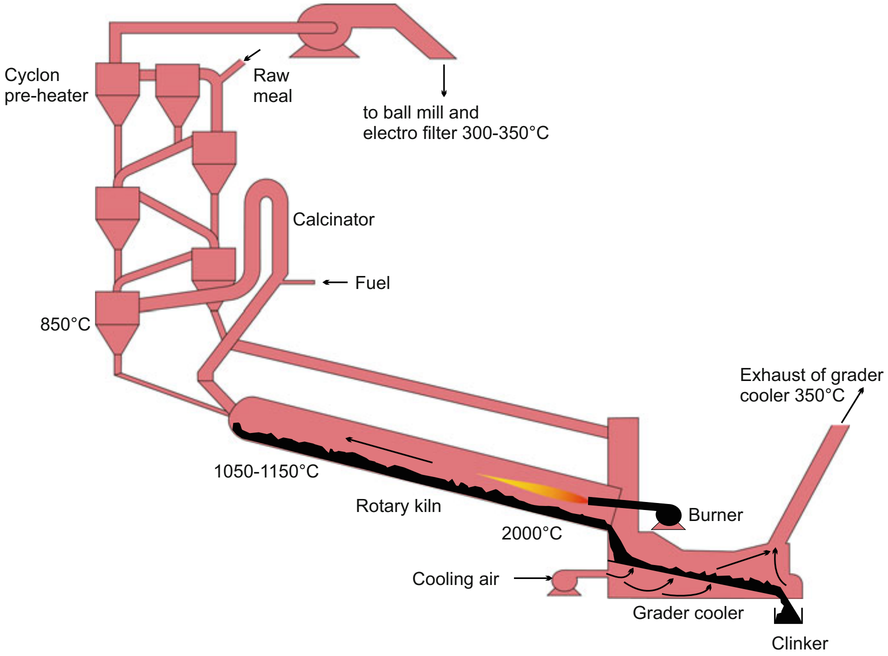

Fig. 6.3 Schematic sequence of the burning process in the rotary kiln during cement production

Table 6.1 Cement phases

Chemical name	Designation	Formula in oxide notation	Chemical formula
Tricalcium silicate	Alite	C_3S	Ca_3SiO_5
β-Dicalcium silicate	Belite	C_2S	β-Ca_2SiO_4
Tricalcium aluminate	Aluminate	C_3A	$Ca_3Al_2O_6$
Tetracalcium aluminate ferrite	Ferrate/Celite Brownmillerite	C_4AF $C_2A \ldots C_2F$	$Ca_4Al_2Fe_2O_{10}$

In the product "cement", the phases C_3S (about 50 mass-%), C_2S (about 25 mass-%), C_3A (about 13 mass-%) and C_4AF occur (Table 6.1).

To explain the phase relationships, a section of the ternary phase diagram C-A-S is shown enlarged in Fig. 6.4.

Actually, the quaternary system CaO-Al_2O_3-Fe_2O_3-SiO_2 should be considered. In practice, however, it is sufficient to consider the ternary edge system. To ensure that the formation of free CaO is avoided, the CaO content of the total cement composition must not exceed the CaO (free lime, lime) and alite (Ca_3SiO_5) field boundaries. In Fig. 6.4 this field boundary is marked in red. The lime standard is given here as a number, and for the value 100 it represents the mathematical description of this field boundary. CaO as a phase in the cement would lead to locally uncontrollable volume

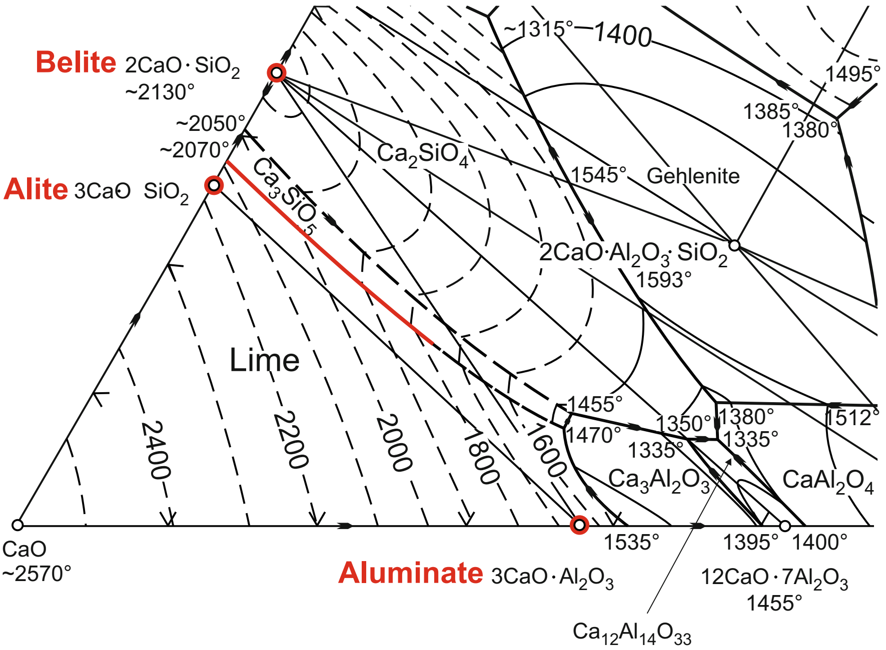

Fig. 6.4 Section of the CaO-Al_2O_3-SiO_2 ternary system relevant to cement production. (Modified according to American Ceramic Society: Phase diagrams for ceramists, reprinted with permission of the American Ceramic Society)

expansion during hydration, which would result in cracks or excessive local heating during hardening and microstructure development.

The conversion or formation of the individual phases with the respective residence time and the temperature development of the fuel in the production process is shown in Fig. 6.5.

For the production of cement, lime, clay minerals and quartz are ground in suitable proportions and introduced into the burning process (I). Iron oxide is introduced as an impurity via the raw materials and is desirable as it improves the sintering behaviour.

Until entering the rotary kiln cycle (II), a drying process of the raw meal takes place, the lime decalcines up to 1000 °C for the most part to CaO, the CO_2 escapes. At 573 °C, low quartz transforms into high quartz. At about 550 °C, the clay minerals decompose and begin to form the $C_2(A,F)$ phase and the Belite (C_2S) cement phase with portions of the high quartz and iron oxide.

From the entrance into the rotary kiln cycle to directly into the rotary kiln (III), all clay minerals have chemically converted, and all $CaCO_3$ has also decalcined.

In the front section of the rotary kiln (IV), CaO and SiO_2 decrease to form dicalcium silicate (belite). The remaining high quartz transforms to cristobalite, reacts further to belite and the last residues form with the other components a first

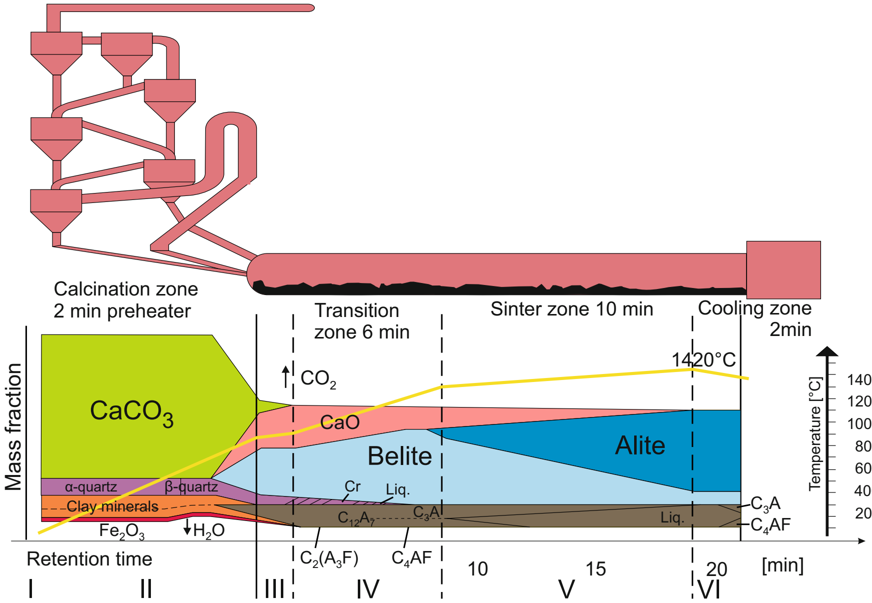

Fig. 6.5 Cement drying and burning process and phase formation over time

Al,Fe-rich melt (Liq.). Due to residues of H_2O in the process, intermediate mayenite ($C_{12}A_7 - Ca_{12}Al_{14}O_{33}$), which combines with this melt and the $C_2(A,F)$ ($Ca_2(Al,Fe)O_5$) reacts into aluminate (C_3A) and tetracalcium aluminate ferrite (C_4AF).

Before moving to the main area of the rotary kiln (V), the tricalcium silicate alite (C_3S) begins to form from belite and CaO. At the same time, a significant amount of melting (Liq.) develops with dissolution of aluminate (C_3A) and C_4AF.

In the cooling zone (VI), the entire clinker is rapidly cooled. In the process, the melt recrystallizes to tricalcium aluminate (C_3A) and tetracalcium aluminate ferrite (C_4AF), a significant portion solidifies glassy. Besides, metastable alite (lower stability at 1250 °C) and belite are found as main phases. The maximum temperature of the material to be fired in the rotary kiln on the clinker is approx. 1420 °C.

The reactions taking place are reflected in the microstructure of the cement clinker. Figure 6.6 shows a typical microstructure with the corresponding formation and quantitative proportions of the cement clinker phases.

Large quantities of CO_2 are produced during cement production, on the one hand from the decalcination of the lime and on the other hand from the use of fuels. A total of approx. 870 kg of CO_2 is released per 1000 kg of clinker.

The clinker is then finely ground and calcium sulphate (approx. 3% by mass) is added. Now the final product, the cement, is available. The sulphate is a mixture of gypsum, anhydrite and hemihydrate, depending on the recipe and the grinding process. The addition of sulphate makes it possible to regulate the setting reaction of cement with water during subsequent processing.

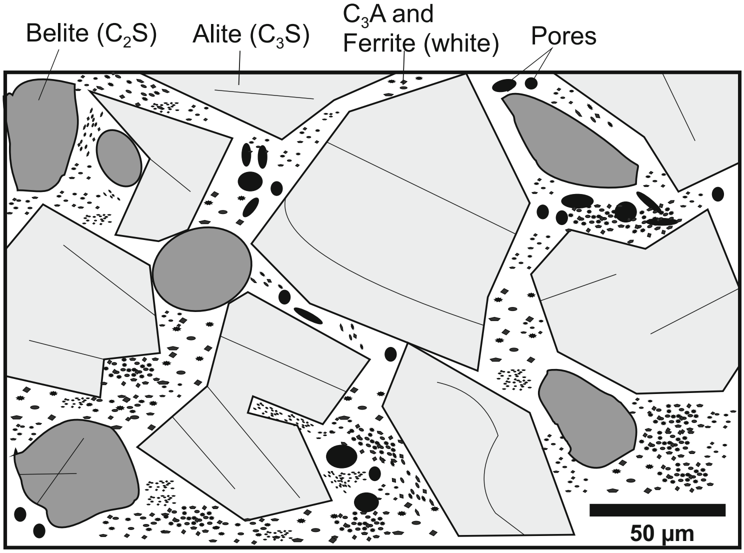

Fig. 6.6 Schematic representation of the microstructure of cement clinker phases. (Modified after Campbell 1986)

6.2.3 Hydration of Cement

The cement is mixed with aggregates such as sand and/or gravel and water in the cement plant or on the construction site. This mixture can now be used to pour building components, walls, ceilings, etc. Mortar and concrete consist of cement with various aggregates of different grain size and water. In mortar the main aggregate tends to be sand (max 4 mm), in concrete sand and gravel. Mortar is mainly used to join bricks or ashlars as a jointing material. Concrete is mostly used to make large building components.

As soon as cement comes into contact with water, hydration begins. During hydration, calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (C-A-H) are formed, which bring about consolidation (Fig. 6.7). The exact processes are quite complex and can therefore only be considered schematically at this point. In addition to the C-S-H and C-A-H phases, portlandite ($Ca(OH)_2$) is also formed, which is responsible for the quite high pH value in the concrete of about 12.5; additional alkalis increase it even further to 13.2.

The Ca-silicates alite and belite react with water in an exothermic reaction to form C-S-H phases and portlandite. The reaction turnover of alite is much faster and ranges from hours to about 1 month, in the case of belite the time frame is from months to years.

The following silicate reactions are important in hydration:

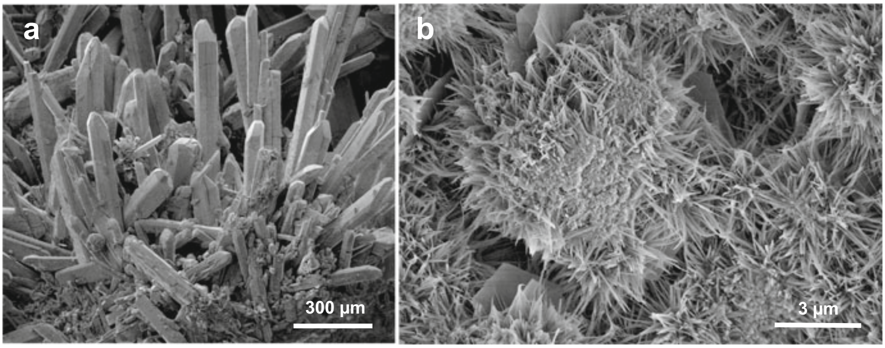

Fig. 6.7 SEM images of ettringite (**a**) and CSH phases (**b**). (Photos: B. Möser, with kind permission)

$$\begin{array}{l}C_3S + 5.3\,H \rightarrow C_{1.7}SH_4 \qquad + 1.3\,CH \\ \text{Alite} + \text{Water} \rightarrow \text{C-S-H-Phase} + \text{Portlandite}\end{array}$$

$$(\text{reaction turnover from hours to one month})$$

$$\begin{array}{l}C_2S + 4.3\,H \rightarrow C_{1.7}SH_4 \qquad + 0.3\,CH \\ \text{Belite} + \text{Water} \rightarrow \text{C-S-H-Phase} + \text{Portlandite}\end{array}$$

$$(\text{reaction turnover from months to years})$$

The hydration of the tricalcium aluminate is also an exothermic reaction, which proceeds very violently and rapidly in the presence of water. In order to make the setting of the cement practicable, gypsum is added to the reaction mixture as a setting retarder. Thus, ettringite is initially formed as an intermediate phase (Fig. 6.7), which is later gradually converted into monosulphate in a further reaction.

It should also be mentioned that the properties of cement and concrete can be modified by adding a wide variety of mineral and chemical agents. In addition to accelerators and retarders of the setting reactions, these can include solid and liquid plasticizers, air-entraining agents, viscosity modifiers, water-reducing agents or colorants. This allows the manufacturing parameters and material properties to be specifically adapted to the specific requirements.

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Refractory Materials

7

Ceramic refractory materials are used in many ways in everyday life and in industry. Fireclay bricks are found in open fireplaces or wood-burning stoves as lining in many homes, and practically all high-temperature processes in industry take place in reaction vessels lined with ceramic materials.

In refractory science, two lines of materials exist: the acidic, and the basic refractory materials. For the acid refractory materials, the binary phase diagram Al_2O_3-SiO_2 is relevant, for the basic refractory materials the binary phase diagram CaO-MgO. Although in recent years this distinct separation has been viewed somewhat more moderately, it is still highly significant for fundamental understanding. As in wet chemistry, acid reacts violently with a base. Also with ceramic materials the rule applies never to combine directly acid with basic, otherwise reactions take place, in the worst case melts are formed.

There is a multitude of components that make up refractory materials. Figure 7.1 shows this basic material pyramid with the material designations.

It is not possible and also not intended to present and discuss the entire refractory science here. Only by means of selected examples the fundamentals of selected aspects are to be presented from the mineralogical point of view.

7.1 Refractory Fabric Systems

7.1.1 The Crystalline Normal Pressure Modifications of SiO_2

Depending on pressure and temperature and on the type of crystal structure, many modifications of SiO_2 exist. For applied mineralogy, however, only the crystalline modifications that are stable at normal pressure are of interest (Fig. 7.2).

Regarding the names of the modifications, it should be noted that internationally there is no uniform rule for the use of the terms α and β for low- and high-

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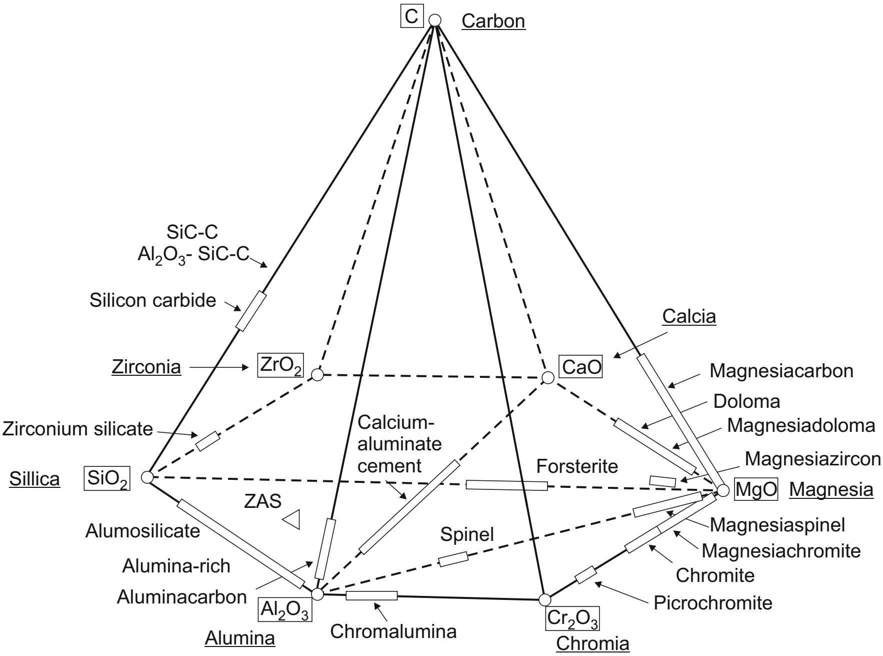


Fig. 7.1 Fundamental material pyramid with the position of the refractory materials. (Modified after Routschka 2001)

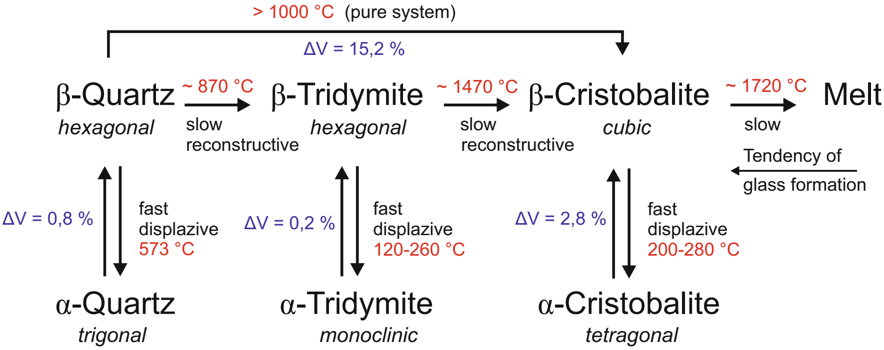


Fig. 7.2 The crystalline modifications of SiO_2 at normal pressure. *α* low-temperature modification, β high-temperature modification

temperature modification, respectively; this often leads to confusion. Two different types of phase transformation occur:

- During the displacive phase transformation from low to high phase and vice versa, the bond angle between the $[SiO_4]^{4-}$-tetrahedra and slightly the bond length change. This phase transformation is not quenchable, it always proceeds and is reversible.

- In the reconstructive phase transformation, a significant remodeling of the structures via bond breaking between the $[SiO_4]^{4-}$-tetrahedra must occur, followed by a new arrangement. This is kinetically inhibited and proceeds slowly. This phase transformation can be frozen.

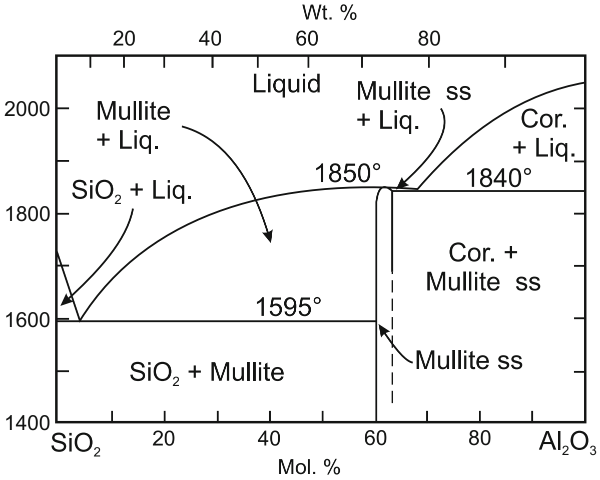
The unary system SiO_2 is special in many respects. If a SiO_2 melt is cooled, no crystals are formed and it solidifies into silica glass. If low-quartz is heated, high-quartz forms at 573 °C, which on further heating transforms into high-tridymite and this then transforms into high-cristobalite, which consequently melts at 1725 °C. In practice, however, high cristobalite often forms after the high quartz, which then successively transforms into the stable high tridymite when remaining in the thermal stability field of the high tridymite. This is due to the presence of traces of K or Na. If high cristobalite is cooled rapidly, metastable low cristobalite is formed, and the same applies to high tridymite, which transforms into low tridymite.

7.1.2 The Binary System SiO_2-Al_2O_3

The binary system SiO_2-Al_2O_3 exhibits one of the fundamental phase diagrams in the refractory field, but also in many other areas of applied mineralogy (Fig. 7.3).

In the phase diagram, three stable, congruently melting phases occur: SiO_2 in its respective temperature modifications, mullite and corundum. The phases disthene, andalusite and sillimanite, which exist in nature, do not occur in the pure system SiO_2-Al_2O_3, since they crystallize only at elevated pressure or in the presence of water.

Fig. 7.3 The binary system SiO_2-Al_2O_3 at normal pressure in air. (According to Phase Diagrams for Ceramists, American Ceramic Society (1964), Vol. I, Fig. 314, reprinted with permission of the American Ceramic Society (1964))



Corundum melts at about 2020 °C, mullite melts at about 1850 °C and SiO_2 as cristobalite at 1725 °C. One always encounters discussions regarding the congruent or incongruent melting behavior of mullite. This discussion is complex, but can be clearly answered with the statement: mullite melts congruently. Mullite exhibits a distinct phase range. The Al-rich composition is called fused mullite $2Al_2O_3 – SiO_2$ (2:1 mullite). These boundary solid solutions occur in fused cast stones with compositions between corundum and mullite, hence the name fused mullite. The Al-poor composition is called sintered mullite $3Al_2O_3 – 2SiO_2$ (3:2 mullite). These boundary solid solutions occur in rocks produced from clays via sintering processes, hence the name sintered mullite. The solidus temperature between corundum and mullite is about 1840 °C, and the associated eutectic is close to mullite. The solidus temperature between mullite and cristobalite is found at 1590 °C, here the eutectic is at about 95 mass-% SiO_2. It is rare to find an exactly formulated structural formula for mullite, almost always the designations 2:1 or 3:2 mullite are used. This is because the crystal structure of mullite is derived from that of sillimanite via suitable defect formation. This is not trivial and leads to confusing formulas.

7.1.3 The Binary System CaO-MgO

The binary system CaO-MgO is an eutectic system with distinct miscibilities of the phases for the other component (Fig. 7.4).

CaO and MgO form distinct phase widths (solid solution – ss) that increase with increasing temperature until they reach their maximum at the solidus. The crystal lattice of CaO can incorporate the smaller Mg^{2+} in greater quantity than the crystal lattice of MgO can incorporate the larger Ca^{2+}. The solidus is at 2370 °C.

7.2 Classification of Refractory Materials

7.2.1 Terminology

The designations of refractory materials are manifold. On the one hand, traditional names such as fireclay have become established, on the other hand, they are named after the raw material, such as dolomite bricks, although they only consist of CaO and MgO after the firing process. The same applies to sillimanite bricks, which are produced from the raw material of a modification of Al_2SiO_5, mostly andalusite or sillimanite, but then consist in the brick of mullite, a SiO_2 modification and possibly a glassy solidified melt.

Regardless of the chemical composition, a distinction is made between shaped and unshaped products. Shaped products are prefabricated stones of various sizes that have been converted into sintered products by a firing process during manufacture. Unshaped products are mixes, mortars or cements that are tamped on site as backfill material in areas where stone shapes would be too complex or expensive. Like cements and mortars, they sinter and solidify when the kiln is started up. The

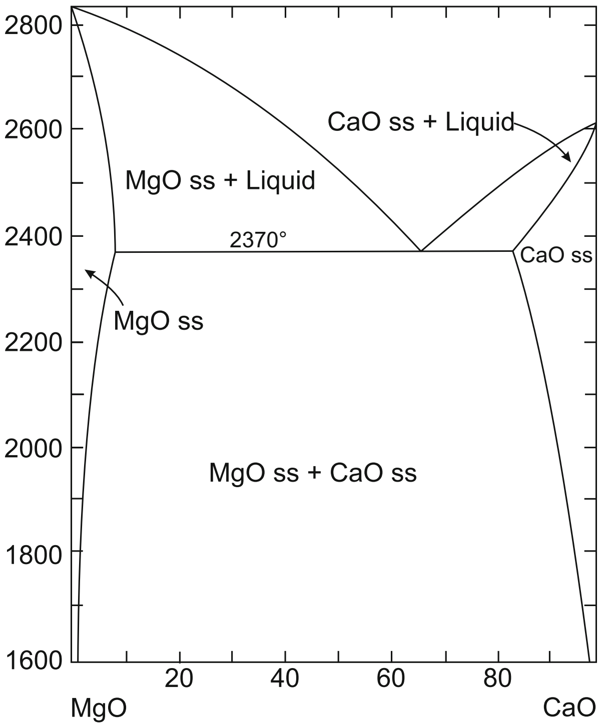


Fig. 7.4 The binary system CaO-MgO at normal pressure in air. (American Ceramic Society (1964), Phase Diagrams for Ceramists, Vol. I, Fig. 229, reprinted with permission of the American Ceramic Society (1964))

firing shrinkage must be compensated for in the process. This is done via the joints of the masonry made of mortar and cements. If necessary, additional burning spacer materials must be added in order to optimally absorb the greater expansion of the bricks during the heating process compared to the shrinkage of the thin joint material. In addition, there are special functional products such as gas purging bricks, sliders, ceramic filters, etc.

Two important terms are “refractory” and “high refractory”. They designate materials according to the characteristic of the occurrence of the first melt. In the case of refractory materials, according to the definition, the first melt may only occur in the brick itself above 1450 °C without external chemical input. For high refractory materials, this temperature is 1840 °C. This can also be read from the binary system SiO_2-Al_2O_3 (Fig. 7.3). Refractory materials have a composition between that of mullite and a modification of SiO_2. Here the solidus temperature is 1590 °C. However, since the raw materials are never pure, but always have impurities of possibly some mass-% of Fe, Mn, K, Na, etc., this lowers the solidus in the resulting polynary system. 1450 °C is the practical value. High refractory materials show compositions between corundum and mullite. Here the solidus temperature is 1840 °C. The raw materials for this are usually very pure, so this 1840 °C also corresponds to the practical value for highly refractory. Basic refractory materials from the

CaO-MgO system easily meet this requirement with the solidus temperature of 2370 °C.

7.2.2 Fireclay Bricks

Fireclay (Chamotte) is probably the oldest and most widely produced refractory material in quantity. At its simplest, it represents fired clay made into either bricks or mixes. In Fig. 7.5, the compositions for various raw materials in the Al_2O_3-SiO_2 system are plotted. Potential raw materials such as kaolin on the one hand and andalusite (respectively sillimanite and disthene) are in the range between mullite and the modifications of SiO_2.

With the raw materials kaolin or other clays and andalusite, the composition can be optimized for the desired use. The difference in fireclay quality does not lie in the solidus temperature, but in the quantity of the first melt that occurs (application of the lever law to determine the quantities of melt and mullite). The higher the Al_2O_3 content, the lower the amount of melt. Furthermore, this melt is also high in SiO_2-content, which makes it very viscous. The different acid refractory materials are classified according to their Al_2O_3-content. High alumina bricks are made using bauxite as the raw material.

If andalusite, sillimanite or disthene are used as raw material, these stones are called sillimanite stones, although they consist of mullite and a SiO_2 phase. In rare

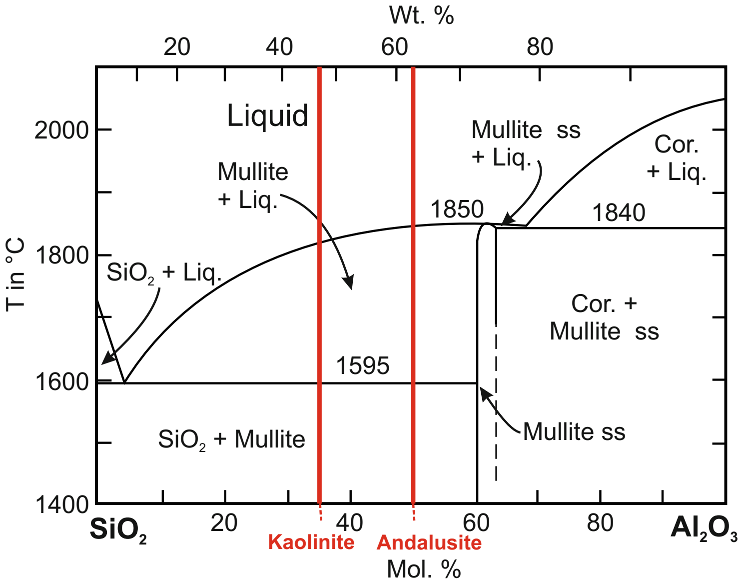


Fig. 7.5 The binary system SiO_2-Al_2O_3 with position of various raw materials. (Modified from American Ceramic Society, Phase Diagrams for Ceramists, Vol. I, Fig. 314, reprinted with permission of the American Ceramic Society)

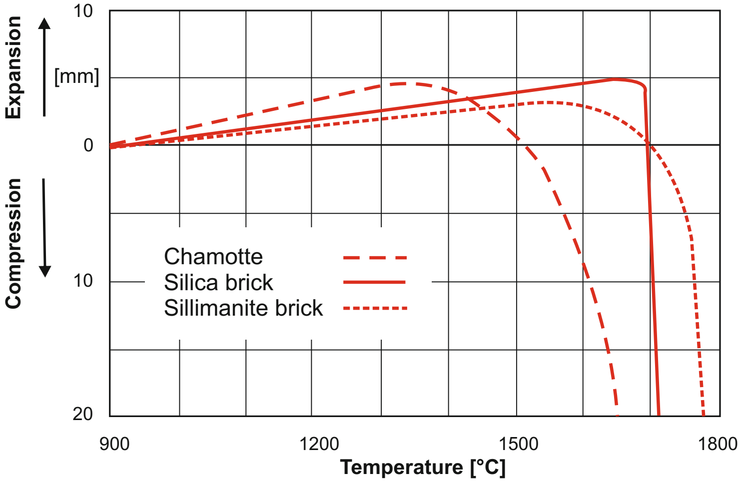


Fig. 7.6 Idealised refractoriness under load curves of fireclay (chamotte), silica and sillimanite bricks (pressure 0.2 N mm^{-2}, height of test specimens 50 mm)

cases, a glassy solidified melt is found in minute quantities, in which impurities of alkalis/alkaline earths have collected.

The quality of a stone is shown by the occurrence of a melt, the amount of melt formed and the structure. One test method shows this particularly clearly, the refractoriness under load curve. The refractory bricks are subjected to the load pressure of the wall above them. In the test, a standardized cylindrical test specimen with a defined superimposed load is therefore continuously heated in a furnace. Figure 7.6 shows a comparison of the test curves of a fireclay brick (chamotte), sillimanite brick and silica brick.

The curves show different behaviour: The fireclay brick (chamotte) expands up to approx. 1330 °C and then slowly begins to increasingly compress until it finally fails above 1500 °C. Fireclay bricks are made from clays. They are good, but not high quality materials. Due to impurities, including those caused by occupation between the layers, the raw material primarily introduces alkali/alkaline earth and, to a lesser extent, iron impurities, which lead to an initial low level of melting at approx. 1330 °C. This causes the grain bonding in the clay to become increasingly deformed. As a result, the grain bond in the microstructure is loosened and displaced by the load. With further temperature increase, the amount of melting and thus the displacement in the microstructure continue to increase until the stone shows no stability, regardless of the fact that it is only partially melted. The test curve of the sillimanite stone shows a comparable picture, the first melt formation and thus the compression do not start until about 1520 °C. The melting of the sillimanite stone is not very stable. Here iron is to be regarded as the main impurity which leads to this temperature of melt formation deviating from the phase diagram, while alkalis occur rather subordinately. Although this first melt is SiO_2-rich and thus should actually be highly viscous, the iron content must still be taken into account. The iron in the melt makes it much less viscous and the drop in stability is then more dramatic. By way of anticipation, the silica stone should be discussed at this point. These stones are composed of SiO_2 with small amounts of calcium for bonding. Alkalis and iron are also present here as minor impurities. The stone shows excellent stability up to 1660 °C, but as we are close to a congruent melting compound here, the increase in melt is quickly very high and the dramatic drop from 1690 °C shows complete melting.

On the basis of these test curves, statements can be made about the behaviour in the limit range. Irrespective of the temperature at which the first melt occurs, the silica stone fails very quickly, whereas sillimanite and fireclay stone can still absorb small amounts of melt forming in the structure and do not fail so dramatically quickly.

Fireclay bricks are used as lining in open fireplaces, wood stoves, rotary kilns in the lime and cement industries, in kilns for coarse and fine ceramic materials, etc.

7.2.3 Silica Bricks

Silica bricks consist of more than 93 mass-% SiO_2, preferably rock quartzite. To support a ceramic bond, approx. 3–4 mass-% CaO is added (Fig. 7.7).

Due to the addition of CaO, small amounts of melt are formed above the solidus at 1436 °C. Due to the small quantity, these are not critical during use. Therefore, the stones also appear slightly yellowish. Iron impurities would lead to brown colouring. Contamination of the raw materials with alkalis should be avoided.

Silica bricks possess excellent properties with respect to thermal shock resistance. Figure 7.8 shows the volume jumps during the phase transformations of various SiO_2 modifications.

Quartz shows the volume jump of 0.8% from low quartz to high quartz at 573 °C. Low quartz shows a clear volume expansion, high quartz even a volume shrinkage with increasing temperature. The volume jump from low cristobalite to high cristobalite is 2.8% at 270 °C, tridymite shows two volume jumps from low to high modification at 117 °C and 163 °C of 0.2% each. How these two jumps are to be explained is rather complex and not yet satisfactorily clarified, but it does not influence the application behaviour of the silica bricks. The largest jump in volume occurs from high quartz to high cristobalite and high tridymite with 15.2 and 15.6% respectively (estimated from diagram). The destructive effect of the phase transformation from high-quartz to high-cristobalite becomes clear in Fig. 7.9.

Figure 7.10 shows the phase development during the production of silica bricks. The diagram was created experimentally for different firing cycles. The phases were determined qualitatively by X-ray powder diffraction after cooling. In each case the low temperature modifications were found. In operation, the respective high-temperature modifications are present in the brick. The glass phase was determined microscopically by image analysis and calculated with the diffractometry data. It is present as a melt during use. Due to the complexity of this determination, the values can only be regarded as qualitative.

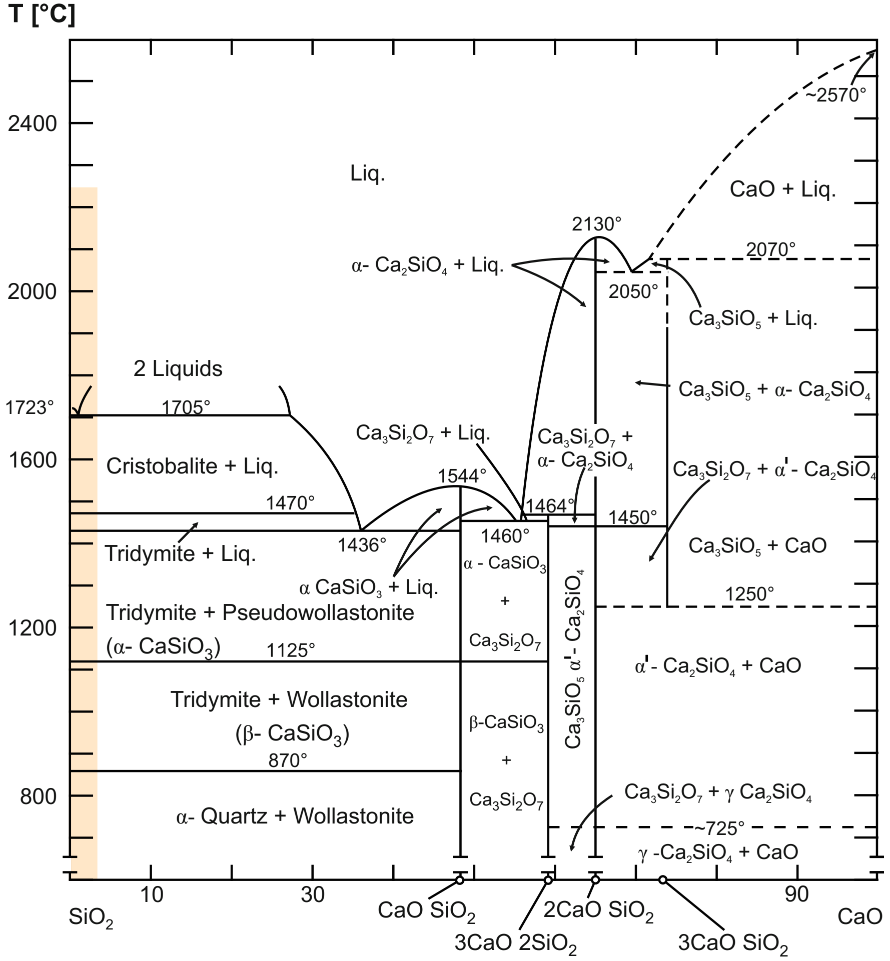


Fig. 7.7 The binary system SiO_2-CaO in mass-% in air with marking of the composition range of silica bricks. (Modified American Ceramic Society, Phase Diagrams for Ceramists, Vol. I, Fig. 237, reprinted with permission of the American Ceramic Society)

The raw materials for the silica bricks are ceramically prepared and shaped, followed by the firing process at approx. 1450 °C in air. At the beginning, approx. 10% melt is formed, which is called glass in the diagram. The quartz transforms into high-quartz and then successively first into high-cristobalite (metastable), then into high-tridymite. During the heating process, the largest jump in volume of the stones takes place at 800–1000 °C, as the transformations to high-cristobalite or high-tridymite take place here. The melt or glass content will always be about 10% during the service life of the bricks. The high-quartz or high-cristobalite content decreases during use and the stone approaches a state of equilibrium. Residual quartz and some residual cristobalite, however, always remain. The reason for this is that some grains

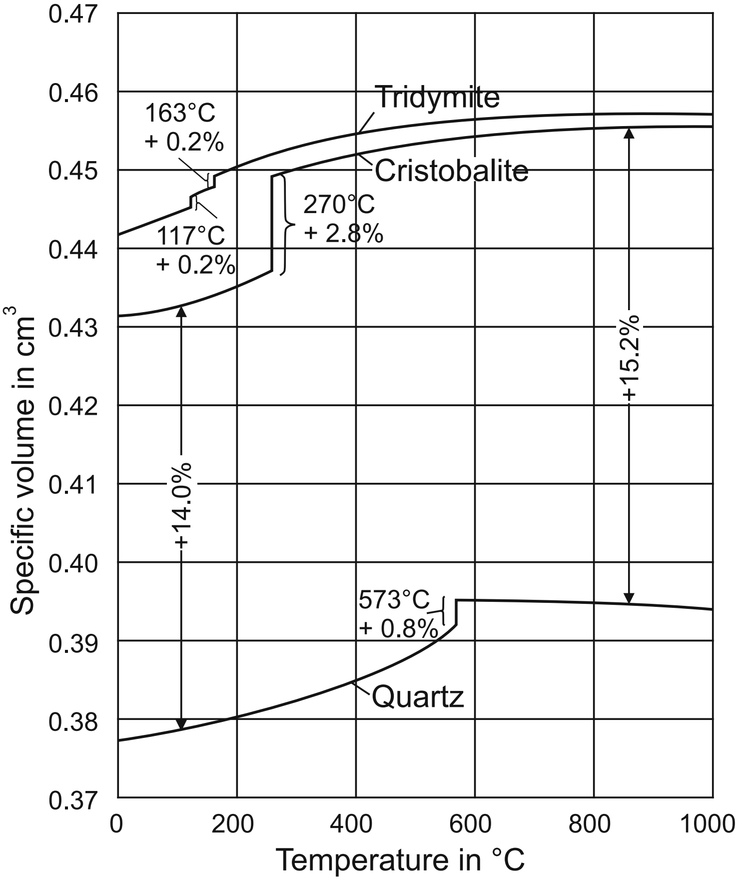
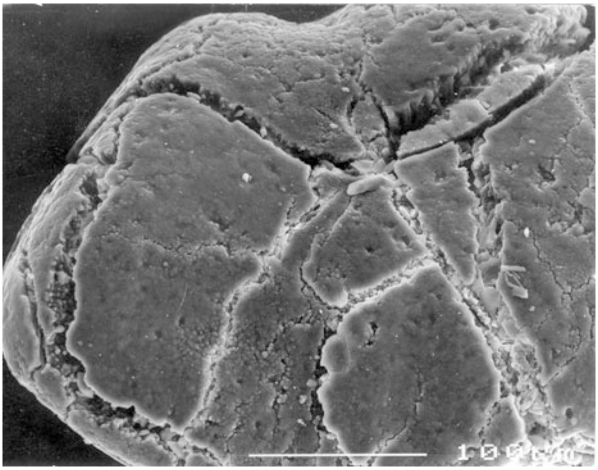


Fig. 7.8 Temperature dependence of the specific volume of quartz, tridymite and cristobalite. (Figure 100, p. 187 from Salmang and Scholze 1982, with kind permission)

in the microstructure are locally put under significant pressure by the phase transformations and microstructural strains. However, high-tridymite and high-cristobalite are not pressure stable, and so cores of high-quartz are obtained. The residual cristobalite is stabilized by small amounts of Na and/or K. When the pre-fired silica brick cools, large volume jumps no longer occur because the high-tridymite, high-cristobalite and high-quartz phases follow the path of displacive transformation due to the nature of the phase transformations (Fig. 7.2) and transform into the respective low-form. The volume jumps there are quite small, and the melt also helps the microstructure to absorb this. Figure 7.11 shows the thermal expansion of silica bricks.

When silica bricks are used, they are only heated once from normal temperature, and the expansion of approx. 1.3% up to approx. 600 °C must be absorbed by the joints. From 600 °C up to the application limit of 1400 °C there is practically no

Fig. 7.9 “Bursting” of a quartz grain during transformation to high-cristobalite



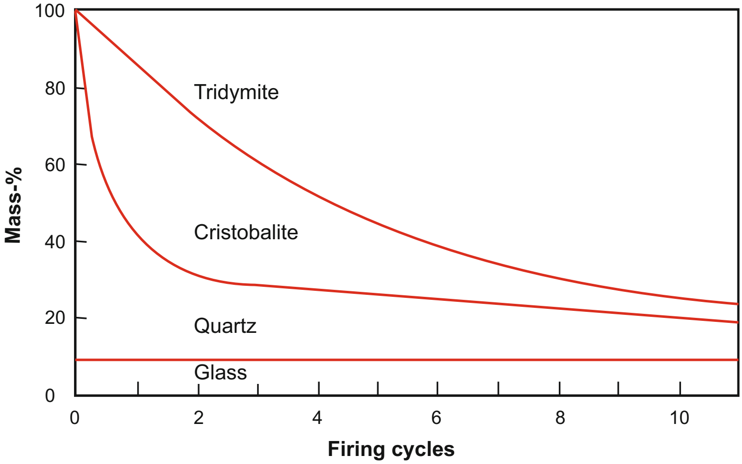


Fig. 7.10 Idealised phase development in silica bricks as a function of the firing cycles at 1450 °C in air for 6 h in each case in mass-%

thermal expansion. This makes these bricks ideal for use in areas where frequent temperature changes are unavoidable, e.g. in coke ovens, where temperature fluctuations between 700 and 1400 °C occur constantly between filling with “cold” coal and pushing the “hot” coke out of the oven. Only increased contents of residual quartz can be critical for the quality of the silica bricks, since quartz subsequently transforms into cristobalite when used at high temperatures and the associated volume expansion leads to “regrowth” of the bricks.

Silica bricks are used in coke ovens, in glass troughs (trough as well as ceiling), on lids of electric furnaces etc.

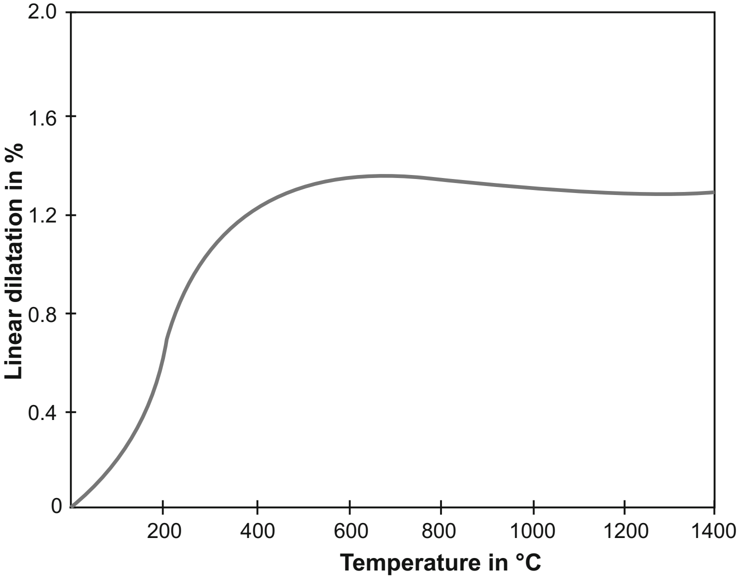


Fig. 7.11 Idealized thermal expansion curve of a silica brick

7.2.4 Basic Refractory Materials

The basic refractory materials are produced from the raw materials limestone, dolomite or magnesite. A special position is occupied by the so-called seawater magnesite (or *dead sea periclase*), in which the magnesium is extracted from brine by means of a special process. After the firing process, microstructures have formed in the stones which correspond to the binary phase equilibria of the CaO-MgO system. The basic side of refractory materials is also referred to as the “black side” of refractory science.

When burning lime, dolomite or magnesite stone, MgO is also formed in addition to CaO. MgO is hardly hygroscopic, whereas CaO is very hygroscopic. This is a major problem during storage and transport. The prepared pre-fired raw materials are bound with carbon pitch or epoxy resin. This prevents hydration during storage and transportation. After the bricks are installed, the pitch, carbon and epoxy resin are burnt out during heating, and this loss of volume is compensated for by the thermal expansion of the masonry.

In addition to the products mentioned, chromium-magnesite bricks (CM bricks) or olivine and chromite as direct raw materials (forsterite and spinel bricks) are also used as basic refractory materials.

Basic refractories are used in transport vessels for the iron and steel industry, in steel converters, etc.

7.3 Test Methods of Refractory Materials

There are countless test methods in the field of refractory science. Often, these methods have been developed empirically or have proven their informative value with regard to the operating conditions, although they sometimes have little to do with reality in terms of their nature. At this point, a few selected test methods will be briefly presented.

7.3.1 Abrasion Resistance

In this process, materials are tested for durability at different temperatures (20, 1000 and 1400 °C) by means of abrasive blasting or grinding. Properties such as porosity, cold/hot pressure behaviour and cold/hot bending strength play a major role as partial aspects. Abrasion resistance decreases with increasing temperature, corrosion of the stone and atmosphere are further critical parameters.

7.3.2 Alkali Oxide Bursting

The reaction of alkali oxides and vapours above 800 °C with refractory bricks often results in a corrosion layer of different phases which, due to the different volumes, can lead to spalling over large areas and thus to dramatic corrosion (Table 7.1). The formation of glaze-like molten surface layers is another type of this corrosion.

Table 7.1 New mineral formations during alkali oxide attack on alumina-silica materials. MP Melting point; DP Decomposition point

Acid firebricks (below 30% Al_2O_3)			
Feldspars	Potash feldspar	$K_2O \cdot Al_2O_3 \cdot 6\ SiO_2$	DP 1150 °C
	Albite	$Na_2O \cdot Al_2O_3 \cdot 6\ SiO_2$	MP 1118 °C
Fireclay and alumina-rich bricks (30–80% Al_2O_3)			
Feldspathic minerals	Kaliophilite	$K_2O \cdot Al_2O_3 \cdot 2\ SiO_2$	MP 1785 °C
	Nepheline	$Na_2O \cdot Al_2O_3 \cdot 2\ SiO_2$	MP 1626 °C (density ~ 2.6 g cm^{-3})
	Leucite	$K_2O \cdot Al_2O_3 \cdot 4\ SiO_2$	MP 1693 °C
	Kalsilite	$K_2O(Na_2O) \cdot Al_2O_3 \cdot 2\ SiO_2$	
	Noseane	$Na_2O \cdot Al_2O_3 \cdot 2\ SiO_2 \cdot Na_2SO_4$	
	(with simultaneous SO_3-attack e. g. in glass tub grids)		
Corundum brick (over 80% Al_2O_3)			
	ß – $Al_2O_3K_2O$ (Na_2O) · 11 Al_2O_3		(density ~3.3 g cm^{-3})
	Alkali aluminate K_2O (Na_2O) · Al_2O_3		(hygroscopic)

Data from Routschka (2001)

7.3.3 Refrectoriness Under Load

In this test method, a test specimen is subjected to a constantly increasing temperature at a constant superimposed load and the expansion or shrinkage is recorded (cf. Figure 7.6). Depending on the type and quantity of melt formed, the stability of the stone changes until complete failure occurs due to destruction/melting. This allows statements to be made about application temperatures and about behaviour in the limit range.

These properties are determined by the microstructure as well as the type, quantity and properties of melting and porosity.

7.3.4 Thermal Expansion Under Load

The compressive yielding test is tested with a specimen at constant superimposed load. The temperature is continuously increased up to 1550 °C and then the development of shrinkage over time is detected. This assesses the deformation over time at constant pressure and temperature (Fig. 7.12).

The stone expands up to 1500 °C. After reaching the test temperature, the bricks show shrinkage of different types. This shrinkage can have different causes. On the one hand, recrystallization effects can be observed, in which the crystallites in the structure change their dimensions. This can occur via solid-state diffusion or accelerated via the presence of a melt. On the other hand, larger amounts of melt

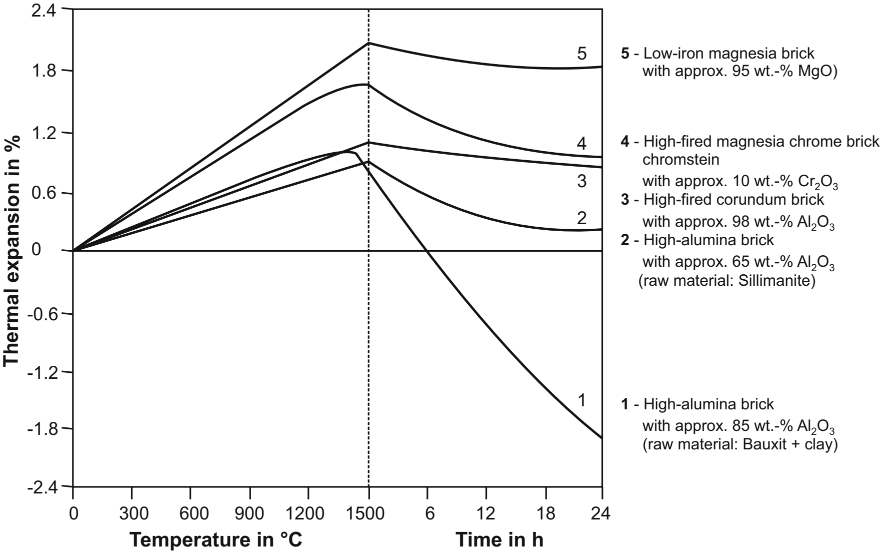


Fig. 7.12 Thermal expansion under load behavior of refractory bricks at 1550 °C and 0.2 N mm^{-2} pressure in air. (Modified after Didier-Werke 1990)

can accumulate over time, causing the microstructure to “set”. The melt is pushed to the side or into the pore space until the non-melted support grain ensures the stability of the microstructure again. In these effects, impurities and the liquidus temperatures of the oxide systems are decisive for the shrinkage behaviour. In most cases, this shrinkage process recovers after some time, and the microstructure has stabilized despite the melt content. The melting amounts responsible for these effects are in the single-digit percentage range.

7.3.5 Elasticity Modulus – E Modulus

The determination of the modulus of elasticity is used to estimate the mechanical and thermomechanical stress. Different methods lead to different values. The modulus of elasticity describes the relationship between stress and reversible deformation.

7.3.6 Gas Permeability

Gas permeability describes the property of allowing gases to flow in the case of a pressure difference. It is essentially determined by flowable pores with diameters >10 μm (Fig. 2.10 in Chap. 2). There is a statistical dependence between open porosity and gas permeability. Fine-pored stones with high porosity can be practically impermeable to gas. Cracks in the stone can greatly alter the behaviour in use.

7.3.7 Hot Bending Strength/Hot Compressive Strength

The hot bending strength/hot compressive strength is carried out under constant temperature on elongated, beam-shaped test specimens that rest on two points. In between, a punch presses from above with increasing pressure on this test specimen and the deformation is measured.

7.3.8 Porosity and Pore Size Distribution

Porosity is an important parameter for the assessment of infiltration and insulation behaviour and stability of refractory materials. Only the open porosity can be determined by different measuring methods. The determination of the closed porosity is not trivial; it can either be roughly estimated by microscopic image analysis in the section or narrowed down, as shown in Fig. 7.13. The mercury injection method gives information on pores between 0.001 and 500 μm, the water-air displacement method on pores between 0.5 and 100 μm. Densely fired bricks typically show pore sizes of 0.1–250 μm, with a main range of 1–50 μm. Refractory concretes are found to have a high percentage of pores below 1 μm. Values of 10–20% total porosity for

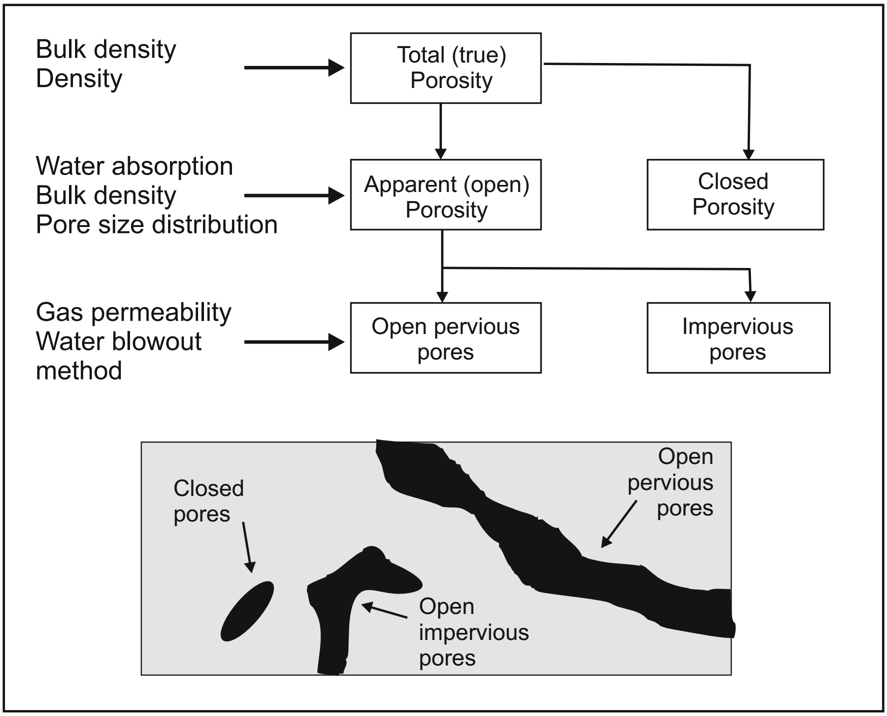


Fig. 7.13 Illustration of the different types of porosity with possibilities of determination. (Modified after Routschka 2001)

non-fused cast bricks are typical. Figure 7.13 shows different types of porosity with ways of determining them.

7.3.9 Thermal Shock Resistance

Thermal shock resistance is probably the most important property of refractory materials. Refractory materials are often subject to large temperature changes. Due to thermal expansion, this ultimately results in disruption and thus destruction of the microstructure. Most refractory materials remain at a constant temperature if possible throughout their entire service life in order to keep wear due to the stress caused by temperature changes as low as possible.

One test method for Thermal Shock Resistance is the *water quenching method.* Here, the specimen is heated to 950 °C and quenched in water. After a defined number of these cycles, the specimen is evaluated for type and severity of cracking. In the *air quench method,* the test cycle consists of heating to 950 °C followed by blowing with compressed air for a defined time. The *ribbon test* consists of a test cycle in which the specimen in the form of a plate is heated on one side with a gas burner and then quenched with compressed air. After a defined number of respective cycles, the test specimen is visually assessed for type and severity of cracking. The damage pattern in all these tests is strongly dependent on the stone format due to the possibility of heat conduction that depends on it.

7.3.10 Thermal Expansion

Thermal expansion measures the geometric expansion of an elongated test specimen as the temperature increases (Fig. 7.14).

7.3.11 Thermal Conductivity

Thermal conductivity is a quantity that is tested by various methods.

In the hot wire method, wires placed in a cross shape on the sample stone are heated and the temperature of the stone is measured at defined intervals. Calorimeter methods are quite complex to perform and have quite high errors with regard to reproducibility and comparability of ±15–20%.

The following general statements can be made:

- With increasing porosity and decreasing pore size, the Thermal conductivity decreases.

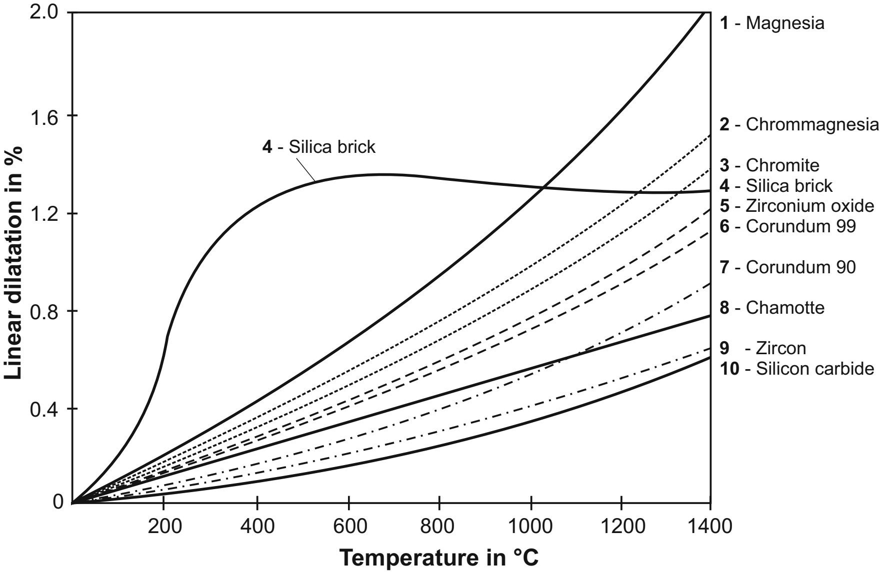


Fig. 7.14 Thermal expansion of refractory bricks. (Modified after Didier-Werke 1990)

- In the case of heat-insulating materials, there is a certain optimum bulk density (porosity) for each temperature.
- Microporous thermal insulation materials can have a lower Thermal conductivity than air.
- For ceramic fibre materials (porosity >90%), the Thermal conductivity decreases with increasing packing density.
- Atmosphere and pressure influence the Thermal conductivity.

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Mineral Materials in Electrical Engineering/Electronics

8

Although metallic materials play a dominant role in electrical engineering and electronics, non-metallic materials are irreplaceable in various fields of application (Hofmann and Spindler 2013). Non-metallic mineral materials are used, for example, as dielectrics or ferroelectrics, piezoelectrics, semiconductors or insulators. In the following, some characteristics of these materials will be discussed.

8.1 Dieletrics and Ferroelectrics

In ceramic materials, unlike metals, the electrons are relatively tightly bound to the nucleus because of ionic or covalent bonding. Therefore, such materials have a low electron conductivity ($<10^{-8}\ \Omega^{-1}\ \text{m}^{-1}$) or a high resistivity ($>10^{10}\ \Omega\text{cm}$). In the electric field, charge transport by electron migration does not occur as in metals, but only a charge shift (= dielectric shift) occurs, which leads to *polarization* and thus to the development of an electric dipole moment. Dielectricity thus describes the formation of electric dipoles by electron and/or ion polarization in the electric field.

According to their occurrence, four types of polarization can be distinguished (Fig. 8.1).

The dielectric behavior of materials is characterized by the dielectric constant ε (or permittivity), which describes the behavior of a non-conductor in the electric field. This property is used in electrical engineering in capacitors by causing polarization to occur due to displacement of an electric charge. The polarizability α of a substance is linked to the dielectric constant ε via the relationship $\varepsilon = 1 + 4\pi\alpha$. Ion polarization plays the most important role in inorganic non-metallic materials.

The dielectric constant can vary widely depending on the composition and structure of the compounds (Table 8.1). Materials with a symmetrical, non-polar structure (e.g. silica glass) have the lowest values, while a number of compounds show strong anisotropic properties (e.g. TiO_2). The microstructure and porosity of ceramic materials also influence ε.

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https://doi.org/10.1007/978-3-662-64867-4_8

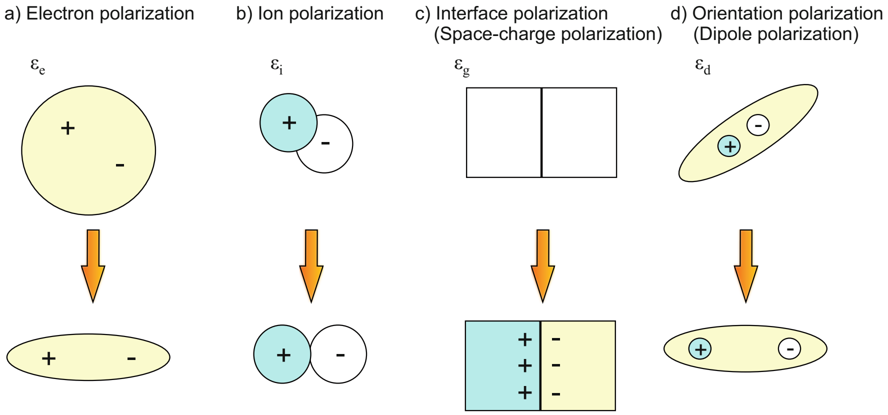


Fig. 8.1 Types of polarization in the electric field

Table 8.1 Dielectric constant ε of selected inorganic non-metallic materials

Material		ε (25 °C, 10^6 Hz)
Barium titanate		>3000
TiO_2	‖ *c-axis*	89
	⊥ *c-axis*	173
Al_2O_3	‖ *c-axis*	8.6
	⊥ *c-axis*	10.5
Lead silicate glass		19
MgO		9.6
CNS glass		7
Mullite		6.5
Quartz		4.7
Silica glass		4

Table 8.2 Dielectric loss for selected materials

Material	Loss angle tan δ (in 10^{-4})
Glasses	4–15
Corundum ceramics	5–10
Titanate ceramics	5–300
Silicate ceramics	200–1000

Since the charges are bound to masses, the charge displacements follow the laws of a forced oscillation. Phase shifts occur between the exciting and generated oscillation, and part of the electrical energy is converted into heat. This is called dielectric loss, measured by the shift δ of the phase angle between current and voltage. The dielectric loss is characterized by the loss angle tan δ (loss factor). Here, too, strong variations occur depending on the material properties (Table 8.2).

The loss angle tan δ increases with increasing temperature but decreases with increasing frequency. For example, tan δ of hard porcelain can be lowered from 200 ·

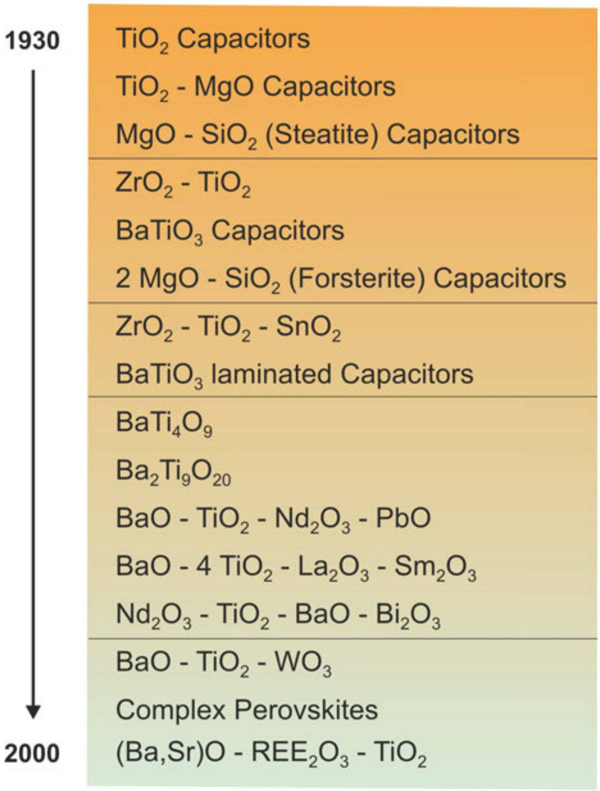


Fig. 8.2 Historical development of dielectric materials

10^{-4} at 50 Hz to $80 \cdot 10^{-4}$ at 1 MHz. Thus, the best dielectric properties are obtained at low temperatures and high frequencies (Baumgart et al. 1984).

The historical development since the 1930s shows that dielectric ceramic materials were and are mainly developed on the basis of titanium oxide (TiO_2 and alkaline earth titanates) (Fig. 8.2). Such materials possess specific properties for dielectric, ferroelectric, and piezoelectric applications. A major advantage of these compounds is mainly the inverse proportionality of dielectric constant ε and geometrical size. This makes them particularly suitable as capacitor materials for the miniaturization of components.

Besides the pure so-called rutile ceramics, alkaline earth titanates are of particular interest. In this group, the dielectric constant increases with increasing atomic mass of the cations: from about 20 for $MgTiO_3$ over ~150 ($CaTiO_3$) and 250–300 ($SrTiO_3$) to 1500 for $BaTiO_3$. Thus, the alkaline earth titanates outperform conventional TiO_2 ceramics in many properties.

In the BaO-TiO_2 system, the congruently melting $BaTiO_3$ has the greatest importance as an engineering material. In this phase system, the hexagonal α-$BaTiO_3$ is stable between the melting temperature and about 1460 °C, changing below 1460 °C to the cubic β-$BaTiO_3$ (perovskite structure) and finally at 120 °C to

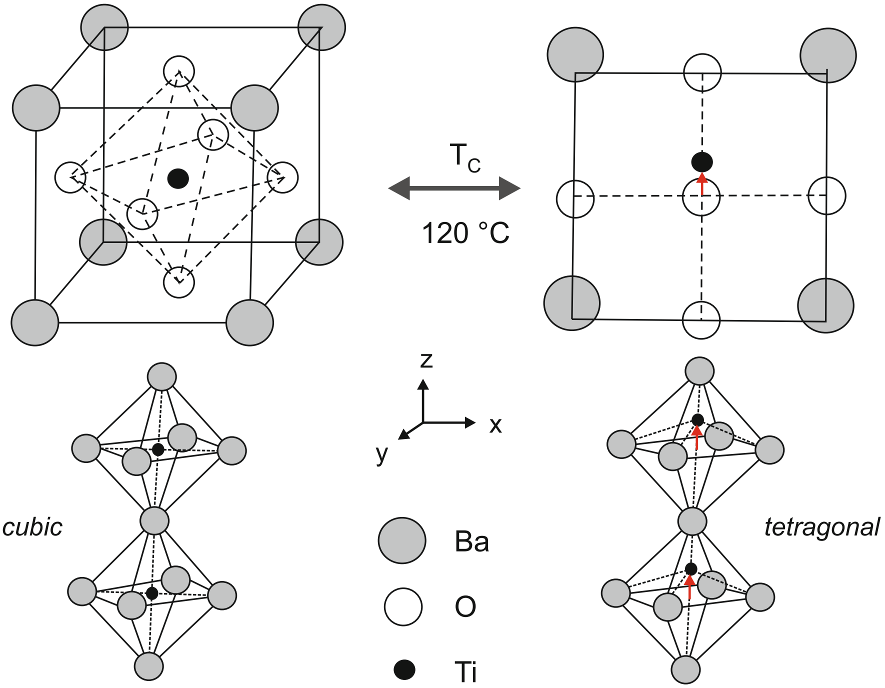


Fig. 8.3 Unit cell of Ba titanate ($BaTiO_3$); above the Curie temperature of 120 °C a centre of symmetry is present (cubic), while below 120 °C the Ti-O chain polarises spontaneously in the *z-direction* (tetragonal without centre of symmetry)

the tetragonal γ-$BaTiO_3$ (Fig. 8.3). The temperature of 120 °C is also known as the Curie temperature (T_C). This is the temperature above which loss of spontaneous polarization (and hence ferroelectricity) occurs. Thus, below 120 °C barium titanate is ferroelectric, while at temperatures >120 °C it exhibits dielectric (paraelectric) properties. The β−/γ-conversion is also of particular interest, since here the dielectric constant has a maximum value.

The basis for the ferroelectricity of barium titanate is the perovskite structure (Fig. 8.3). Due to the large barium ion, steric effects are induced at temperatures below 120 °C, which cause a tetragonal distortion. The titanium ion can occupy two equivalent positions in the *z-axis* direction, resulting in the formation of dipoles when charged ions are displaced. The dipole moments of several cells can be coupled at the microscale and spontaneous polarization occurs, leading to the formation of ferroelectricity. Microdomains of equal polarization are also called Weiss domains (Fig. 8.4). Ferroelectricity thus occurs only in crystals in which the structure permits a polar axis. By applying a voltage, the electrical polarization in ferroelectrics can also be reversed.

The dielectric properties of barium titanate can be modified by combining it with other alkaline earth titanates. For example, the Curie temperature can be shifted from

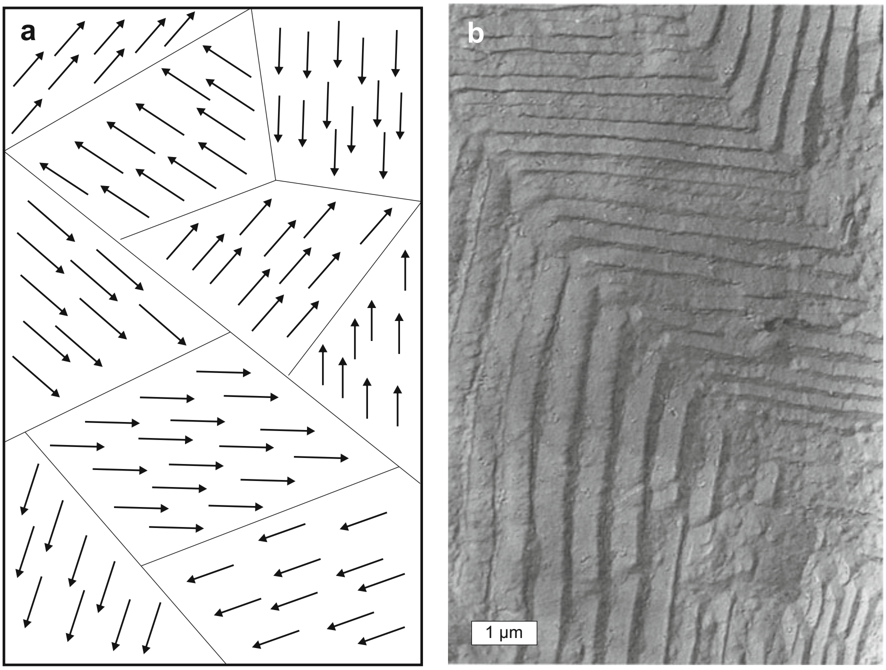


Fig. 8.4 (**a**) General scheme of microdomains of the same polarization (Weiss domains); (**b**) electron micrograph of a domain structure in ferroelectric material. (Modified after Baumgart et al. 1984)

120 °C to room temperature and thus the maximum of the dielectric values can be shifted to a more favourable application range (Fig. 8.5).

In addition to titanates, various zirconates, niobates, tantalates and stannates with perovskite structure are also potential ferroelectric materials that also show piezoelectric and pyroelectric properties. Based on the general formula

$$ABO_3$$

with:

A K^+, Na^+, Ca^{2+}, $Sr^{2+,}$ Ba^{2+}, Pb^{2+}, La^{3+}
B Ga^{3+}, Ti^{4+}, Zr^{4+}, Sn^{4+}, Ta^{5+}, Nb^{5+}

various combinations are possible. By coupled substitution, “complex perovskites” of different composition with optimized properties can also be produced. For example, in the system $PbTiO_3$-$PbZrO_3$ there exists a continuous series of solid solutions which have even better properties than $BaTiO_3$. These materials are referred to as PZT ceramics. They are more ferroelectric, have a higher Curie temperature and a larger remanent polarization.

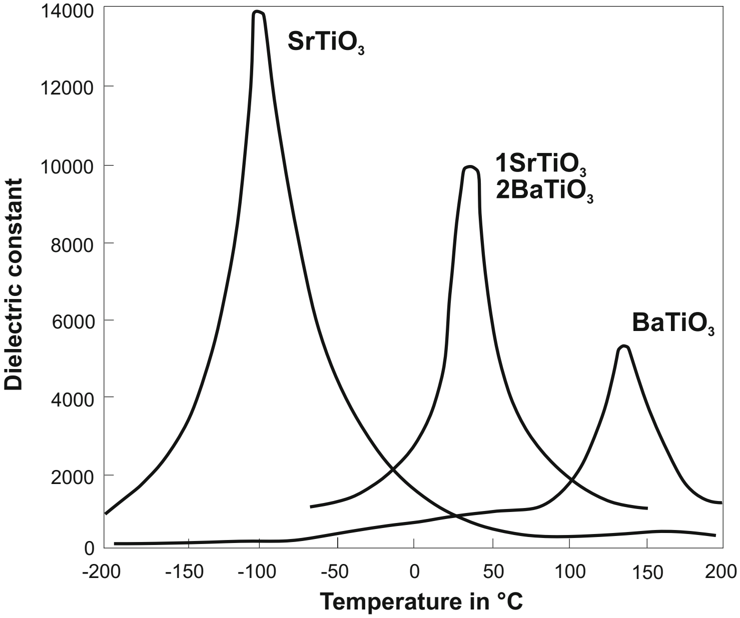


Fig. 8.5 Dielectric constants of $SrTiO_3$, $BaTiO_3$ and a mixture of both as a function of temperature. (Modified after Hecht 1976)

Due to their excellent properties, di- and ferroelectric ceramic materials find many applications in modern industry and technology. They are used as sensor materials for temperature measurements and switches or as dielectric resonators in microwave oscillating circuits in communication technologies. Further applications can be found in the military sector (radar, weapon guidance systems), in mobile phones or satellite systems.

So-called ceramic PTC resistor materials based on barium titanate should also be highlighted. These are ferroelectric ceramic resistors with semiconductor properties. Characteristic for these materials is the strong increase of the resistance at the Curie temperature. Below the so-called transition temperature T_T normal semiconductor behavior is present. Above T_T, the resistance rises sharply and then falls again at T_{max}, which corresponds to normal semiconductor behavior.

8.2 Piezoelectric Materials

Piezoelectricity (also piezoelectric effect) describes the change in electrical polarization and the associated occurrence of an electrical voltage on solids during directed elastic deformation. The piezoelectric effect was first observed in 1880 by the Curie brothers on tourmaline crystals.

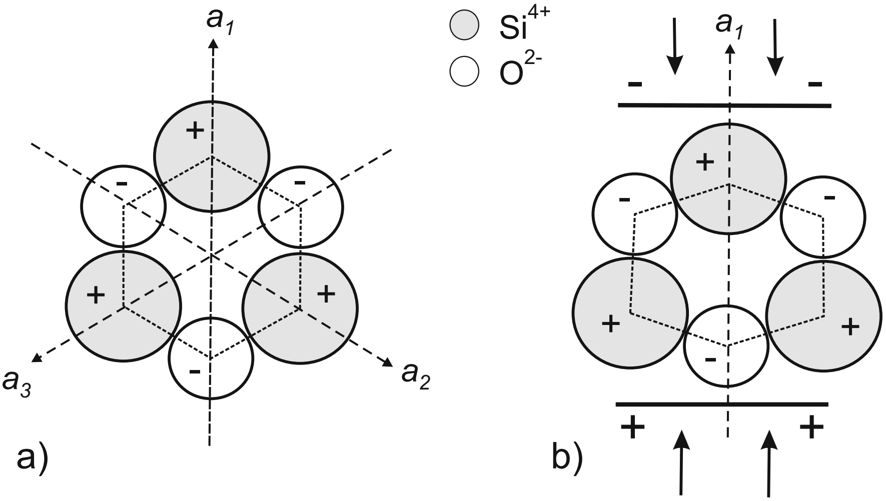


Fig. 8.6 Scheme of the piezoelectric effect in quartz; the uniformly distributed charges (**a**) are displaced by directed pressure (**b**), resulting in the build-up of a voltage. (Modified after Kleber et al. 1998)

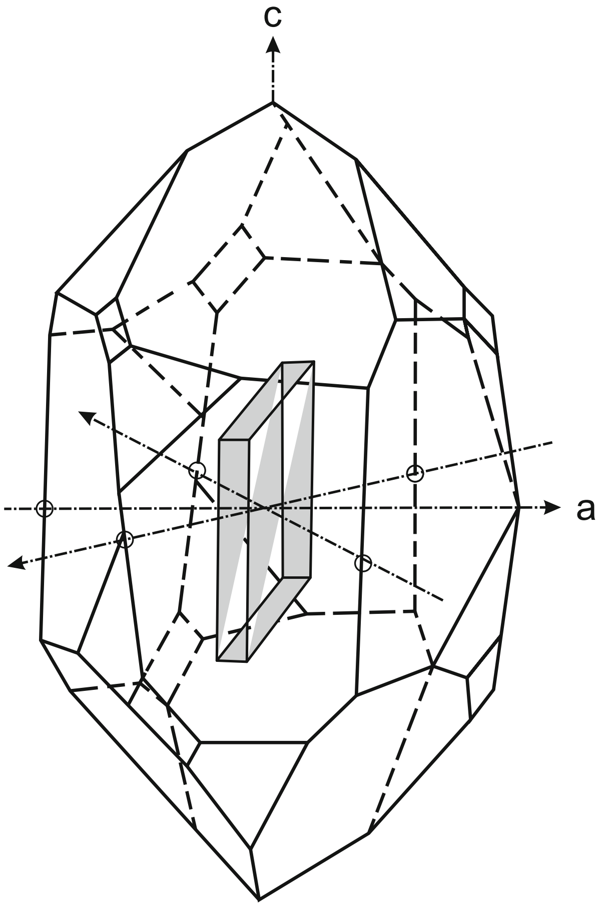
Piezoelectricity is observed in crystals without a center of symmetry (e.g. quartz, $BaTiO_3$, $LiNbO_3$). Mechanical pressure or pull in the direction of the polar crystallographic axis causes dipoles to form within the unit cell due to the displacement of the centers of charge (cations, anions), which in sum result in opposite charges at the crystal ends (Fig. 8.6). Conversely, the application of an electrical voltage causes the mechanical deformation of the crystal. This effect is called electrostriction or inverse piezoelectric effect.

For a long time, quartz with its excellent piezoelectric properties was the preferred crystal material in many fields, especially for frequency stabilization in oscillating circuits (so-called vibrating quartz). High-purity natural crystals from pegmatites and hydrothermal deposits as well as synthetic crystals grown in hydrothermal processes were used for this purpose. Important for the function is the crystallographic orientation of the vibrating plate, which must be prepared perpendicular to the polar *a-axis* from the quartz crystal (Fig. 8.7).

With suitable mounting, the natural frequencies of the piezoelectric crystal are hardly changed by environmental influences, which is why this material is ideally suited for use in precise oscillators. Probably the best known use is the stabilization of vibration frequencies in quartz watches.

However, piezoelectric applications of quartz are not possible at high temperatures. The displacive phase transformation at 573 °C from trigonal low-temperature quartz to hexagonal high-temperature quartz is associated with a loss of the polar axis and thus piezoelectricity. This limitation forced the search for new piezoelectric materials, especially for use in the high-temperature range (Fig. 8.8).

Fig. 8.7 Position of a "vibrating plate" in a quartz crystal. (Modified after Blankenburg et al. 1994)



The figure shows that the representatives of the langasite family (CGG crystals) can be generally considered as new potential materials in acoustoelectronics and microacoustics. The family of crystals with calcium gallium germanate (CGG) structure includes more than 60 compounds formed by complex ion substitution from the general formula

$$A_3BC_3D_2O_{14}$$

with:

A	Ca, Sr, La
B	Ga, Nb, Ta
C	Ga
D	Si, Ga.

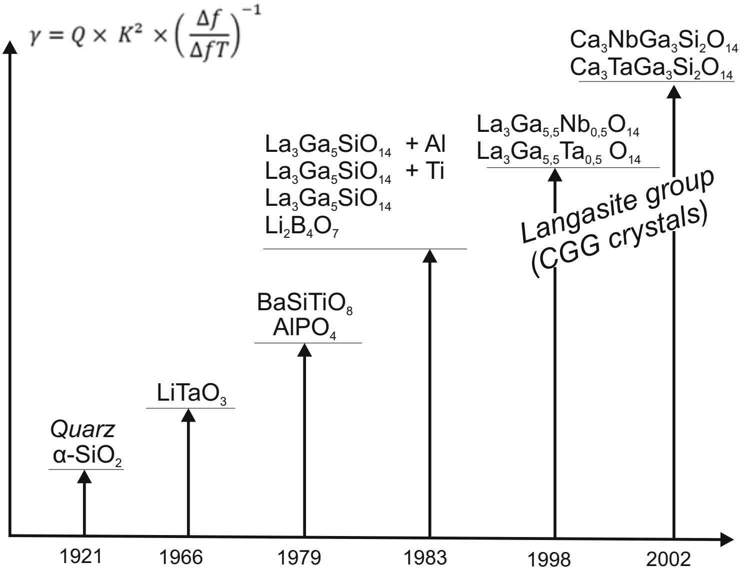


Fig. 8.8 Development of piezoelectric materials. *Q* mechanical quality factor; *K* electromagnetic coupling coefficient; *f* frequency. (Modified after Andreev 2004)

Fig. 8.9 Synthetic piezoelectric single crystal of SNGS ($Sr_3NbGa_3Si_2O_{14}$) grown from the melt by the Czochralski method

From this structural group, ternary oxides such as langasite (LGS, $La_3Ga_5SiO_{14}$), the homologous compounds with niobium (langanite, LGN) and tantalum (langataite, LGT) or even quaternary oxides with Sr-Nb-Ga-Si (SNGS) and Sr-Ta-Ga-Si (STGS) are synthesized. The single crystals are predominantly grown from the melt using the Czochralski process (Fig. 8.9).

Due to the absence of phase transformations, these materials can be used for piezoelectric applications even at high temperatures >1000 °C. The langasites are ideally suited as functional oxide ceramics for pressure, acceleration and force sensors as well as surface acoustic wave (SAW) filters in many areas of telecommunications. Further applications are frequency stabilizers, band-pass filters or optical memories and displays in electro-optical devices.

The search for further alternative materials with even better properties or application parameters *(p, T) is* constantly leading to the development of new materials. In the field of piezoelectrics, CaREE oxoborates may have promising potential for the future.

8.3 Semiconductors

Semiconductors are electron-conducting solids whose resistivity is higher than that of metals and lower than that of insulators (~10^{-4}–10^{10} Ωcm). The classification of insulators, semiconductors, and conductors can be explained schematically using Fermi's band model (Fig. 8.10).

According to the band model, semiconductors have a fully occupied valence band and an almost empty conduction band. The width of the forbidden zone (band gap) is about 1 eV, but at most 2–3 eV. This allows electrons to be lifted from the valence band to the conduction band by thermal excitation, thus creating positive holes (defect electrons) in the valence band. Electrical conductivity is based on the migration of charge carriers (electrons or ions or defect electrons).

If electrons and defect electrons are supplied by the ground lattice alone, then this is intrinsic conduction (number of electrons = number of defect electrons; Fig. 8.11). Extrinsic conduction occurs when, due to dopants and defects, defect centres are generated which donate electrons to the conduction band (= donors) or accept them

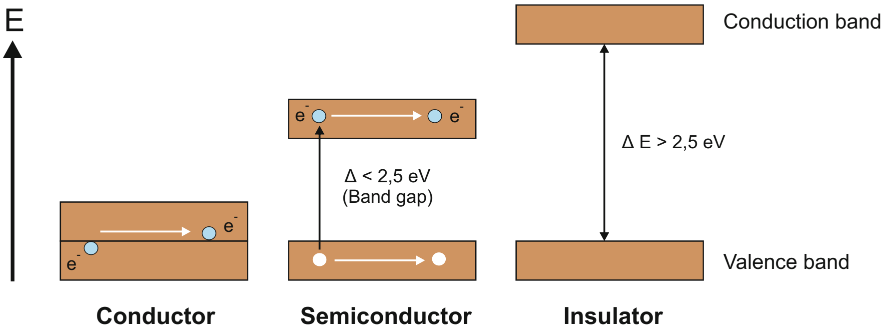


Fig. 8.10 Fermi's band model for electrical conductors, semiconductors and insulators

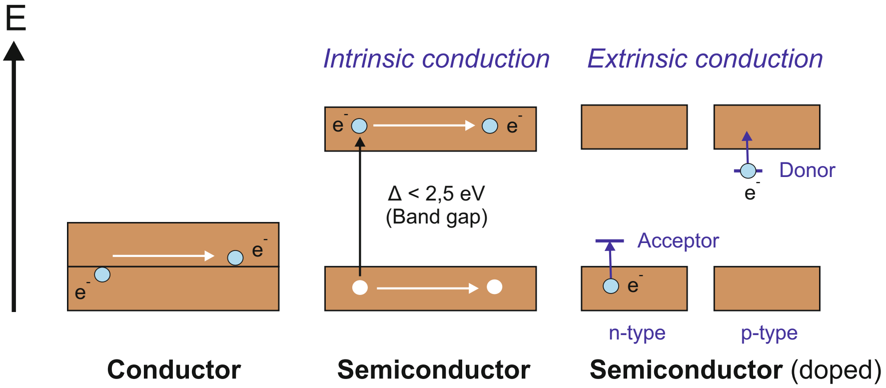


Fig. 8.11 Schematic representation of different conduction states in semiconductors

from the valence band (= acceptors). When there is an excess of electrons as charge carriers, so-called n-conduction (negative excess conduction) occurs, while an excess of defect electrons causes p-conduction (positive excess conduction or electronic deficiency conduction). In silicon or germanium semiconductors, an increase in conductivity is achieved, for example, by doping with P (P^{5+} = n - Typ) or B (B^{3+} = p - Typ).

The total conductivity is composed of:

$$\sigma_{\mathrm{ges}} = \sigma_{\mathrm{n}} + \sigma_{\mathrm{p}} \quad (+ \quad \sigma_{\mathrm{ion}})$$

with:

n	excess electron count
p	number of defect electrons (electron holes)
ion	number of ions.

Ion conductivity σ_{ion} is important for ion-conducting ceramics, e.g. zirconium oxide ZrO_2, which exhibits high oxygen ion diffusion (anion conductor). Addition of CaO or Y_2O_3 as stabilizing ions creates oxygen vacancies in the structure. When an electric field is applied, the vacancies move, generating charge transport.

The most important semiconductor is silicon, of which more than 10,000 t a^{-1} are currently produced for microelectronics and the solar industry. The production of high-purity silicon requires a complex and multi-stage process (Fig. 8.12).

The primary starting material for silicon production are natural quartz raw materials such as quartz gravels and quartzite, which are reduced to metallurgical silicon in a thermal process at 1700–1800 °C. The silicon raw metal contains $\geq$98% Si and various impurities (Al, Ca, Fe, etc.). The raw metal is ground to a grain size of about 0.2 mm and treated with HCl in a fluidised bed reactor at 300–400 °C to obtain trichlorosilane $SiHCl_3$. This process results in a noticeable reduction of the impurity content to approx. 0.2 mass-%.

In a further process, trichlorosilane is evaporated and fed together with hydrogen into a reactor in which thin, polycrystalline Si rods are attached. At temperatures of 1100–1300 °C, chemical reactions and thermal decomposition of $SiHCl_3$, occur and Si is deposited on the rods. This polycrystalline silicon is in turn the starting product for the growth of high-purity, single-crystalline silicon by the Czochralski or floating-zone technique. The material receives its final utility value through the production of semiconductor wafers and, if necessary, appropriate doping (e.g. B, P).

The overall process of manufacturing semiconductor Si is extremely costly and energy-intensive. The value added from raw quartz to the finished Si wafer is estimated at a factor of approx. 80,000 (Blankenburg et al. 1994).

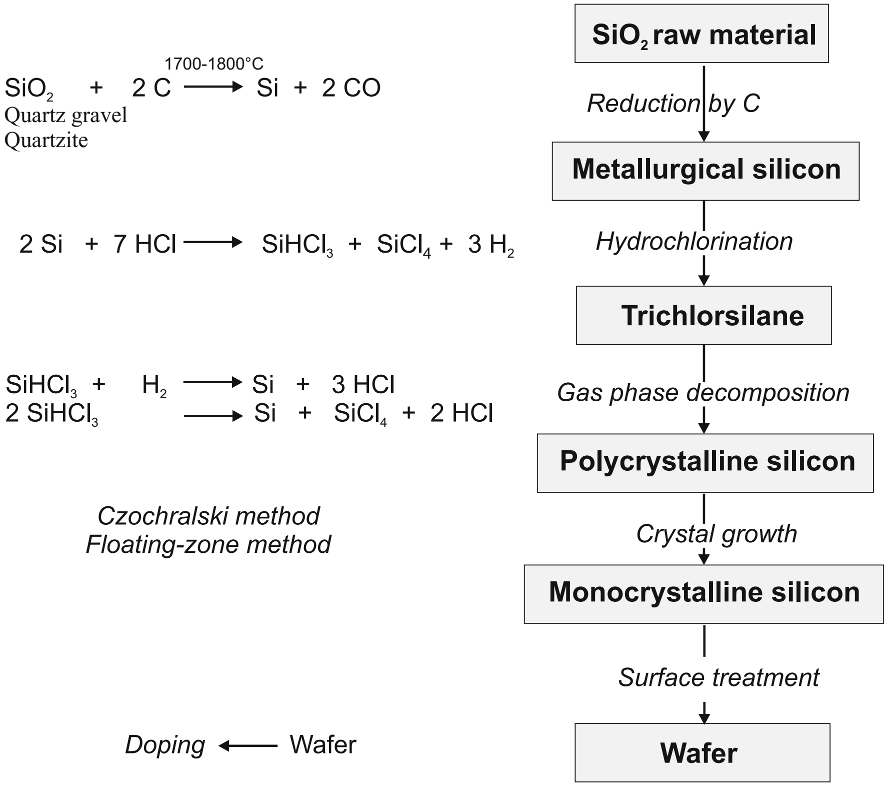


Fig. 8.12 Process chain for the production of high-purity semiconductor silicon. (Modified after Blankenburg et al. 1994)

8.4 Insulators

The most commonly used mineral insulator material in the world is muscovite $KAl_2[(OH, F)_2/AlSi_3O_{10}]$. Due to the difficulties in the realization of mica syntheses, natural raw materials are mainly used in the industry (Sect. 3.7). A distinction is made between so-called block mica on the one hand and splittings or mica waste on the other hand. Block mica and the splittings made from it have traditionally been used in receiver tubes, mica capacitors or semiconductor components (Fig. 8.13). Fine-grained mica products are processed and are required as insulating material in radiators, electric motors and generators.

In addition to the excellent machinability of mica sheets, it is above all the extremely good insulating effect (high dielectric constant) as well as the high chemical and thermal resistance that condition the use of muscovite in a wide variety of electronic components. Despite the sharp decline in its use in electrical engineering/electronics due to the development of modern materials, it is impossible to

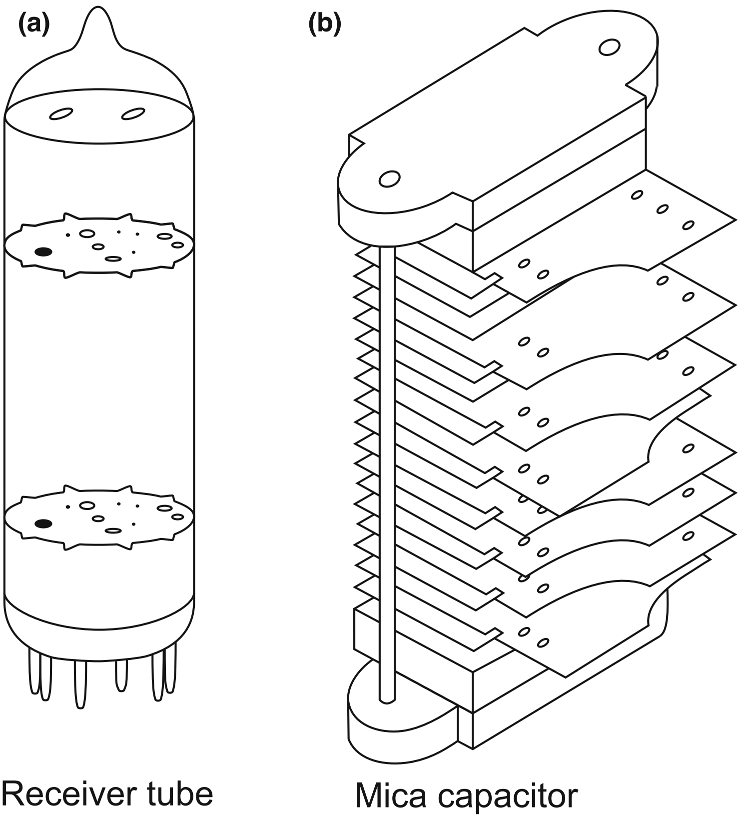


Fig. 8.13 Use of formatted block mica as insulator in receiver tubes (**a**) and mica capacitors (**b**)

imagine modern technical devices without muscovite as an insulator material. Various plastics and glasses cannot match the outstanding range of properties of muscovite.

In modern microelectronics, silicon dioxide SiO_2 is the dominant insulator along with some glasses. The excellent insulator properties are explained by the wide band gap between the valence and conduction bands (Fig. 8.10). As a result, even at higher temperatures, the energy of the band gap cannot be overcome. However, a prerequisite is a high purity and defect-free SiO_2, since otherwise additional energy levels for electron transitions are created.

Another important aspect for the application of SiO_2 in microelectronics is its good compatibility with semiconductor silicon. SiO_2-insulator layers can be deposited on the semiconductor devices by growth or deposition processes, resulting in metal-oxide structures (MOS technology) (Hübner 1984).

The most important growth process is the thermal oxidation of the Si substrate surface. An amorphous SiO_2 layer is formed between 900 and 1200 °C by reacting Si

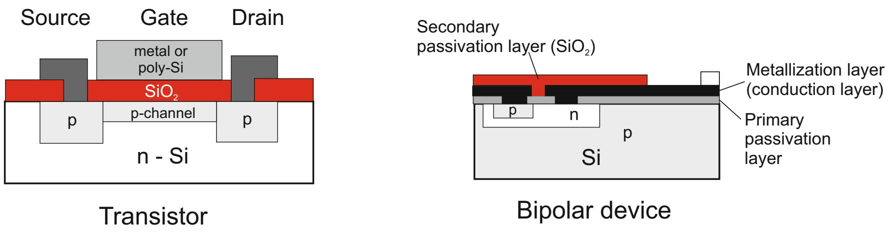


Fig. 8.14 Schematic representation of SiO_2-insulation layers and SiO_2-passivation layers. (Modified after Blankenburg et al. 1994)

with dry or moist oxygen with the addition of HCl. The layer thickness can be influenced by the reaction conditions and reaction times.

Deposition processes from the gas phase are realized by chemical deposition, vapour deposition or cathode sputtering. The advantage of these processes is the lower temperature and the independence from the substrate. *Chemical vapour deposition (*CVD*)* processes, in which amorphous SiO_2 layers are formed by oxidation of monosilane SiH_4 at temperatures ≤1000 °C, are widely used:

$$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$$

Average deposition rates of 30–300 nm min^{-1} are achieved in this reaction. Other starting materials for CVD processes are organic Si compounds (e.g. tetraethoxysilane), Si halides or mixtures with phosphine PH_3.

SiO_2 layers are used in many areas of microelectronics (Hübner 1984). They are used for primary and secondary passivation, gate and conductive path insulation or as diffusion and implantation masks (Fig. 8.14).

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Natural and Synthetic Hard Materials

9

Hard materials are materials that are characterized by very high hardness and wear resistance. The classification of hard materials has changed several times in the course of history, which is mainly due to the changing properties and technical applications. In general, a subdivision can be made into natural and synthetic, but also into metallic and non-metallic hard materials. This classification is not always unambiguous, since, for example, pure carbides, borides, nitrides and silicides sometimes have properties like ceramic materials, but also like metals.

Metallic hard materials include compounds of carbon, nitrogen, boron and silicon with the transition metals of the IVth to VIth main groups of the periodic table. In addition to the naturally occurring minerals diamond, corundum and garnet, the group of non-metallic hard materials primarily includes carbides and nitrides of silicon, boron and aluminium.

Composite materials made of ceramic materials in a metallic matrix are called cermets (*ceramics* + *metals*). Al_2O_3 and ZrO_2 are often used as ceramic components, while Nb, Ti, Mo, Co, Cr or Zr act as metallic components. The advantages of these composites are high hardness and wear resistance.

Since hard materials in technical use must exhibit a high level of resistance to various impact mechanisms, characterization is primarily carried out using hardness and wear tests. These include, for example, scratch tests, various abrasion tests, impact abrasion/erosion tests or the measurement of indentation hardness. By means of these test methods, the mechanical wear of materials is to be recorded qualitatively and quantitatively, which can take the form of adhesive, abrasive or diffusion/dissolution wear. Among the various factors affecting strength and wear of materials, microstructure plays a prominent role. Wear increases exponentially with increasing porosity, and increasing grain size also results in increasing wear (so-called Hall-Petch relationship, Fig. 9.1). Thus, an increase in the strength of materials is generally possible through grain refinement and reduction of porosity.

The following section will focus on the group of non-metallic hard materials. At the beginning, the metallic hard materials are presented in a short overview.

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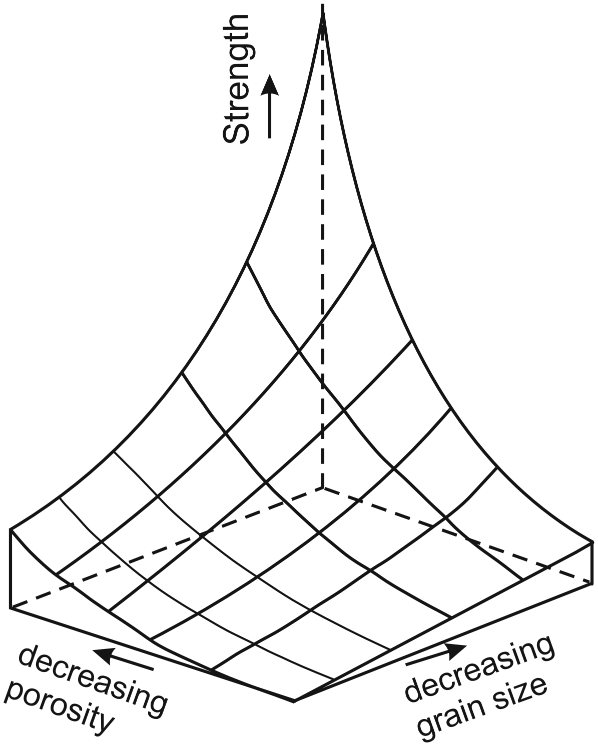


Fig. 9.1 Basic dependence of material strength on grain size and porosity

9.1 Metallic Hard Materials

Metallic hard materials include the compounds of carbides, nitrides and borides of Ti, Zr, Hf, V, Nb, Ta, W, Cr, U and Th. Many of the carbides, nitrides and some borides are called intermediate compounds because of their metallic-nonmetallic interaction.

9.1.1 Structure and Properties

The structure of metallic hard materials is characterized by densely packed metal atoms with small N or C atoms in the interstices, where there are no N-N or C-C interactions. Carbon or nitrogen atoms thus lie on an intermediate position in an octahedron or a trigonal prism, with the intermediate atoms and the next metal atom forming a unit.

The materials in this group are characterized by metallic properties (e.g. electrical conductivity), but often also exhibit good thermal conductivity. Most carbides and

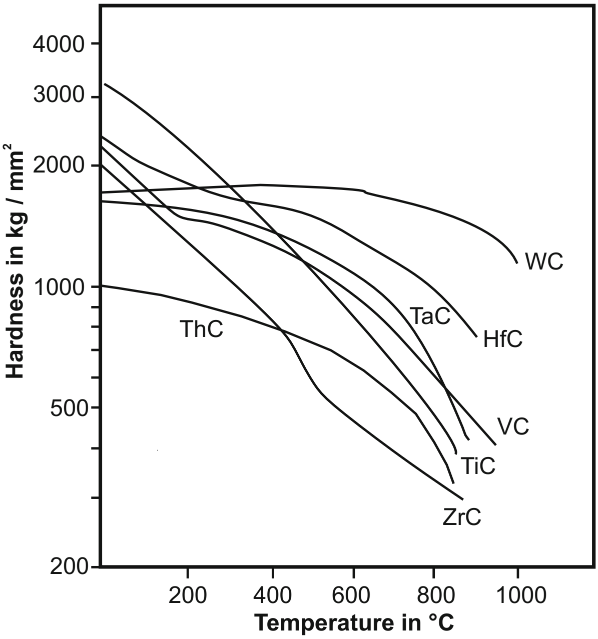


Fig. 9.2 Temperature dependence of microhardness of various carbides. (Modified after Campbell and Sherwood 1967)

nitrides have extremely high melting points, which is why these materials are also called refractory carbides and nitrides.

Strength and hardness show partly strong temperature dependencies (Fig. 9.2). Titanium carbide (TiC) has the highest hardness at room temperature (approx. 3000 kg mm^{-2}), while above 400 °C tungsten carbide (WC) is the hardest material. Metallic hard materials are often brittle at low temperatures; at high temperatures, high strength is achieved primarily by dense, fine-crystalline material bodies.

9.1.2 Manufacture

The production of metallic hard materials can be realized in different ways depending on the requirements and the intended use. Carbides and nitrides are mainly synthesized by melting or sintering reactions of the respective metals or metal oxides with carbon or nitrogen in inert gas atmosphere or vacuum. In addition, deposition by means of CVD *(chemical vapour deposition) processes* with various starting materials is also possible.

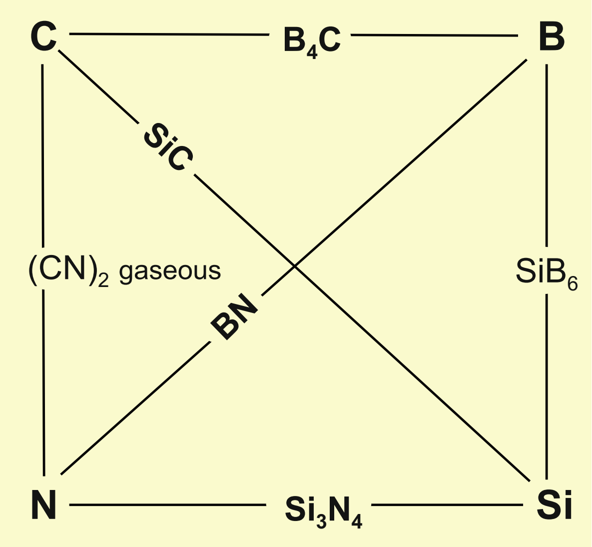


Fig. 9.3 Occurrence of non-metallic hard materials in the C-N-B-Si system. (Modified after Kiefer and Benesovsky 1963)

9.2 Non-metallic Hard Materials

The group of non-metallic hard materials can be represented predominantly in the C-N-B-Si system (Fig. 9.3). Besides the pure, cubic carbon modification diamond, which also occurs naturally, it is mainly synthetic phases such as boron carbide, boron nitride, silicon carbide and silicon nitride. In addition, Al_2O_3 (corundum) and ZrO_2 are still important as non-metallic hard materials.

9.2.1 Synthetic Non-metallic Hard Materials

Boron Carbide B_4C

The hexagonal boron carbide B_4C is the only compound in the boron-carbon system. Boron carbide is an insulator and has a high melting point (2450 °C). Boron carbide is the second hardest material after diamond.

The synthesis is carried out at 2600 °C with a mixture of molten boric acid and graphite. It must be noted that it is not possible to mix in a metallic matrix, otherwise metal borides will be formed. Solid and dense moulds are produced by hot pressing or sintering of cold pressed moulds. The enormous volume shrinkage (approx. 20%) must be taken into account here.

Boron carbide is mainly used as an abrasive in grains and pastes for grinding hard materials. Another interesting application is the use as a neutron flux regulator and protection material against thermal neutrons in nuclear reactors.

Boron Nitride BN

Boron nitride can occur in two different structural modifications. Cubic BN has a sphalerite structure, where each B atom is connected to four N atoms and vice versa. In contrast, a graphite-like hexagonal layered structure of boron nitride with alternating C and N layers also exists. In contrast to the metal bonding in graphite, however, ionic and atomic bonding occurs here.

Hexagonal boron nitride is synthesized by the reaction of boron oxide B_2O_3 with nitrogen or ammonia at high temperatures and using tricalcium phosphate as catalyst. A conversion to cubic boron nitride (kBN) is carried out at high temperatures (1500–2200 °C) and pressures (50–90 kbar) using alkali nitrides as catalysts.

Due to the similar structure, the hardness and abrasion properties of cubic boron nitride come close to those of diamond, with even higher temperature resistance. It is mainly used as an abrasive.

Silicon Carbide SiC

In the Si-C system, there is only one compound of the formula SiC (70.2 mass-% Si, 29.8 mass-% C), which should theoretically melt incongruently at 2700 °C. However, the melting point is only a theoretical value, since SiC starts to decompose or sublime into Si_g and C_f already at 2300 °C (Petzold 1991).

Silicon carbide occurs in two modifications, a hexagonal α-SiC with wurtzite structure and a cubic β-SiC with sphalerite structure. In cubic SiC, there are two face-centered cubic Si and C lattices, respectively, displaced from each other by a quarter of the space diagonal, and tetrahedral [Si–C] coordination with sp^3-hybridized atomic orbitals and a high proportion of covalent bonding (Fig. 9.4). It is characteristic for SiC that, apart from the two modifications mentioned, there are other stacking sequences leading to innumerable polytypes, which are also influenced by the Al content (up to 0.2%). Depending on the formation of regions with a high C content or the incorporation of various foreign ions (e.g. Al, B, N) in the lattice, SiC can exhibit different colorations.

Silicon carbide (also carborundum) occurs extremely rarely as a natural mineral (moissanite) and is therefore synthesised for technical purposes. Traditionally, technical production is carried out using the *Acheson process* from petroleum coke and quartz sand in an electric furnace at 2000–2300 °C:

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

The disadvantage of the process is the very high temperature (>2000 °C) required for a complete chemical reaction. In addition, the material accumulates in large blocks and thus requires complex grinding and cleaning steps for the production of SiC grains.

For the above reasons, alternative processes for silicon carbide synthesis have been developed. Known are the direct synthesis of β-SiC from Si and C at 1800 °C or the formation of β-SiC by heat treatment of a silica gel in a sugar solution at 1800 °C in an inert atmosphere.

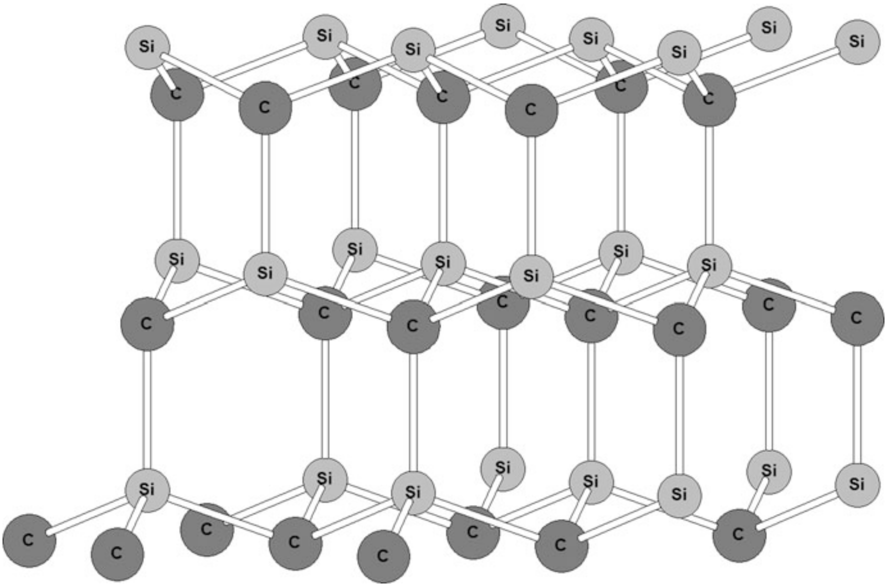


Fig. 9.4 Schematic structure of α-SiC

Another elegant solution was developed by thermal treatment of rice husks containing up to 20% SiO_2 and cellulose. Burning at 1200–1600 °C produces a very fine powder (~0.1 μm) of predominantly β-SiC. The advantage of this process lies not only in the utilization of rice husks from rice processing, which are produced in large quantities as waste, but also in the extremely favorable particle size distribution of the resulting SiC powder, which can be used primarily in the ceramics industry.

Last but not least, surface layers of SiC can also be generated by gaseous phase synthesis. Here, both the reaction of SiH_4 or $SiCl_4$ with CH_4, C_2H_4, and CCl_4 is possible, as well as the thermal decomposition (CVD) of CH_3SiCl_3 or CH_3SiH_3 at ~1000 °C.

Silicon carbide is used in a wide variety of technical applications, whereby the basic properties of pure SiC can be modified by manufacturing processes, degree of densification, sintering conditions, additives, etc. Besides the high hardness (directional hardness up to $45 \cdot 10^3$ MPa), the most interesting properties for technical use are the thermal conductivity (60 $Wm^{-1} K^{-1}$ at room temperature to 15 $Wm^{-1} K^{-1}$ at 1400 °C) and the semiconductor properties.

SiC is mainly used as an grinding and abrasive material in loose grain size or in binder-bonded form (abrasives). However, numerous SiC materials are also used in sintered form as refractory materials, structural ceramics or electrical conductors. Last but not least, SiC is also an important component in high-temperature protective coatings.

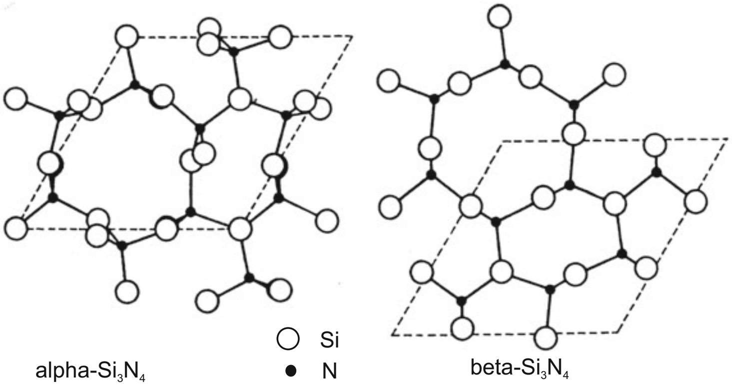


Fig. 9.5 Schematic structure of α- (low)Si_3N_4 and β- (high)Si_3N_4. (Modified after Petzold 1991)

Silicon Nitride Si_3N_4

In the Si-N system, apparently only one compound of the formula Si_3N_4 exists, which melts or decomposes at 1900 °C:

$$Si_3N_4 \rightarrow 3Si_l + 2N_{2,g}$$

Silicon nitride has not been observed in nature and occurs only as a synthetic product. It is mainly produced at high temperatures by nitriding silicon (reaction sintered):

$$3Si + 2N_2 \rightarrow Si_3N_4$$

or by a carbothermic reaction with quartz:

$$3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO$$

Surface coating is possible by CVD *(chemical vapour deposition)* processes (Petzold 1991):

$$3SiCl_4 + 4NH_3 \rightarrow Si_3N_4 + 12HCl$$

The structure of silicon nitride is derived from that of phenakite (Be_2SiO_4), with the Be atoms replaced by Si and the O atoms replaced by N. Distorted [SiN_4]-tetrahedra are each connected by the corners of the tetrahedra, so that each N atom belongs to three tetrahedra (Fig. 9.5). The two occurring hexagonal α/β modifications arise from different stacking sequences of the tetrahedra layers. During the synthesis of silicon nitride, both modifications are formed, with an irreversible transformation to the thermodynamically stable high-temperature modification (β-Si_3N_4) above 1300 °C.

In addition to high hardness, Si_3N_4 also exhibits good hot strength and chemical resistance. This combination of properties allows it to be used as a high-quality ceramic in metallurgy and high technology.

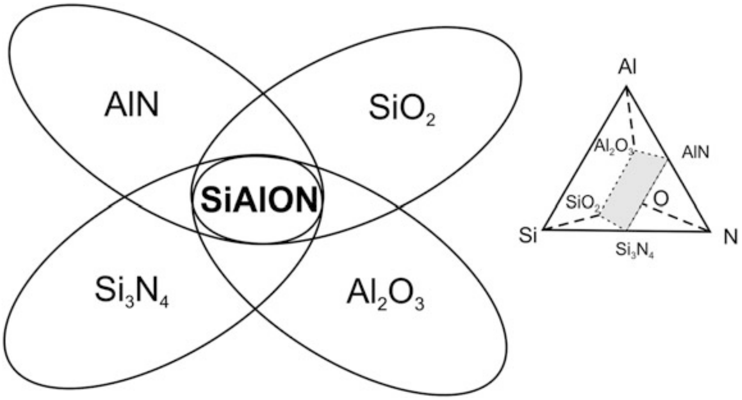


Fig. 9.6 Position of the sialons in the Si-Al-O-N system

SiAlONs (Silicon Aluminium Oxynitride Alloys)

By incorporating various compounds into the structure, Si_3N_4 can form a series of *solid solutions* with excellent properties. Of particular note is the combination with Al_2O_3, leading to the formation of the sialons in the Si-Al-O-N system (Fig. 9.6).

The substitution of $Si^{4+}N^{3-}$ durch $Al^{3+}O^{2-}$ results in a complex chemical composition of the resulting compounds, so it is difficult to give a specific stoichiometric composition for the sialons. Starting from β-Si_3N_4, $Si_{6-y}Al_yO_yN_{8-y}$ angegeben can be given as a general formula for the β’-sialons, with $y = 0$ up to 4.2. For example, $y = 0$ then results in β-Si_3N_4 and $y = 4$ in $\beta' - Si_2Al_4O_4N_4 = \beta' - SiAl_2O_2N_2$ (“SiAlON”).

The structure of the compounds in the Si-Al-O-N system can be derived from the structure of β-Si_3N_4, which is why they are also called ß’-sialons. Basic building blocks are [(Si,Al)(O,N)]-tetrahedra, which are linked three-dimensionally via common corners (Fig. 9.7).

Sialones are usually made from common raw materials that occur in large quantities. Known syntheses are, for example:

$$\text{Kaolinite} + \text{Coke} + \text{Nitrogen} \rightarrow Si_3Al_3O_3N_5\,(y = 3)$$

$$\text{Volcanic ash} + \text{Al} + \text{Nitrogen} \rightarrow Si_2Al_4O_4N_4\,(y = 4)$$

The mechanical and chemical properties of Sialon materials are similar to those of silicon nitride or Al_2O_3. The high hardness is coupled with a comparativecly higher resistance to aggressive media such as oxidizing acids, alkalis or slags. The oxidation of the sialons at temperatures above 1100 °C causes the formation of a protective layer of resistant mullite.

In practice, the properties of β’-sialons can be further improved by the addition of Y_2O_3. Corresponding commercial sialon ceramics show higher fracture toughness and wear resistance, as well as excellent oxidation resistance, which allow their use under extreme conditions. The exceptional high-temperature strength can be used,

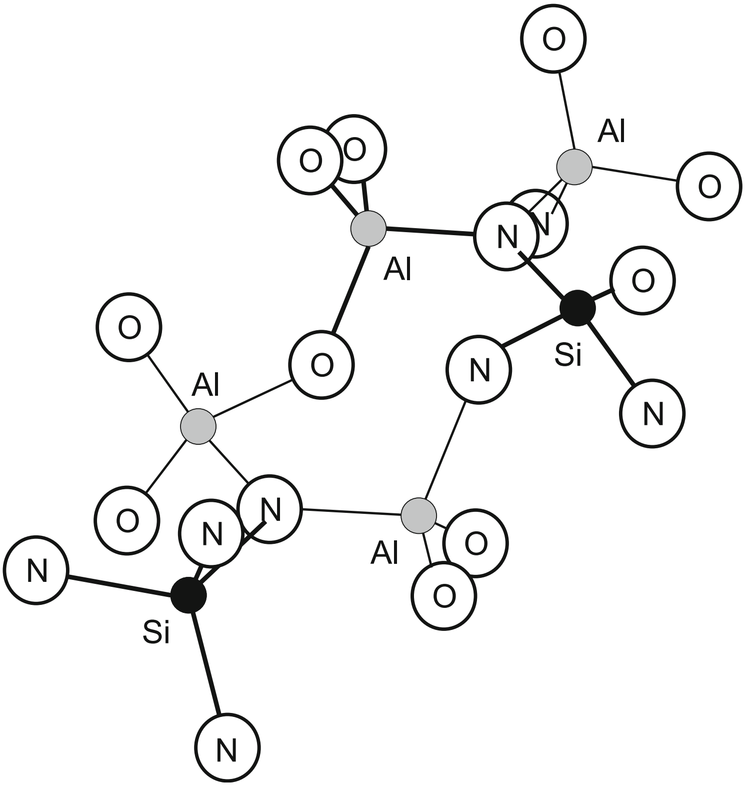


Fig. 9.7 Schematic structure of sialons β'-$(Si,Al)_3(O,N)_4$ with $[(Si,Al)(O,N)_4]$-tetrahedra linked via corners

for example, for special high-temperature cutting tools or needle valves in carburetors and injection nozzles.

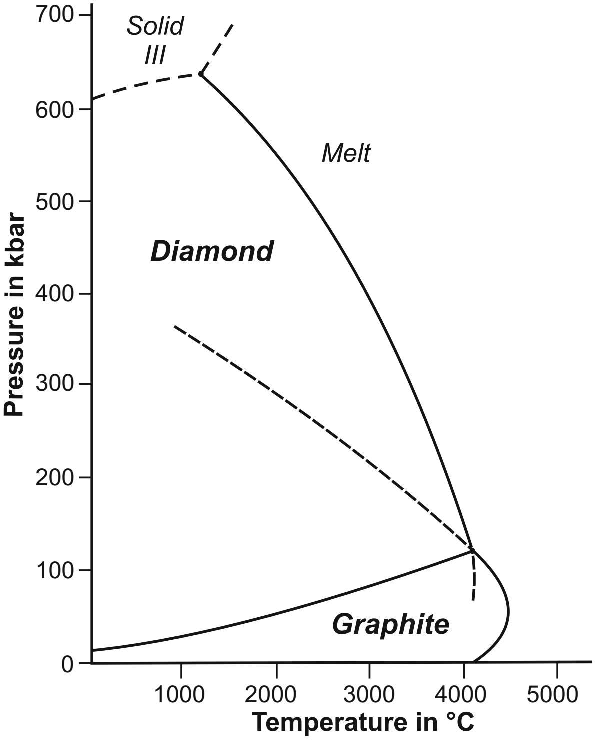
9.2.2 Natural Non-metallic Hard Materials

Diamond β-C

In hardly any other system the structure-property relationships can be demonstrated more impressively than in the carbon system (Fig. 9.8). Two carbon modifications have been known for a long time: the cubic diamond (β-C) and the hexagonal graphite. Graphite, which is stable under normal conditions, can be converted to diamond in a thermodynamically stable manner only at extremely high pressures ($>10^3$ MPa) and temperatures (>2000 °C).

A relatively new compound, with a different structure and bond type, is hexagonal carbyne. Besides natural occurrences in graphite gneisses of the Ries crater and in meteorites, carbyne was produced by sublimation from graphite and amorphous

Fig. 9.8 Temperature-pressure diagram of the unitary system of carbon. (Modified after Bergeron and Risbud 1984)



carbon. In addition, londsdaleite ("hexagonal diamond") was first discovered in chemical experiments and later in impact craters of meteorites.

Cubic diamond is the most important natural hard material due to its extreme properties. The structure of diamond results from the juxtaposition of two face-centered cubic unit cells, each of which is displaced from the other by a quarter in the three spatial directions (cubic-holohedral crystal class m3m). Each carbon atom is surrounded by four others in a tetrahedral arrangement at a distance of 1.54 Å (Fig. 9.9). The extraordinary hardness of diamond is due to covalent bonding (sp^3-hybrid orbitals).

The varying arrangement of the carbon atoms on the most important crystallographic surfaces (Fig. 9.9) results in a number of anisotropic properties (e.g. hardness, cleavability, optical properties), which are also of great importance for technical applications. One of the most important mechanical properties of diamond is its extreme hardness. Figure 9.10 illustrates that it has both the highest scratch hardness and Vickers hardness of all natural minerals.

The microhardness varies considerably for different methods and shows distinct anisotropy effects (Table 9.1). The grinding hardness also shows marked anisotropy, which has to be considered for grinding and processing.

A clear temperature dependence can also be observed for the microhardness of diamond. The hardness decreases linearly up to approx. 1500 K and exponentially

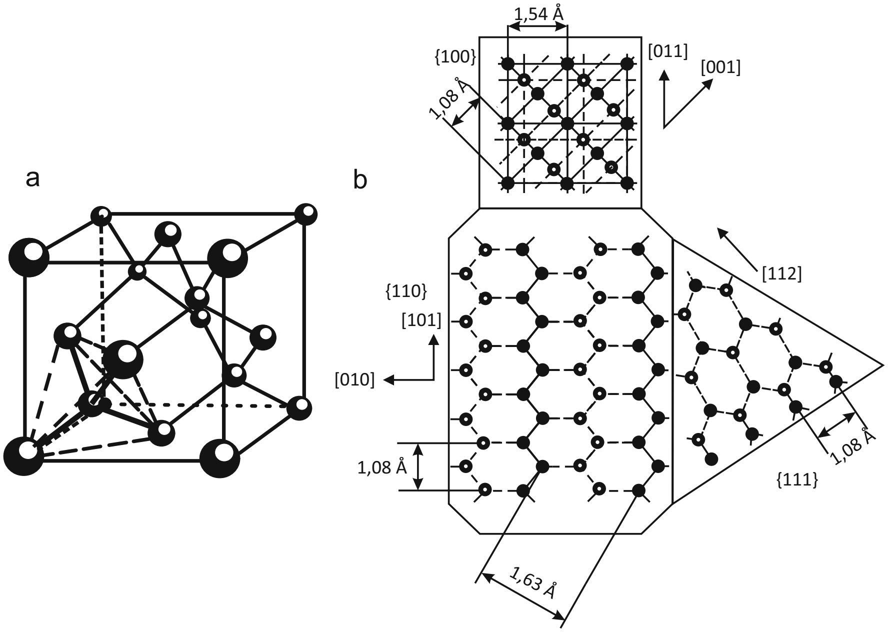


Fig. 9.9 (**a**) Cubic face-centered unit cell of diamond (sphalerite structure); (**b**) Arrangement of carbon atoms on different crystallographic cross-sections. (Modified after Schmidt and Malzahn 1979)

thereafter up to a hypothetical melting temperature of 4000 K. At 1500 K a transition from brittle to plastic behaviour can also be observed, so that above this temperature cracks no longer occur.

In addition to its high hardness, diamond has a number of other extreme properties such as high thermal conductivity, high electrical resistance and very low thermal expansion. It is only attacked by strongly oxidizing substances at high temperatures and burns in air above 800 °C.

The technical use of diamond can be traced back very far in history. Already about 2000 years ago Pliny the Elder reports about the use of diamond as an engraving tool. Industrial use began at the end of the eighteenth century, when precision screws were turned with a diamond tool. Since the first successful diamond synthesis using a high-temperature belt press in 1954, there has been a significant increase in the technical use of diamond. Today, about 10 tons of synthetic diamonds are produced per year, most of which are used as industrial diamonds..

Diamond tools are used in modern industry in many areas for machining almost all materials. The majority of industrial diamonds (approx. 90%) are used as tools with an undefined cutting edge, i.e. with diamond grit in metallic, ceramic or organic bonding, on carrier materials (e.g. on drill bits). Since the entire volume of the crystals is stressed in these multi-grain tools, a high volume strength is required. In the case of so-called single-grain tools with a defined cutting edge (e.g. turning,

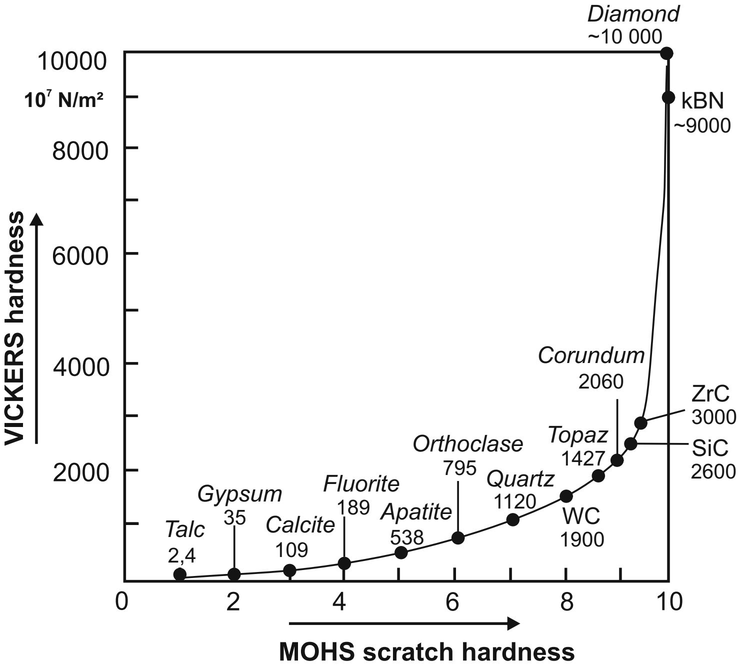


Fig. 9.10 Relationship between scratch hardness according to Mohs and indentation hardness according to Vickers for selected minerals and synthetic hard materials. (Modified after Rösler 1981)

Table 9.1 Comparison of the microhardness of different hard materials

Hard material	Face	Microhardness in kp mm^{-2} according to Knoop	According to Berkovič	According to Vickers
Diamond	(111)	7500–9000	11,000	10,000
	(100)	6900–9600	15,000	–
kBN	(111)	4500	5000	4780
Sapphire	(0110)	1400–1800	1950–2100	2200
	(0001)	1350	1800–2050	2200

Data from Schmidt and Malzahn (1979)

milling, profiling or scribing diamonds for shaping), on the other hand, it is above all the hardness anisotropy that must be taken into account.

Corundum α-Al_2O_3

In the Al_2O_3 system, only one thermodynamically stable phase occurs up to the melting temperature of 2050 °C, the trigonal corundum (α-Al_2O_3). The structure is built up by layers of oxygen atoms perpendicular to the c axis, with the small Al atoms incorporated in their spandrels (Fig. 9.11). Unstable compounds, such as the

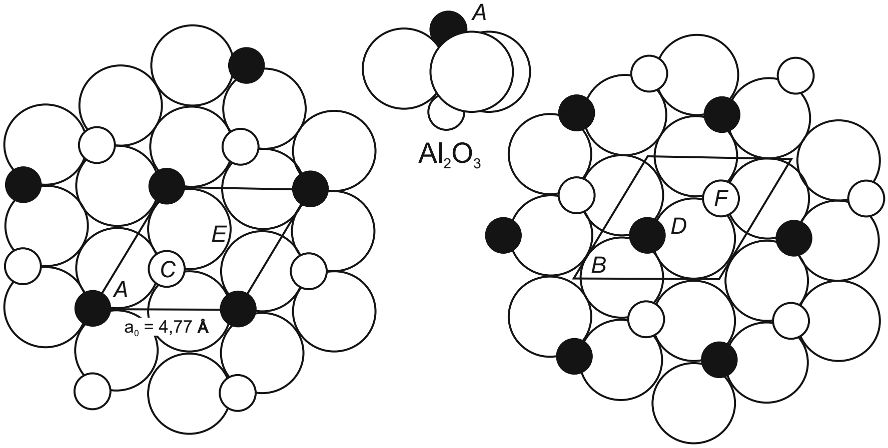


Fig. 9.11 Structure of corundum with two layers in projection on (0001); in the hexagonal cell, six Al-O layers with ABCDEF follow each other in [0001] direction. (Modified after Rösler 1981)

hexagonal β-Al_2O_3 (stabilization by alkali oxides) or the cubic γ-Al_2O_3 (defect spinel) are formed only during the dehydration of Al hydroxides.

Corundum crystals of the ruby (red) and sapphire (blue) colour varieties are particularly popular and sought after as high-quality gemstones. But corundum is also one of the oldest natural hard materials due to its enormous hardness. There are early reports of the use of emery (compact, fine-grained corundum with admixtures of quartz and iron oxides) from Naxos as an abrasive material.

After the first corundum monocrystals were synthesized by August Verneuil in 1894, Ernst Moyat realized the commercial production of corundum using an electric melting furnace in 1916. So far, the vast majority of corundum for use as abrasives is produced in this way.

High-grade bauxite or pure technical alumina (>99% Al_2O_3) are used as raw materials for corundum smelting. Synthetic Al_2O_3 raw materials are obtained by the Bayer process from bauxite, which consists essentially of various aluminium hydroxides (gibbsite, boehmite, diaspor) and admixtures of Ti and Fe oxides. In a multi-stage process, sodium aluminate ($NaAlO_2$) is first formed by treatment with NaOH at elevated temperatures and pressures (250 °C, 40 bar) and the impurities are separated in the so-called red mud. $Al(OH)_3$ (hydragillite) is precipitated from the sodium aluminate solution, from which a fine-grained powder of high-purity α-Al_2O_3 is obtained after calcination at 1200–1300 °C. These powders are also suitable starting materials for sintering high-quality alumina ceramics.

The production of fused corundum starts with the melting of the Al_2O_3 raw materials in electric arc furnaces at 2000–2100 °C (Fig. 9.12a). The melt is poured off in large blocks and cooled down (Fig. 9.12b). The corundum microstructure can be influenced by varying cooling rates. Rapid cooling leads to a microcrystalline texture, while slow cooling causes macrocrystalline corundum with a stalk-like fracture. After smashing with hydraulic hammers (Fig. 9.12c), fine comminution

Fig. 9.12 Main operations for the production of synthetic corundum grains: (**a**) melting of Al_2O_3 raw materials in electric arc furnaces at 2000–2100 °C; (**b**) casting in blocks and cooling; (**c**) coarse crushing with hydraulic hammers. (Source: Imerys Fused Minerals, Zschornewitz GmbH, with kind permission)

to the appropriate grain sizes follows. The comminution process can also be used for the production of specific properties of the corundum grains. Impact comminution in roller mills produces stalky, sharp grains, while preparation in screen ball mills results in predominantly isometric grain shape. Finally, specific grain sizes for consumers are produced by multi-stage screening.

Corundum powders are used for a wide variety of grinding and polishing materials as well as for the manufacture of abrasive discs, papers and cloths. These abrasives are used for the surface treatment of various materials by blasting, lapping and grinding. The properties of the corundum material can be specified by using different raw materials, varying cooling rates and types of comminution or by adding mineralisers (e.g. Ti, Cr). In addition, fine corundum powders are also used to improve the surface properties of resistant industrial flooring, screeds and plastic coatings.

Garnet Group

Minerals of the garnet group crystallize in the cubic system and can be described by the general formula

$$A^{2+}{}_3B^{3+}{}_2[SiO_4]_3$$

with

$$A^{2+} = Mg^{2+}, Fe^{2+}, Ca^{2+}, Mn^{2+}$$

$$B^{3+} = Al^{3+}, Fe^{3+}, Cr^{3+}$$

Garnet as an industrial mineral is usually an almandine-bearing solid solution (almandine: $Fe_3Al_2[SiO_4]_3$) with a density of 3.6–4.3 g cm^{-3} and a Mohs hardness of 7.5. Garnet is formed predominantly in geological environments of contact and regional metamorphism, but can be enriched by secondary processes in placer deposits. Currently, about 200,000 t per year are mined worldwide.

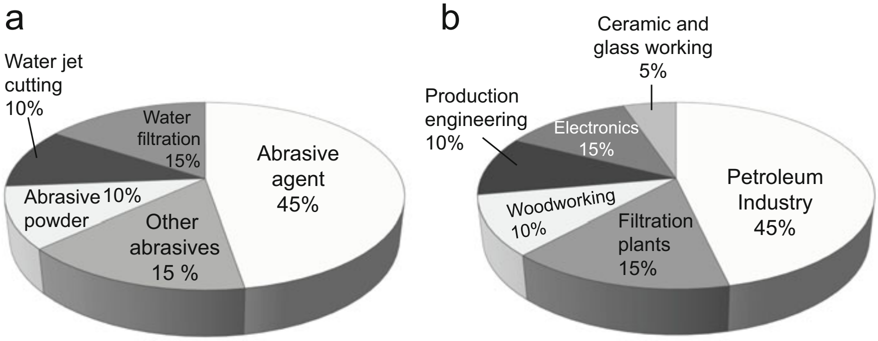


Fig. 9.13 Main applications (**a**) and industrial sectors (**b**) for minerals of the garnet group

The advantage of garnet over other abrasive and blasting media is primarily that the conchoidal fracture constantly creates new, sharp edges during use, maintaining the abrasive effect. Because of the higher density and the non-occurring danger of silicosis, garnet is preferred as an abrasive to the traditional quartz sand.

Figure 9.13 summarises some of the main applications and industrial sectors. Garnet is used as an abrasive for surface cleaning and surface preparation (e.g. roughening, engraving) in shipbuilding, aircraft construction, the petroleum industry or in glass and natural stone processing. Another field of application is water jet cutting, where garnet powder (0.06–1.0 mm) is mixed with a high-pressure water jet. The advantages of this method are three-dimensional manageability and the absence of heat generation, chips and dust. Bonded abrasives and polishes based on garnet are nowadays used for almost all materials (wood, leather, plastics, ceramics, metal, glass) with very good results.

As an alternative to garnet, staurolite and olivine are also used as mineral hard materials.

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Crystal Growing

10

If a mineral or material is created in nature, it is called natural. If a natural material is synthesized in the laboratory, it is called synthetic. Materials that do not have a model in nature, on the other hand, are called artificial.

In crystal growth, the goal is to produce materials in single crystal form in a controlled manner in the desired size, composition and quality in the laboratory. Often, natural crystals are too small, too contaminated or not available in consistent quality, since, for example, many chemical components are present in natural formation processes and this can also vary in each location.

Let us consider ruby as an example. The red color of ruby is due to the incorporation of Cr^{3+} in the crystal lattice of the corundum. The depth or intensity of colour depends sensitively on the Cr^{3+} content. If this rises above about 10% by mass, the crystal becomes green. If minute amounts of Fe^{3+} are present, the color shifts to orange. Since ruby is a frequently used laser material, natural crystals are not suitable for technical applications, since on the one hand their composition is too "uncontrolled", and on the other hand crystals of a corresponding size (up to 10 cm) are not available.

Oscillating quartz find versatile application as clocks in electronics. Natural crystals are available in high purity, but the structural quality is often insufficient. High-quartz transforms displacively to low-quartz at 573 °C (and vice versa). This phase transformation is not quenchable. Only the low-quartz modification is piezoelectric. However, a pure natural crystal does not necessarily show the temperature at which it was grown. If the beginning of the growth is above the temperature of the phase transformation, the crystal will transform into the low-quartz modification when the temperature falls below this temperature during crystallization. Since this is very rapid, this transformation occurs simultaneously at various points in the crystal lattice. Both a left-hand and a right-hand form of low-quartz exist. During the spontaneous high-low transformation, both right- and left-quartz regions are formed, thus leading to twinning of the crystals. The grown single crystal is not destroyed by this, it builds up lattice stresses. For piezoelectric applications, such spatially

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uncontrolled twinning is detrimental, since the property is impaired or extinguished. However, the physical investigation of prepared piezo components individually for the selection of structurally suitable parts is not economically reasonable.

These two examples show that there is a great need for growing synthetic crystals. Even when researching new materials with optimized properties, crystal growth is the only viable way to obtain suitably large and high-quality crystals.

Crystals that grow in nature are often subject to many external influences, the so-called millieu factors. These include, for example, complex melt compositions, geometric obstructions in material transport and heat dissipation, spatial and chemical competition from secondary crystals of the same or different composition. In the processes developed in the laboratory, these obstructive framework conditions are excluded or minimized as far as possible. However, the main question is which growth methods and experimental parameters are suitable. This is not trivial; nature can usually serve as a model, but often a long empirical path is necessary to determine suitable experimental conditions.

Only the growth of single crystals will be presented here. The synthesis of fine- or coarse-crystalline single- or multiphase aggregates will not be considered in detail.

Crystal growth builds on the relationships discussed in Chap. 2. A very comprehensive overview of the fundamentals of crystal growth and the different processes with their variations are given in the book “Kristallzüchtung” by Wilke and Bohm (1988).

The growth of high quality crystals with controlled chemical composition can follow different principles:

- Crystallization from solution/melt
- Vapour sublimation
- Recrystallization from solid phases without the presence of a melt
- High-pressure and/or high-temperature process

The path of formation from solid phases hardly leads to high-quality crystals and shall not be considered further here. Condensation from the gas phase is also of academic rather than economically feasible interest.

In our linguistic usage we intuitively distinguish between solutions and melts. With solutions we tend to think of aqueous solutions, with melts we tend to think of higher temperatures, e.g. molten metals. Yet aqueous solutions are also melts. Water is the melt of ice, salt water is a melting solution from which the solid salt can crystallize under suitable conditions. In the crystallization from the melt, we must distinguish two cases:

- Materials with congruent melting point: Here, melting and crystallization take place via the temperature change and thermal gradients in the range of the melting point. Melt and crystal have the identical chemical composition.
- Materials with incongruent melting point: In this case, fluxes or solvents are used to obtain the possibility of indirect crystallization. Melt and crystal differ in their chemical composition.

Furthermore, a distinction must be made as to whether crystal growth is to be carried out with or without a seed crystal as nucleus. A seed crystal as nucleus is always helpful, as the orientation of the growing crystal can be predetermined. Crystal growth without seed is less controllable and more undefined. It is only used in exceptional cases.

Four crystal growing methods will be presented in more detail below:

- the Verneuil method
- the Czochralski method
- the zone melting method
- the hydrothermal process

10.1 The Verneuil Method

The Verneuil process is a crucible-free process in which the material to be grown melts in an oxyhydrogen flame and the flame pressure conveys the molten droplets onto a growing crystal (Fig. 10.1). It was developed around 1900 by the French chemist Auguste Verneuil for the production of synthetic gemstones.

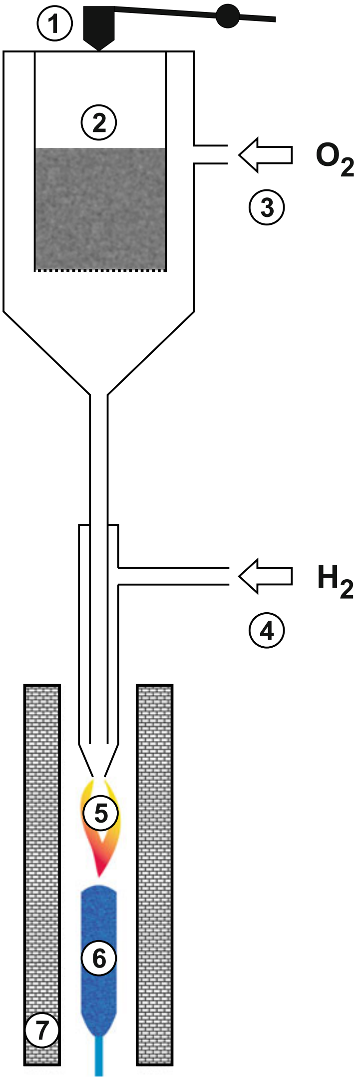
The Verneuil process uses an oxyhydrogen flame, which is created when oxygen and hydrogen burn at over 2500 °C to form H_2O. The principle is to use this temperature to melt materials. Small quantities of powder are continuously fed via a hammer mill and are melted in the oxyhydrogen flame. The flame pressure "sprays" the melt droplets onto a cooler growing crystal (shown in blue in Fig. 10.1). There they crystallize and the crystal grows. Only congruent melting materials, mostly of oxide composition, can be grown by this method.

Due to the high temperatures, it is also essential that the melting point is not too low so that the boiling point of the melt is above the flame temperature to prevent complete evaporation of the material. The material powder must be very fine grained and not agglomerated to ensure uniform melting and deposition. The material powder is introduced into the oxygen gas stream, as introduction into the hydrogen stream could possibly lead to premature ignition or undesirable reduction of the materials. The powder is fed into the gas stream through a sieve via a mechanical shaker or percussive hammer. This is simple, robust, reliable and breaks up any agglomerations. A crystalline seed is used to ensure orientation and single crystallinity. The process produces single crystals in the form of an elongated melting bulb (Fig. 10.2).

The growth rate is very high, up to 1 cm h^{-1}. Therefore, the crystals are of lower quality and are not suitable for laser applications, for example. They have a high mechanical strain, which causes the fusion bulb to split in two when the surface is scratched. Significant gas inclusions are found accumulated in the core region of the crystals.

The Verneuil process is a robust and fast crystal growing method. Typical materials are corundum and spinels of different colorations. The crystals are

Fig. 10.1 The principle of the Verneuil process. *1* hammer mill; *2* material powder; *3* O_2-supply; *4* H_2-supply; *5* oxyhydrogen flame; *6* growing crystal in shape of a bulb; *7* thermal shielding



processed as bearing stones for watch movements, jewelry stones or, in the case of colorless corundum (precious corundum, leucosaphire), into watch glasses.

The advantages of this process are that it works crucible-free, high temperatures are achievable, a nucleation specification is possible, it is "simple", i.e. well automatable, and fast. The disadvantages would be the facts that only a high temperature is available, the crystals are of relatively poor quality, have high stresses due to rapid growth and cooling, and that only congruent materials can be grown.

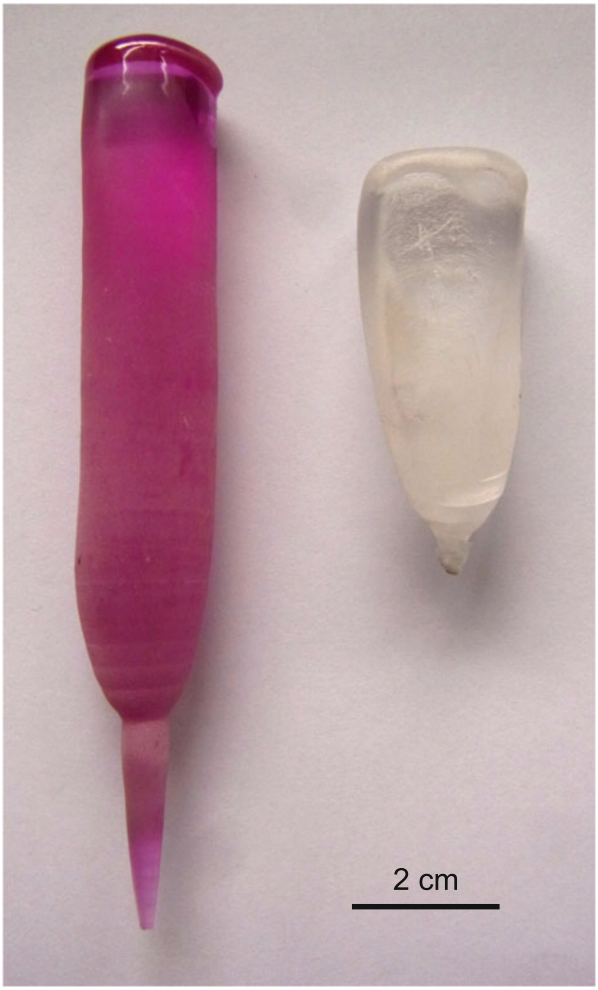


Fig. 10.2 Verneuil fused pears of ruby (*left*) and colorless corundum (*right*) with remnants of the nuclei in the lower part of the aggregates

10.2 The Czochralski Method

The Czochralski method is a very widely used crystal growth technique that can synthesize crystals larger than 20 cm in diameter and 50 cm in length (Fig. 10.3).

The crystals are grown from a melt in a crucible. The seed, and later the crystal that grows from it, cools the melt, which leads to a crystallization and growth of the seed. By moving the seed/crystal upwards, the crystal grows in length. It is practically pulled out of the melt. The melt is constantly in contact with the growing crystal, where it forms what is called a meniscus. The growth of the crystal causes the amount of melt to decrease. This would cause the melt level to lower due to crystallization, which would cause a break off of the melt contact with the crystal..

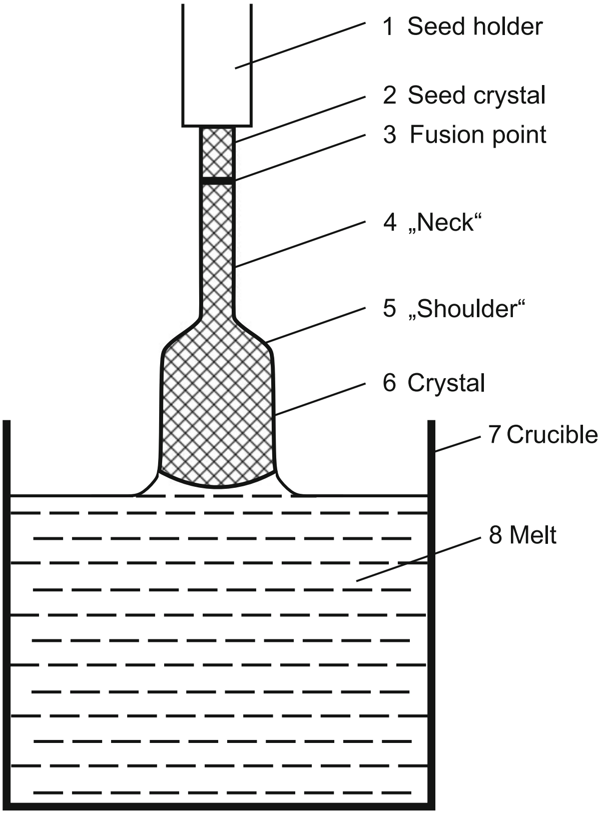


Fig. 10.3 The crystal growing method according to Czochralski

To prevent this, it is essential that the absolute position of the melt and crystal relative to each other be kept exactly the same during the growth process. Therefore, the crucible must be tracked according to the reduction of the melt. This necessary additional tracking movement of the crucible is precisely controlled via the loss of mass in the crucible, which is measured with a balance.

To compensate for low thermal heterogeneities and to mix the melt, the crystal and crucible are also rotated in opposite directions. All of this means a high control effort, which is reliably carried out by means of complex control electronics. Depending on the melting point and the material to be grown, suitable crucible materials must be selected. These are usually platinum or iridium crucibles. The entire crystal growing process takes place under suitable atmospheric control, oxidizing, neutral or reducing, depending on the material.

The shape of the meniscus determines the diameter of the crystal (Fig. 10.4).

The most critical moments are the start and the end of the crystal growth process. At the start of growth, the seed must cool the melt slightly to allow material to crystallize in order to initiate growth. This stage leads to growth defects that greatly affect crystal quality. After crystallization of a certain length of new crystal, the diameter is reduced to reduce these ingrown defects (dislocations, etc.). They grow

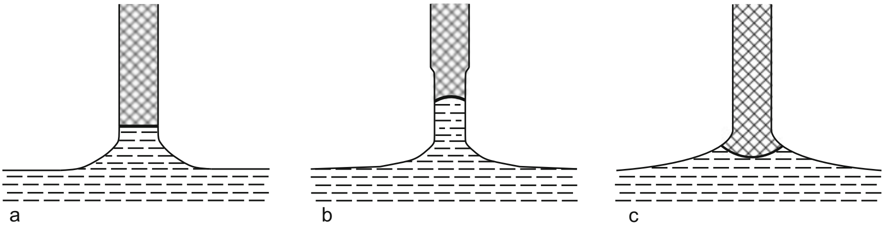


Fig. 10.4 Dependence of the crystal diameter on the shape of the meniscus. (**a**) constant diameter; (**b**) decrease of the diameter; (**c**) increase of the diameter

Fig. 10.5 Single crystal of strontium-gadolinium borate $Sr_2Gd_2(BO_3)_4$ grown by the Czochralski method with remnants of the crystal seed (size about 10 cm)

out to the side. A so-called *neck/necking* is formed. After a suitable length/time, the diameter is slowly increased to the desired final crystal size, the so-called shoulder is formed. Smallest parameter fluctuations can lead to small diameter fluctuations on the one hand or in the case of doped crystals to doping fluctuations. So-called striations are formed, which lower the crystal quality. These can be healed to a limited extent by subsequent annealing treatments. This is done by solid-state diffusion. However, if the crystalline quality is very high, the necessary defects that allow this solid-state diffusion are missing.

The advantages of the Czochralski process are that large crystals can be grown, high temperatures are achievable, nucleus specification is possible and the process can be automated. Therefore, a whole range of materials is synthesized by this process, such as metals, semiconductor materials (Si, GaAs) or oxides (corundum, spinel, garnets, niobates; Fig. 10.5). With more than 10,000 t a^{-1} of growth quantity, the Czochralski process is the dominant method of single crystal growth worldwide.

Disadvantages are the need for a high quality crucible, a suitable crystal seed, a rather high control effort and the fact that only congruent materials can be grown.

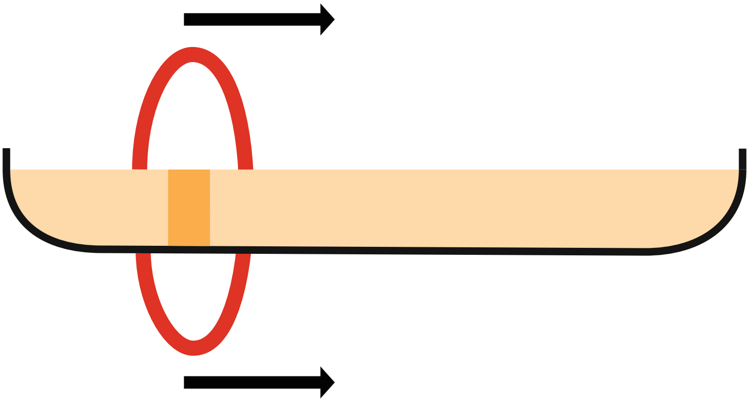


Fig. 10.6 The principle of zone cleaning of a material in a flat crucible with heating ring

10.3 The Zone Melting Process

The zone melting process was used in its origins for material cleaning. The basis of this cleaning principle is that a material-specific distribution coefficient of impurities (chemical components, dopants) is established between crystal and melt (Fig. 10.6).

Usually the content of foreign components in the melt is higher than in the solidifying crystal. During purification, a melt is generated at one end by means of heating rings in a boat or a similarly suitable crucible. This melt zone accumulates impurities, as the crystal solidifying from it has a higher purity. The movement of the melt zone through the crystal thus produces a purification effect.

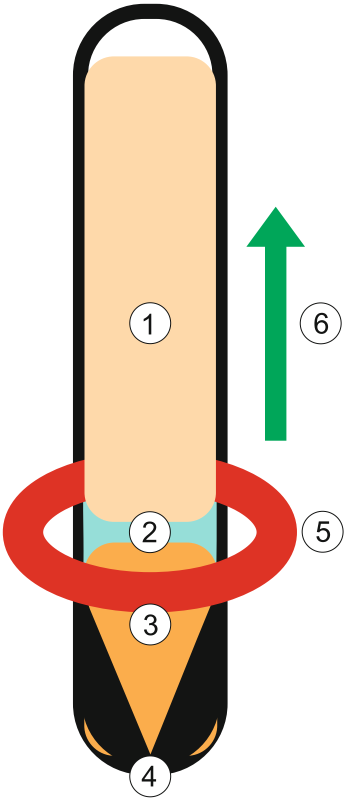
However, this principle can also be used for crystal growth if the setup is placed vertically (Fig. 10.7) and carried out in an ampoule.

Melting is started at the lower tip of the ampoule and the melting zone is slowly moved upwards. The crystal grows by means of crystallization “behind” the melting zone. By suitable shaping of the lower tip of the ampoule, a single crystal can ultimately be produced from a few nuclei forming without nucleus specification. If nuclei are specified, this rather arbitrary selection is bypassed and single crystals of defined orientation can be grown in a targeted manner (Fig. 10.8).

This is also possible without a crucible/ampoule, as the melt is held between the raw material (ceramic rod) and the growing crystal/orientated seed via its own surface tension. Thus, high melting materials can be grown at low cost as the expensive crucible is not necessary. In addition to the use of a heating ring, optical constructions are also used in modern apparatus to generate a local melt (so-called mirror furnaces).

Similarly, the zone melting process is also used to produce a single crystal from polycrystalline starting material while achieving a reduction in defects and impurities. The best-known example of this is the growth of high-purity, single-

Fig. 10.7 The principle of zone melting in an ampoule with heating ring *(5)*. The direction of movement of the heating ring is indicated by the arrow *(6)*; *1* starting material, *2* melting zone, *3* growing crystal, *4* start of melting



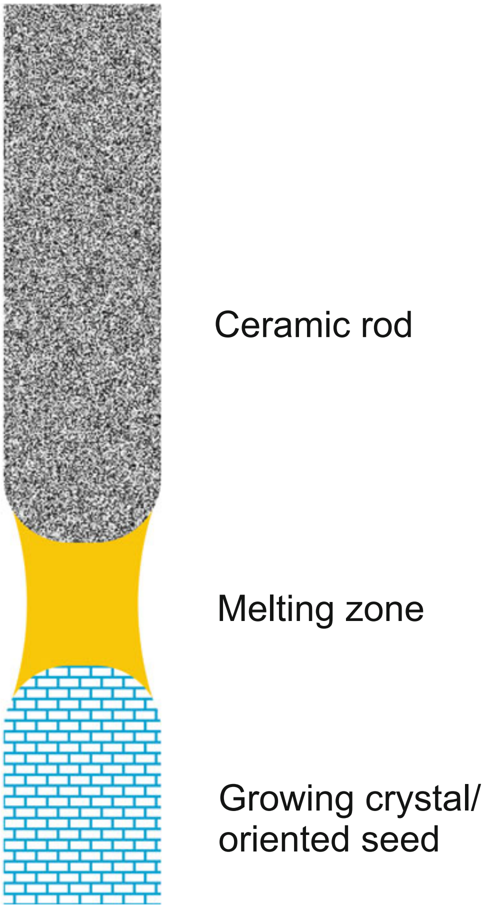
crystal semiconductor silicon. By moving a heating ring along a polycrystalline Si rod, a melt is generated in a spatially limited part, which "migrates" along the rod, leading to the gradual formation of a single crystal.

10.4 The Hydrothermal Process

Crystal growth from solution is one of the oldest methods of single crystal synthesis. The basic principle is based on the crystallization of a dissolved component from a solvent by increasing the concentration. The increase in concentration can be achieved by cooling, evaporation of the solvent or a change in temperature. In order to bring soluble compounds into solution, it is often necessary to work at elevated temperatures and/or pressures.

The hydrothermal process is a crystal growing process under pressure. It takes place in so-called autoclaves. With the solvent H_2O, material is dissolved in a hot area of the autoclave, which is deposited on predetermined seed crystals in a colder

Fig. 10.8 The principle of zone fusion with nucleus specification



area. Here, quartz crystal growth will be presented as an example. The basis is the unary phase diagram of H_2O (Fig. 10.9).

Crystal growth in the hydrothermal process takes place beyond the critical point of H_2O above 374 °C and 218 atm, at which H_2O exists as a supercritical fluid. A supercritical fluid is characterized by the property that at the critical point the density of the liquid state is equal to that of the gaseous state.

The basis for knowing the breeding parameters such as temperature, solubility etc. is the work of Kennedy (1950). The pressure in the autoclave can be adjusted by the degree of filling correlated with the temperature (Fig. 10.10).

Since the principle of growth works first via dissolution and then, due to lower temperature, via precipitation with the circulating fluid between the thermally different regions, the solubility of SiO_2 is a critical parameter. Figure 10.11 compares the relative solubility of different SiO_2 sources in H_2O.

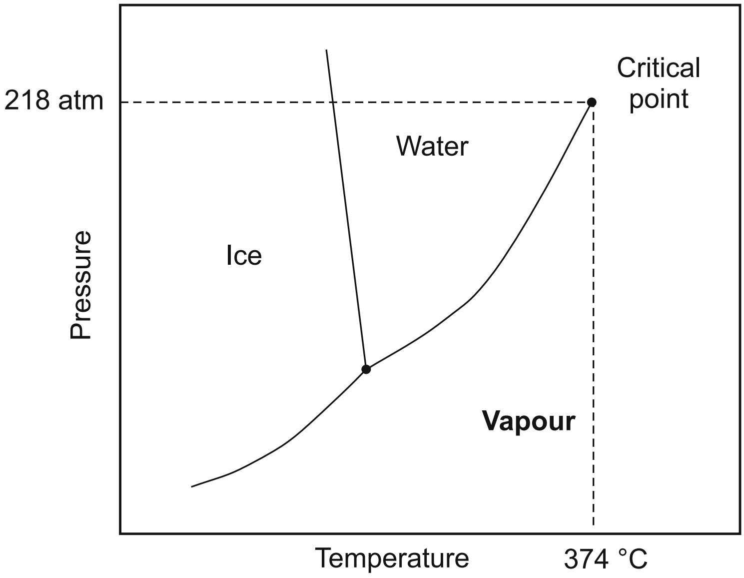


Fig. 10.9 The unary system H_2O

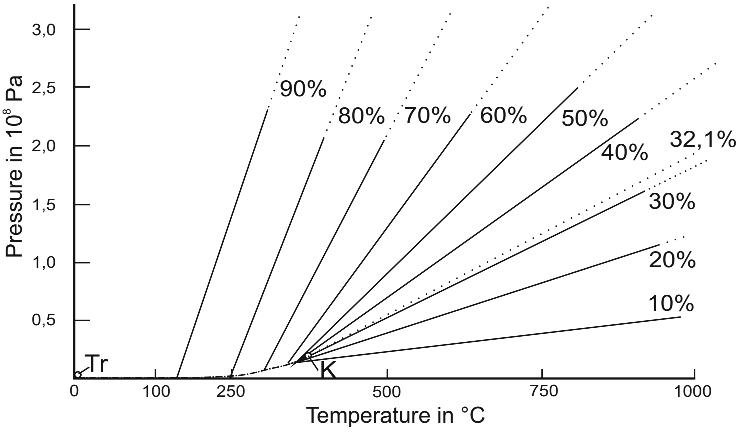


Fig. 10.10 p-T plot of H_2O with isochores correlated with degree of autoclave filling; *K* critical point, *Tr* triple point. (Modified after Wilke and Bohm 1988)

It can be seen that, for example, the highest solubilities are present at just under 360 °C. Silica glass shows twice the solubility (approx. 0.20 mass-%) as α−quartz (just below 0.10 mass-%). Amorphous SiO_2 has even extrapolated a slightly higher value (about 0.24 mass-%), where amorphous SiO_2 is difficult to handle experimentally. Furthermore, the use of silica glass requires a prior melting of SiO_2, which

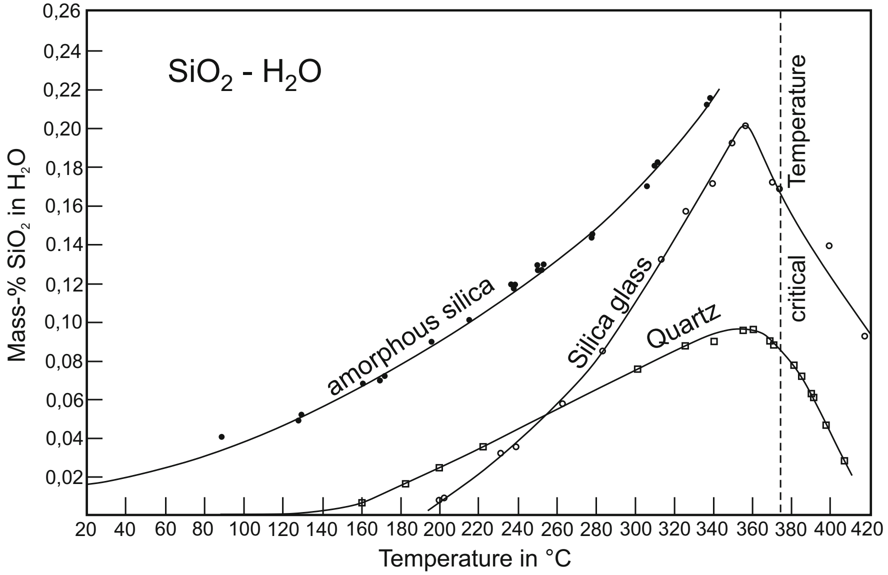


Fig. 10.11 Comparison of the relative solubility of different SiO_2 sources in H_2O. (According to data from Kennedy 1950)

means an additional process step. The influence of pressure as a parameter is shown in Fig. 10.12.

If the values for 360 °C are used here for comparison, about 0.14 mass-% SiO_2 would dissolve at 1000 bar, and about 0.16 mass-% extrapolated at 1500 bar. More important than these numbers, however, is the fact that under pressure the solubility continues to increase with increasing temperature. Crystal growth of quartz usually occurs at about 400–440 °C in the dissolution range. This would correspond to solubilities at 1500 bar of about 0.195–0.275 mass-%, and at 1750 bar of about 0.23–0.32 mass-%. However, all these values are quite low and would end up in a low efficiency of the production. However, if NaOH is added to the system, the solubility is dramatically increased by the change in pH (Fig. 10.13).

Addition of 0.5 n NaOH increases the solubility at 400–420 °C to about 2.38–2.47 g/100 g, which is approximately a factor of 9–10. From all these data, a pressure of about 3000 atm can be derived at this temperature of 400–420 °C and 80% filling ratio. NaOH thus increases the solubility of SiO_2 by a factor of about 10.

The basic structure of an autoclave is shown in Fig. 10.14. The lower part of the autoclave contains the nutrient material. This can be fragments of highly pure quartz crystals (so-called lascas) or silica glass. In the upper part there are the predefined seed plates made of monocrystalline α-quartz, which determine the crystallographic orientation of the growing crystal. These areas are separated from each other by a sieve barrier (screen or baffle) to prevent the nutrient material from swirling upwards. A temperature gradient is set to adjust the circulation of the supercritical solvent: approx. 400–440 °C in the hot dissolution area, 350–380 °C in the colder

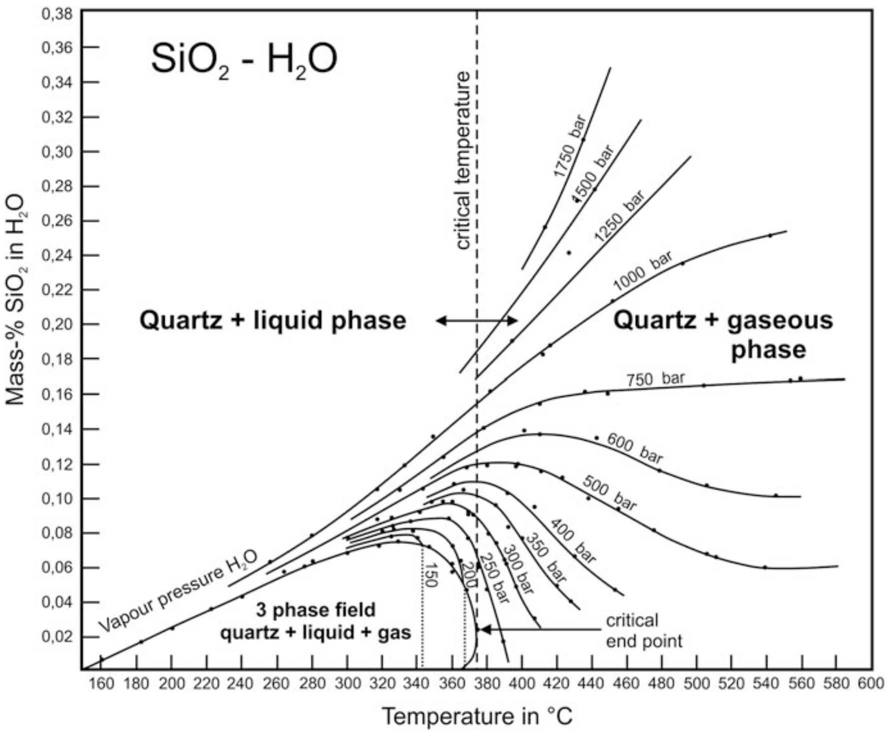


Fig. 10.12 Isobaric solubility curves of quartz. (According to data from Kennedy 1950)

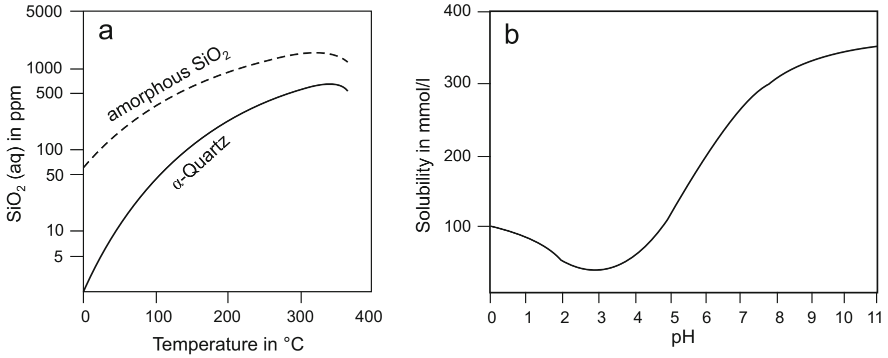


Fig. 10.13 Solubility of α-quartz compared to amorphous SiO_2 as a function of temperature (**a**) and pH (**b**)

precipitation area. The pressure is set via the filling level of 80–85%, but since there is a thermal gradient, the values in Fig. 10.10 do not apply directly. Overall, the pressure is between 1500 and 2000 bar.

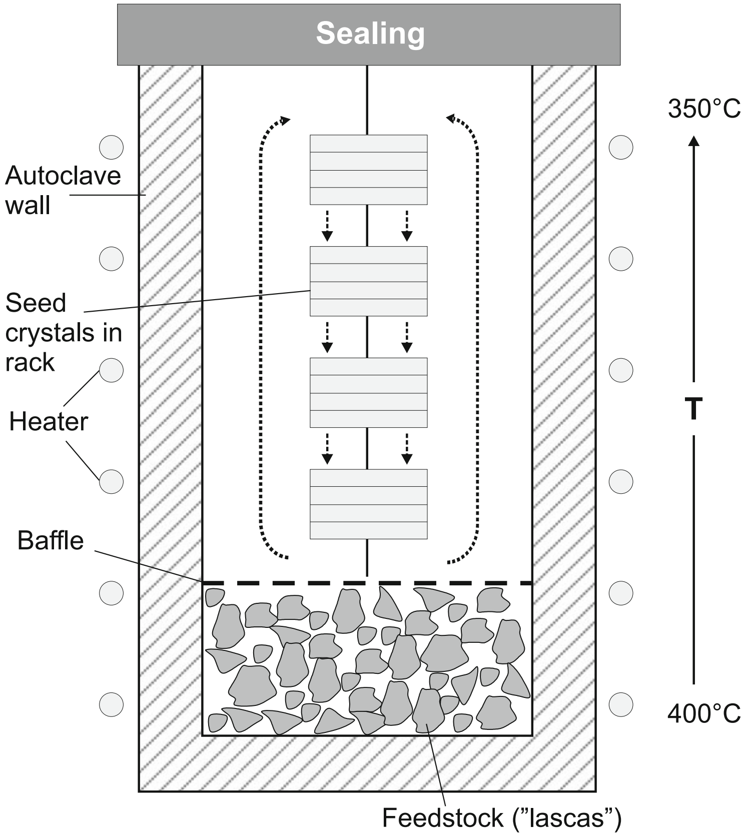


Fig. 10.14 Basic design of an autoclave for hydrothermal synthesis. (Modified after Götze 2012)

Both temperature ranges must be well below 573 °C to ensure controlled growth of low-quartz. The average cultivation time is about 3 months to obtain low-quartz crystals of about 20 cm length (Fig. 3.24). The morphology of the grown synthetic quartz crystals differs significantly from natural crystals. This is due to the nucleation specification, which is chosen to optimise the preparation of vibrational quartz crystals. This forced morphology leads to the formation of disequilibrium surfaces that are not flat but structured (so-called vicinal surfaces).

The hydrothermal process can also be used to grow other materials such as emerald. In principle comparable with quartz, the experimental parameters such as solvent composition, temperature and pressure are adapted to the respective material.

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Mineralogical Aspects in Power Engineering

11

A secure energy supply is the basis of every modern industrial society. Three main forms of primary energy sources have emerged in recent years: fossil fuels (oil, natural gas, coal), nuclear fuels and regenerative (renewable) energy sources. The shares of the individual sectors have shifted significantly over time and will continue to change. While fossil and nuclear energy sources still dominate worldwide at present, the ratio will shift significantly in the direction of renewable energies such as wind, water, solar energy, biomass and geothermal energy in the future. Completely new processes, such as fuel cells or nuclear fusion, will also play an increasing role in the future. This trend is primarily driven by two factors: the limited reserves of fossil fuels and the aim of reducing the environmental impact of energy production.

What all energy sources have in common is that a whole series of geological-mineralogical and material-technical problems arise in the entire cycle from the raw material sources, through extraction and use, to the recycling of residues and waste management. Some of these aspects will be discussed in the following chapter. There are also many overlaps with environmental aspects, which are addressed in Chap. 12.

11.1 Mineralogical Aspects of Coal Energy Production

Despite the increasing use of alternative energy sources, a large part of the world's energy supply is secured by conventional techniques. Coal continues to play a decisive role in this. In addition to the task of raw material exploration, the activities of mineralogists in power plants essentially comprise three areas of responsibility:

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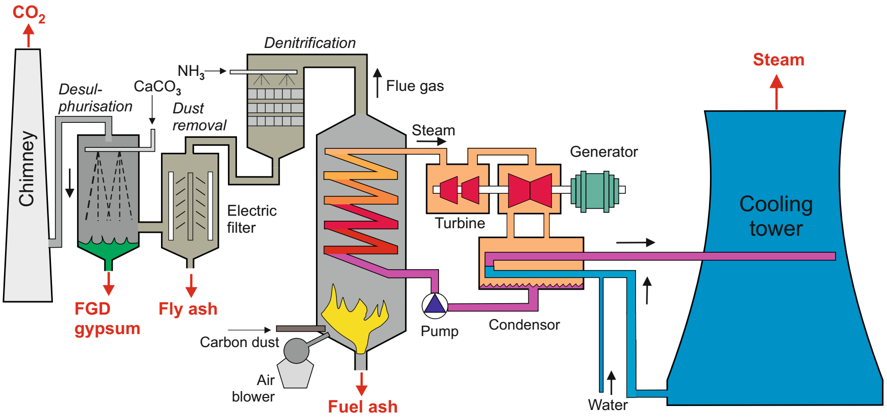

Fig. 11.1 Schematic diagram of a coal-fired power plant

- the assessment of fuels,
- the investigation and control of matter deposition, corrosion, erosion, etc. in boilers and steel pipes as well as steam turbines, and
- the evaluation and dumping of power plant residues (slags, ashes).

Figure 11.1 shows a schematic diagram of a coal-fired power plant. The fine-grained fuels are introduced into the combustion chamber, where they remain for a very short time. The energy released is used to heat steam, which drives the turbines to generate energy.

The gas flow within the power plant causes erosion and corrosion of the steel pipes by sulphurous gases, ash particles and magnetite, which is formed during the oxidation of the pipe surfaces, due to an aggressive environment and the high kinetic energy of entrained particles. Various material engineering solutions are possible to reduce or prevent these wear phenomena. The formation of magnetite particles can be minimized by applying chromium diffusion coatings to the inside of the boiler tubes. Coating the steel tubes with hard materials such as cermet materials (e.g. chromium carbides Cr_3C_2) or iron borides also increases the erosion and corrosion resistance of the materials used.

In addition to material wear, various residual materials are produced during the operation of the power plant, such as bottom ash (fuel ash), fly ash and flue gas. A 1000 MW coal-fired power plant produces as waste materials per day approx. 230 t CO_2, 48 t NO_x, 15 t fly ash and 10 kg toxic heavy metals such as Hg, As, Cd and Se. To reduce the emission of power plant residues, various flue gas cleaning processes are applied (Fig. 11.2).

The solid particles in these combustion residues can be attributed primarily to the non-combustible inorganic constituents in the coal (Fig. 11.3). The most common minerals in lignite are clastic constituents such as quartz and feldspar, clay minerals (kaolinite, illite) and sulphur compounds such as gypsum and pyrite/marcasite.

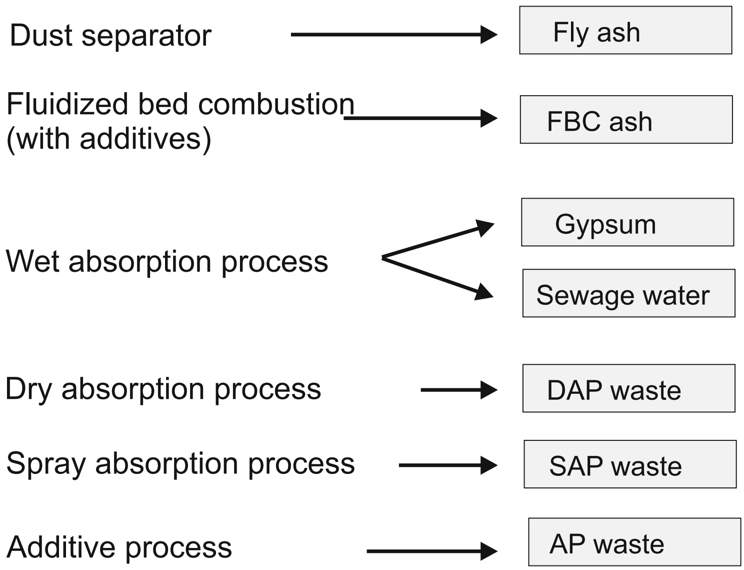

Fig. 11.2 Types of power plant residues depending on the flue gas cleaning process

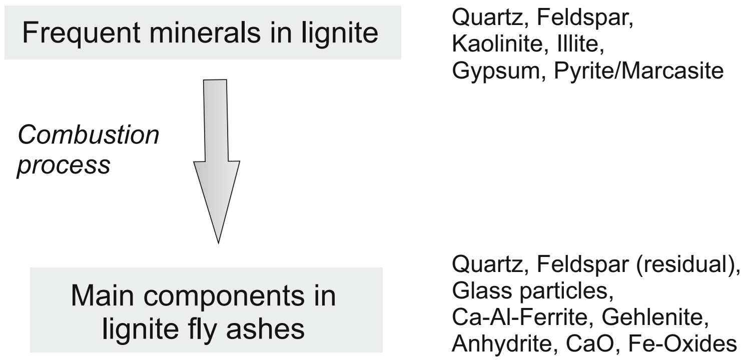

Fig. 11.3 Most important inorganic constituents in lignite and the resulting phases of the combustion process

In the combustion process, the relatively coarse-grained quartz and feldspar are hardly transformed due to the short residence time in the high-temperature range, while gypsum dehydrates to anhydrite and the Fe sulfides are mainly transformed to Fe oxides. Ca-Al ferrites and/or gehlenite $Ca_2(Al,Mg)[(Al,Si)SiO_7]$ can also be formed. The bulk of the fine-grained clay minerals are converted to glass particles, which dominate the lignite fly ashes as small globules of variable chemical composition (Fig. 11.4).

The complex chemical and phase composition of coal ashes essentially determines possible technical uses of the ashes or their chemical behaviour during

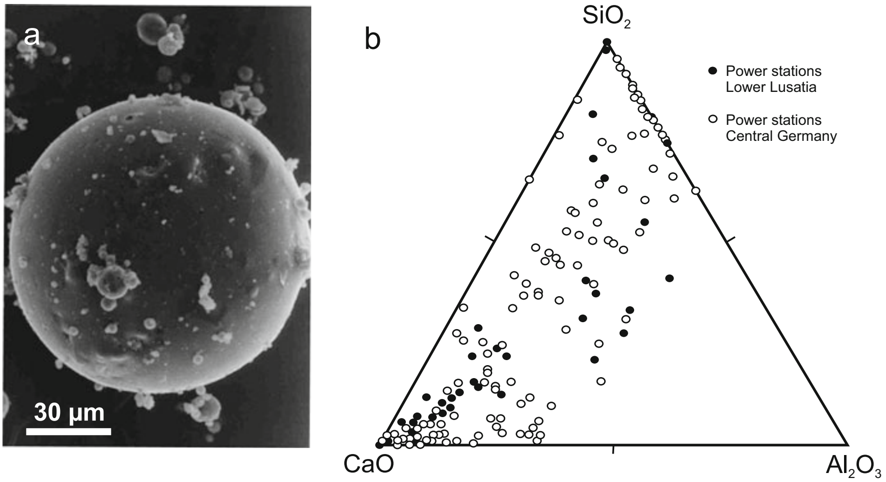

Fig. 11.4 (**a**) SEM image of glass beads from lignite fly ash; (**b**) chemical composition of glass particles from different German power plants. (Data from Münch and Götze 1994)

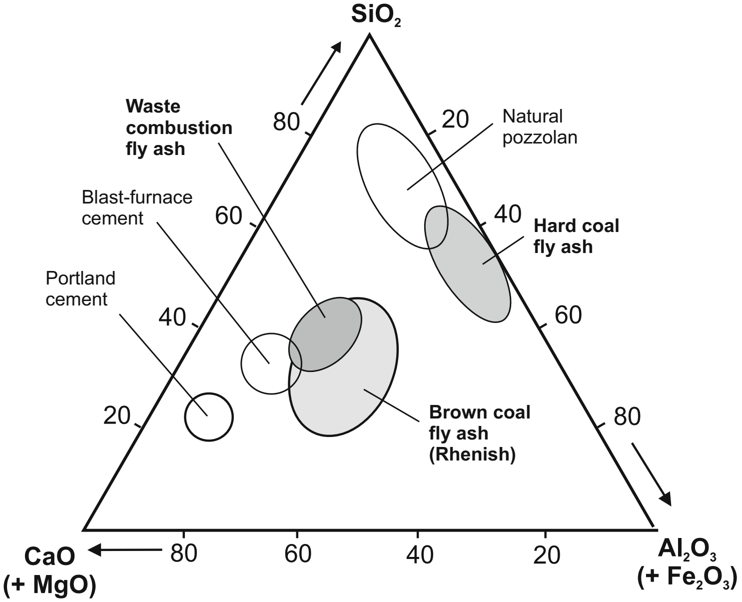

Fig. 11.5 Chemical composition of various combustion residues compared to binders

landfilling. The chemical composition in the system CaO-SiO$_2$-Al$_2$O$_3$ (Rankin diagram) shows proximity to cement phases (Fig. 11.5). In particular, the glass particles affect the reactivity of the ashes in the aqueous environment. Glasses with low CaO contents (so-called inert glasses) are relatively stable, while glasses

Table 11.1 Mineralogical composition of power plant residues (in % by weight)

	Coal	Fluidized bed combustion		Melting furnace	TAV fly ash
	Fly ash	Bed Bag	Fly ash	Fly ash	$CaCO_3$ absorber
Amorphous					
Glass	50–80	–	–	70–95	–
X-ray amorphous	0–5	20–30	20–30	–	–
Crystalline					
Mullite	2–15	–	–	1–6	–
Quartz	2–8	5–10	2–10	1–4	–
Anhydrite	1–2	15–38	15–35	0.1–0.4	20–25
Magnetite	2–10	–	–	1–5	–
Hematite	1–9	1–5	1–3	1–7	–
Calcite	Traces	5–7	Traces	Traces	10–20
CaO	Traces	3–25	3–25	Traces	25–35
Clay/Mica	Traces	40–80	40–60	–	–
Accessories	Traces	Traces	0.5–3	Traces	Traces

Table 11.2 Accumulation of heavy metals in power plant residues

	Boiler ash	Filter dust	Sorption sludge
Element	Mean value (mg kg^{-1})	Mean value (mg kg^{-1})	Mean value (mg kg^{-1})
Cl	22,100	38,000	166,000
F	53	105	40
Pb	2440	4900	2785
Zn	6200	16,600	6400
Cd	60	300	170
Cr	275	450	186
Cu	690	1050	385
Ni	168	145	835
Hg	1.4	8	1900
Tl	2.1	–	0.45

with high CaO contents (so-called active glasses with >35–40 mass-% CaO) show similar chemical compositions and analogous latent hydraulic reactions as cement clinker phases. Thus, such ashes can show setting reactions during landfilling, which produce self-consolidation and thus stabilization. An admixture to conventional cements as hydraulic phases is thus also possible for use in building materials (Chap. 6). However, due to the possible pollutant problems, very strict guidelines must be hold for concrete admixtures.

Table 11.1 shows an overview of the average mineralogical composition of power plant residues.

Problems can arise in the further treatment of residual materials from coal combustion due to the accumulation of various toxic heavy metals (e.g. Cd, Hg, As, Pb, Zn) during the thermal processes (Table 11.2). Volatile components can be volatilized in the combustion process and accumulate on the surface of the solid particles. The heavy metals thus represent a potential hazard in the further use or landfilling of the residual materials and must be firmly bound. Elution tests of the ashes are therefore necessary in advance to test the solubility of the components.

In addition to the high CO_2 emissions, a major problem in energy generation from coal-fired power plants is the high S content of the fossil fuels, which leads to the emission of sulfur compounds (SO_2 and SO_3). For this reason, processes have been developed to significantly reduce the S content of the exhaust gases. One of these residues of coal combustion is FGD gypsum (flue gas desulphurisation gypsum), which is produced in large quantities during flue gas desulphurisation (Fig. 11.2).

Various processes can be distinguished for flue gas desulphurisation, with wet processes being the most common:

- Wet process: Flue gases are cooled with the absorbent contained in aqueous solution and saturated with water vapour. This is usually done in a countercurrent scrubber, the absorber. Various substances are used as absorbents, such as lime or limestone suspension (so-called lime scrubbing) or ammonia (wet ammonia process).

$$SO_2 + CaCO_3 \rightarrow CaSO_3 + CO_2$$

$$2CaSO_3 + 4H_2O + O_2 \rightarrow \underset{\textit{FGD gypsum}}{2(CaSO_4 \cdot 2H_2O)}$$

$$2NH_3 + H_2O + SO_3 \rightarrow (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow \underset{\textit{FGD gypsum}}{CaSO_4 \cdot 2H_2O} + 2NH_3$$

- Dry process: Flue gas constituents react with lime-milk suspension in a spray absorber, producing a dry, fine-grained end product of gypsum ($CaSO_4 \cdot 2\,H_2O$).
- Additive process: Flue gas desulphurisation using limestone powder as a neutralising agent mixed with the fossil fuel. Part of the SO_2 reacts with the limestone and is converted into calcium sulphate.

$$SO_3 + CaCO_3 \rightarrow CaSO_4 + CO_2$$

A large part of the FGD gypsum produced in immense quantities is sent to landfills due to its high residual moisture or can only be used as backfill material (e.g. landscaping and road construction, mining mortar). An application of FGD gypsum is mainly possible in the construction industry, where it is used as building gypsum, as a setting regulator in cements or for gypsum building boards. Potential new applications have been created by autoclaving FGD gypsum. The resulting reactive hemihydrate has rapid binding properties and can be used as stucco or model plaster.

Even the flue gas desulphurisation processes cannot solve all the environmental problems of energy generation from coal. Wet flue gas desulphurisation processes, for example, produce waste water that accumulates various soluble components from the coal and the absorbent, such as heavy metals and halogen compounds (Table 11.1). These wastewaters must therefore be treated before being discharged into the water cycle.

11.2 Nuclear Energy

The generation of energy from radioactive nuclear fuel is a complex issue that polarizes like hardly any other energy source. The highly efficient technology is coupled with a whole series of risk factors and potential dangers that have led to a move away from nuclear energy in Germany. In particular, the problem of the final storage of radioactive residues will continue to occupy scientists and engineers for decades to come, despite the closure of nuclear power plants. In the following, an overview of the complex aspects of nuclear power generation will be given.

The physical and technical basis of energy generation from radioactive raw materials is nuclear fission. In 1938, the German physicists Otto Hahn and Fritz Strassmann discovered at the Kaiser Wilhelm Institute in Berlin that uranium is split into two moderately heavy elements by irradiation with slow neutrons (Fig. 11.6).

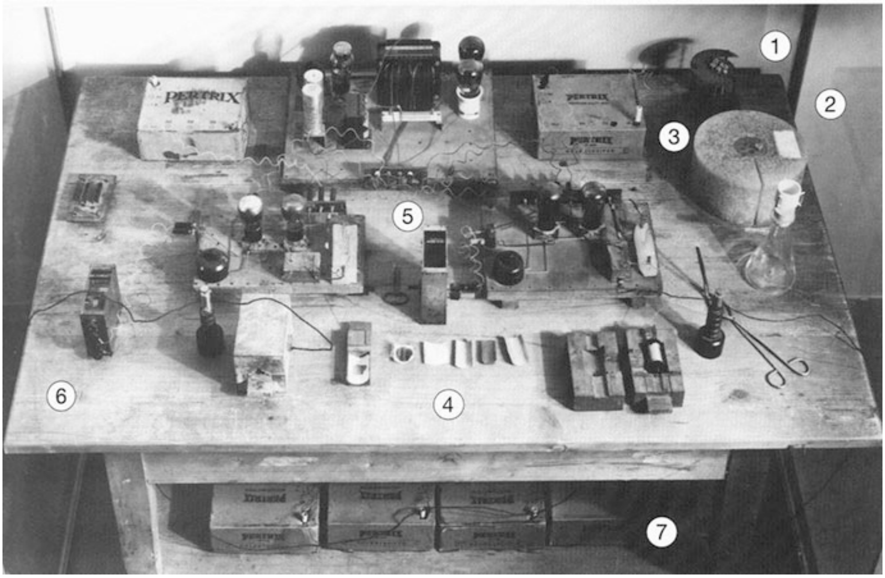

Fig. 11.6 Original set-up of the first nuclear fission experiment in 1938. 1 Neutron source; 2 Uranium; 3 Paraffin block for slowing down the neutrons; 4 Geiger-Müller counting tube; 5–7 Additional electrical equipment. (Source: Deutsches Museum Munich)

$$^{235}\mathrm{U} + \mathrm{n} \rightarrow {}^{144}\mathrm{Ba} + {}^{89}\mathrm{Kr} + 3\mathrm{n} + 200\mathrm{MeV}$$

The complete fission of 1 kg ^{235}U releases an energy of approx. 24 GWh, which corresponds to the amount of energy in the combustion of 3000 t of hard coal. This comparison shows the enormous potential of radioactive fuels for energy production.

The main raw materials for nuclear energy are above all uranium and thorium minerals. Of the approximately 70 known uranium minerals, crystalline uraninite (UO_2) and colloidal pitchblende (U_3O_8) play the most important role. In addition, coffinite ($USiO_4$), brannerite (UTi_2O_6), various uranium micas, thorite ($ThSiO_4$) and monazite ($(Ce,Th)PO_4$) are of interest. Uranium deposits are mainly associated with acidic igneous rocks (granites), hydrothermal veins, and sedimentary deposits (placers, red-bed type, black shales, or in phosphorites and coal deposits). Although uranium is usually diffusely distributed in granites and occurs in relatively low concentrations, these deposits are now being mined on a large scale through the use of modern mining and processing technologies.

As an example of the extraction and processing of uranium ores, the Rössing mine (Namibia), one of the largest uranium deposits in the world, should be mentioned. The primary uranium mineralization here consists essentially of uraninite, with grades in the rock of only about 10–50 ppm. The uranium is extracted from alaskites (alkali leuco-granite) by a complex and multi-stage leaching process:

1. Blasting in large open-cast mines and mining with bucket wheel excavators
2. Transport and coarse crushing in crushing plants
3. Multi-stage wet grinding
4. Combined oxidation and leaching process by ferrous sulphate and sulphuric acid
5. Separation into sand and sludge fractions in the hydrocyclone
6. Separation of the uranium-containing liquor from the sludge
7. Separation of uranium from solution by ion exchange on exchange resin; subsequent release of uranium from resin by strong acid
8. Liquid extraction by mixing the uranium-containing solution with organic liquid and ammonium sulphate solution
9. Precipitation of ammonium diuranate (*yellow slurry,* $(NH_4)U_2O_7$) by addition of ammonia (pH increase).
10. Dewatering in drum filters (filter cake = *yellow cake*)
11. Drying and oxidation to uranium oxide U_3O_8

The finished uranium oxide powder is finally processed into fuel rods for the reactors (Fig. 11.7). The powder is pressed, sintered and processed into formatted pellets of approximately 10 × 20 mm. These pellets are packed into tubes made of a special alloy (Zircaloy) and sealed. Several tubes are assembled into bundles, which are used as finished fuel rods.

The group of nuclear materials includes a wide range of materials used in nuclear power plants. In addition to nuclear fuels, another important group of materials in the nuclear field is various construction ceramics, which are used directly in the reactor as cladding tubes (Zr-Sn/Zr-Nb alloy Zircaloy) or cover material (e.g. graphite). In

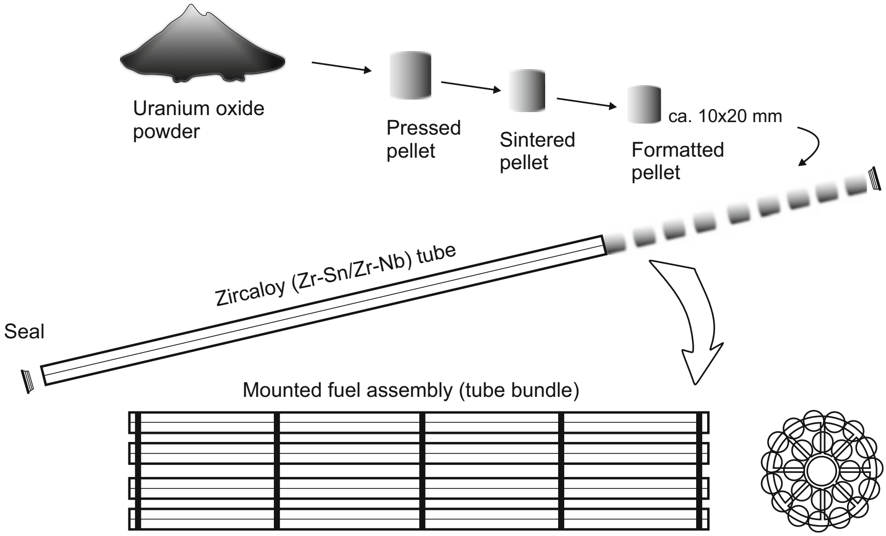

Fig. 11.7 Schematic diagram of the production of uranium fuel rods

addition, there are absorber materials (Be, Cd, B_4C) and moderator materials (e.g. graphite), which serve to regulate the neutron flux or slow down the neutron velocity. Not to be forgotten are special cements/concretes used as construction materials in the power plants.

One of the main problems of the use of nuclear energy is the recycling and disposal of the resulting waste and residues. In particular, the high-level radioactive waste that cannot be reprocessed must be converted into a form that minimises the hazard potential. One possible way is the vitrification of highly radioactive waste from the reprocessing of spent fuel elements (Hofmann and Kuczera 2001). In a multi-stage process, the fuel assemblies are broken down, the uranium and plutonium released are enriched and incorporated in a melt of special glass (borosilicate glass) (Fig. 11.8).

The final disposal of spent nuclear fuel and vitrified high-level radioactive waste (HLW glass) is subject to a number of preconditions. Disposal must take place in deep geological formations where long-term (at least 100,000 years) safe confinement with isolation from the biosphere is ensured. Even under the conditions of possible accidents, no inadmissible radiation exposure may occur (IPPNW 1995).

Salt domes, but also crystalline rocks (e.g. granites) or massive clay formations are under discussion as potential rocks for radioactive disposal. Salt domes in particular have the advantage that they remain stable over geological periods, have a high thermal conductivity, no fluid phases occur and the thermoplastic behaviour of the salt causes a rapid containment of the stored waste.

For the final disposal of radioactive waste, a multi-barrier system for long-term safety has been developed (Fig. 11.9). This system includes a technical, a geotechnical, and a geological barrier which, in combination, should ensure a high level of

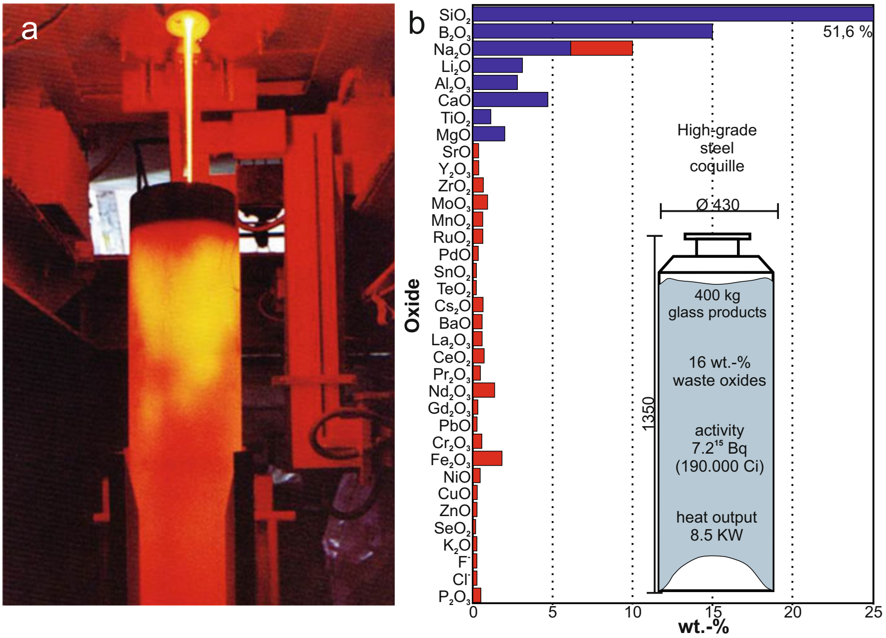

Fig. 11.8 Filling of a glass melt containing uranium and plutonium into a stainless steel mould (**a**) and composition of the special glass (HLW glass, (**b**); blue characterises the composition of the basic glass, red the extension to the HLW glass). (Source: H. Pentinghaus with kind permission)

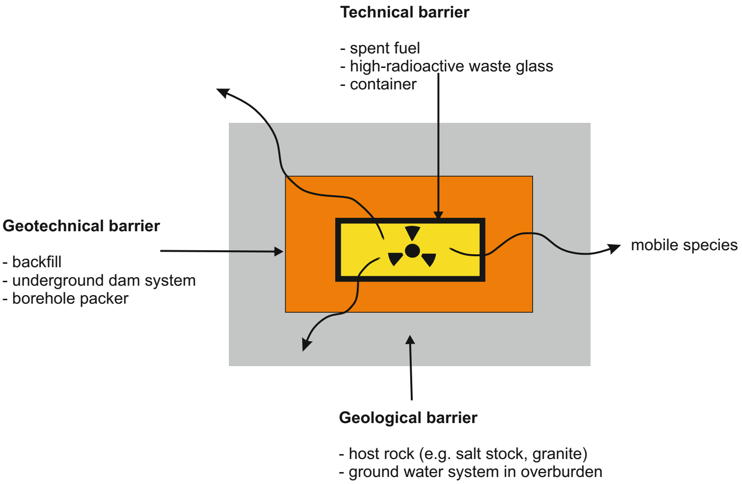

Fig. 11.9 Scheme of the multi-barrier system for the final disposal of radioactive waste materials

safety of the repository. The multi-level arrangement of the individual protective components is intended to prevent the escape of mobile species.

In the search for alternative storage media for radioactive waste, natural minerals are also increasingly coming to the fore. Zircon ($ZrSiO_4$), for example, is a mineral that in nature sometimes has high contents of uranium and thorium, which have been safely incorporated in the crystal over hundreds of millions of years. Synthetic phases of zircon are therefore potentially suitable as stable storage minerals for uranium, thorium or plutonium.

11.3 Alternative Energies

Problems with the availability of conventional energy raw materials as well as growing environmental problems have led to the development and application of alternative and renewable energies becoming increasingly important. Above all, the direct and indirect use of solar energy has great potential, as this energy source supplies huge amounts of energy and is almost inexhaustible (Fig. 11.10). In 20 min, the sun supplies an amount of energy equivalent to the entire annual world consumption. The energy can be used in the form of heat (collector – solar heating), electrical energy (solar cell – solar power) or indirectly stored as chemical energy in biomass (Wokaun 1999).

Photovoltaics is the direct conversion of solar energy into electrical energy. In 1954, an American scientist discovered that electrical voltage occurs on electronic

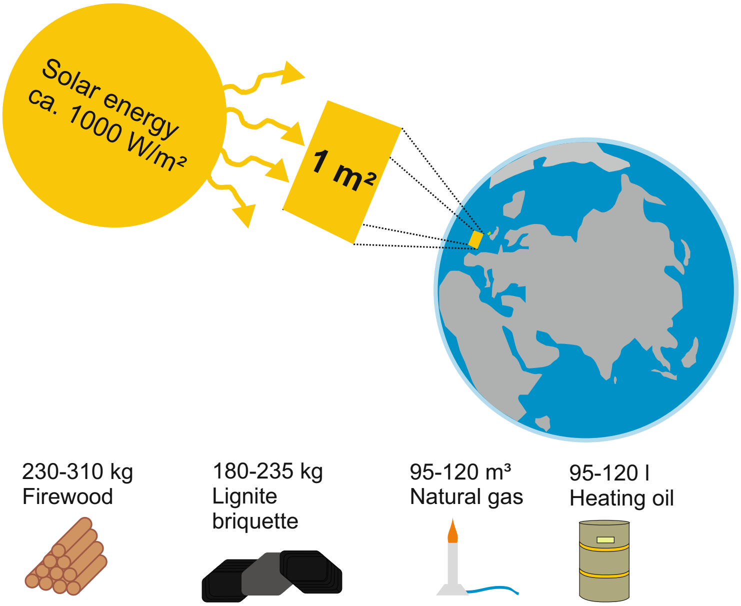

Fig. 11.10 Solar energy per square metre with comparable amounts of energy from fossil fuels

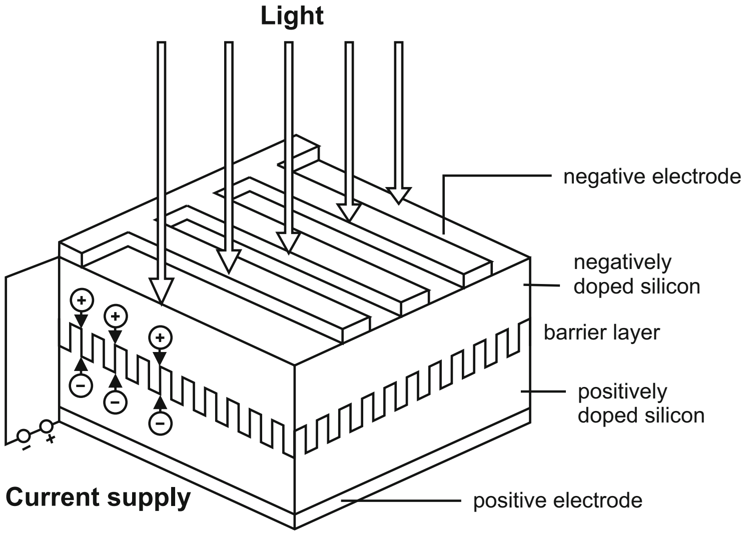

Fig. 11.11 Schematic structure of a solar cell made of semiconductor silicon

semiconductor components as soon as they are exposed to light (photoelectric effect). “Solar” silicon, which is used as a synthetic semiconductor material in photovoltaics, plays a major role in this process (Chap. 8). The silicon is synthesised in a multi-stage process (Fig. 8.12) and incorporated into solar cells as a base material (Fig. 11.11). The solar cells consist of two layers in which negative and positive charge carriers predominate, respectively, due to the introduction of impurity ions (in silicon e.g. P^{5+} and B^{3+}). In the doped semiconductor materials, solar energy is converted directly into electrical energy by exciting electron transitions. One disadvantage of photovoltaics is the low efficiency of energy conversion, which is currently around 15–20%.

Solid oxide fuel cells (SOFC) represent a modern material and technology development (Fig. 11.12). Here, oxygen is ionised at the anode by means of electrons. The oxygen ions are transported through an ion conductor to the anode, where the reaction of hydrogen with oxygen ions forms water with the release of electrons. Electric current is generated by these reactions.

The materials used for fuel cells are optimized for the function. For example, Sr-doped $LaMnO_3$ (perovskite structure) is used as the material for the cathode, Li-doped Co_3O_4 (spinel structure) for the anode and Y-stabilised zirconium oxide as the ion-conducting electrolyte (Fig. 11.13). Doping is done to increase the conductivity and catalytic effect of the components or for phase stabilization. Solid electrolyte fuel cells are an elegant solution for energy generation. At present, the storage of the fuel hydrogen in sufficient quantities is still problematic. Suitable materials are being sought for this purpose.

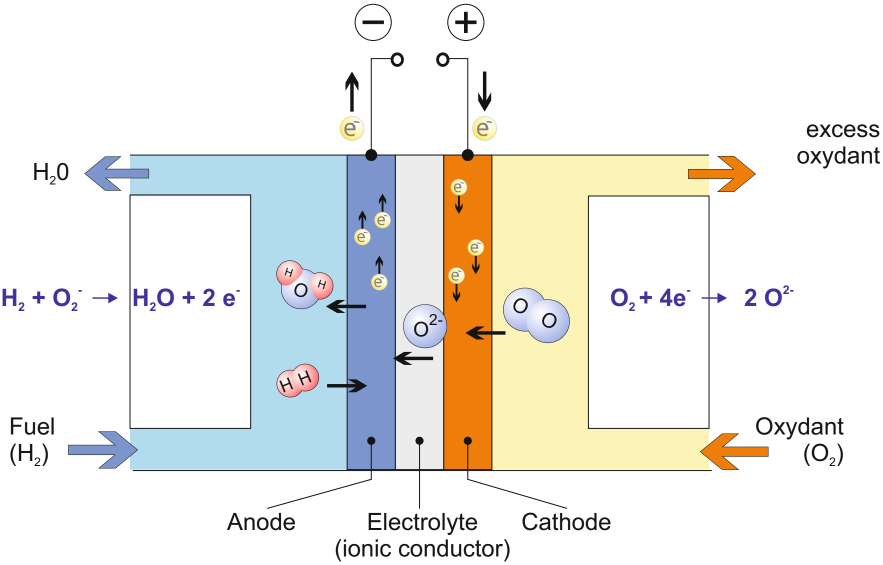

Fig. 11.12 Schematic structure and mode of operation of a solid oxide fuel cell

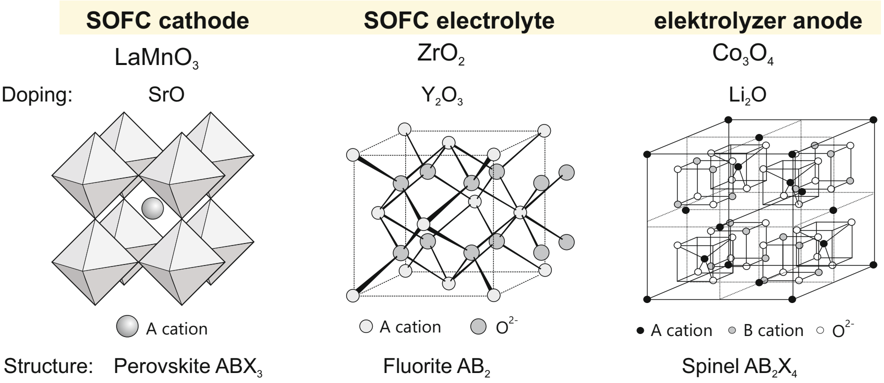

Fig. 11.13 Chemical composition and structure of materials for solid oxide fuel cells (SOFC)

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Environmental Mineralogy

12

The development of modern civilization bears a number of environmental problems, since the consumption of vast amounts of energy and raw materials simultaneously generates corresponding amounts of waste, residual materials and pollution (Fig. 12.1). This issue can only be solved in its entirety if the interrelationships and the character of the material cycles are recognised in detail.

Due to the fact that minerals are important components of the geosphere, atmosphere and technosphere, mineralogical aspects play a major role for the evaluation of environmental problems. On this basis, the subfield of environmental mineralogy has developed, which deals with complex topics of mineralogy in environmental issues (Fig. 12.2).

Some of these environmentally relevant mineralogical aspects that occur in connection with energy technology (residues from coal combustion, radioactive waste) have already been discussed in the previous chapter (Chap. 11).

12.1 Characterisation of Residues and Waste Disposal

Waste and residual materials as well as intermediate products from the extraction and processing of raw materials play a dominant role in environmental problems, as they are constantly produced in large quantities and can sometimes contain enormous pollutant potential. Above all, the solubility of toxic elements and their possible introduction into the water cycle must be taken into account when recycling and dumping these residual materials. Characteristic elements of such anthropogenic contaminations are e.g. Hg, Pb, Cd, Cr, Tl or As.

A typical example is ferrous and non-ferrous metallurgy, where hundreds of millions of tonnes of slag are produced worldwide every year. The precise knowledge about mineralogical and chemical properties of residual materials is an important prerequisite for deciding whether these materials are to be recycled

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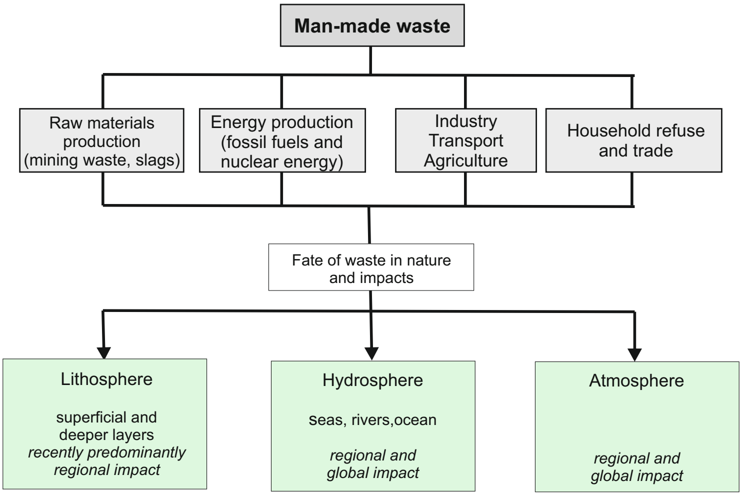


Fig. 12.1 Generation and fate of anthropogenic waste and residues

Fig. 12.2 Important topics of environmental mineralogy

- ▶ Characterization and reutilisation of waste materials
- ▶ Mineralogical aspects of combustion processes (slags and ashes of coal and waste combustion)
- ▶ Storage minerals
- ▶ Environmental aspects of clay minerals
- ▶ Radioactive waste
- ▶ Minerals in the atmosphere (aerosols)
- ▶ Mineralogy and health (asbestos, silicosis)
- ▶ Weathering and conservation of natural stone

(e.g. building industry) or landfilled, or whether secondary metal extraction makes sense, (Table 12.1).

In general, residues are produced in almost every production and consumption process, and are divided into secondary raw materials and wastes depending on their recyclability. The characterization of these materials with regard to material composition (type of material, structure, degree of decomposition, etc.) and granulometric condition (piece or particle size) is a prerequisite for the assessment of the technological properties and a possible hazard potential. Particularly in the case of modern composite materials, the detailed evaluation of their properties is required for

Table 12.1 Characteristics of slags from various pyrometallurgical processes

	Iron/steel slags	Non-ferrous slags
Main elements	Ca, Si, (Al, Mg, Fe)	Fe, Si, (Al, Ca)
Main phases	Ca-rich glass	Glass
	Ca-containing olivine	Olivine group
	Melilite group (Al, Mg)	Pyroxene
	Miscellaneous oxides	Melilite group
	(CaO, sulfides, metals)	Spinel and SiO_2 phases
		(sulfides, metals)
Eluate	Alkaline	Acidic
	(Ca compounds)	(sulfide oxidation)

Data from Piatak et al. (2015)

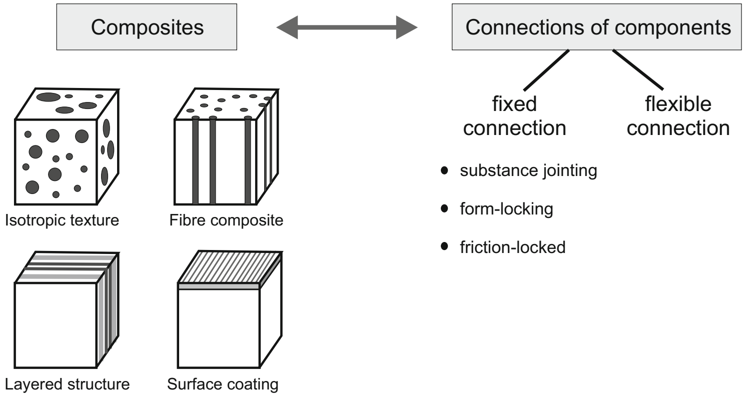


Fig. 12.3 Characterization of composite materials

optimal processing or recycling in analogy to natural mineral raw materials (Figs. 12.3 and 12.4).

Thus, a large number of different compounds from different materials occur in modern technical equipment, the separation of which is of decisive importance for the questions of waste disposal or recycling. Based on this premise, the special field of environmental processing has developed and established itself in analogy to the processing of raw materials. The main aim of these processes is to recover recyclable components as secondary raw materials.

Non-recyclable residues can be disposed in various ways (Fig. 12.5). The largest quantity of waste materials is sent to landfills, where in many cases prior chemical or thermal treatment is carried out. The main purpose of this pre-treatment is to reduce the volume and to bind possible pollutants. Only high-caloric residues remaining after several processing steps such as mechanical treatment (separation of iron/non-iron), shredding, drying and screening of mineral components are thermally treated and landfilled as residual waste.

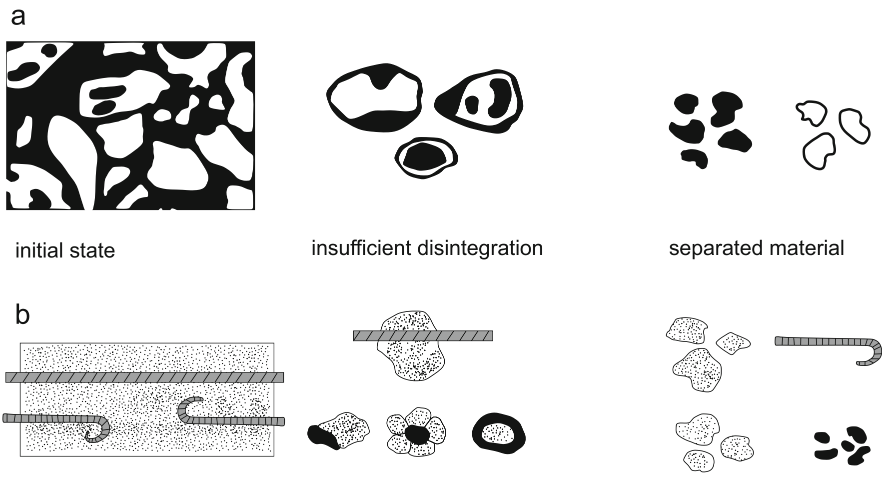


Fig. 12.4 Evaluation of intergrowth (**a**) or bonding (**b**) and state of disintegrationin waste and secondary raw materials

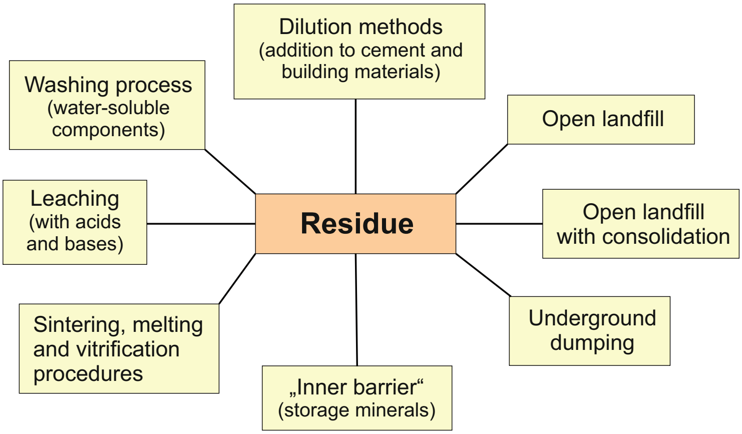


Fig. 12.5 Principle disposal routes for polluted industrial residues

A major problem is the safe storage of industrial residues contaminated with pollutants, such as electroplating sludges, sewage sludges or flue gas cleaning residues. Due to a lack of possible applications, these toxic and/or heavy metal contaminated wastes are in many cases treated by means of thermal processes. The aim is to store the pollutants in a matrix that is as stable as possible, i.e. to render them inert.

The chemical and mineralogical composition of the thermal products is usually very complex, and the microstructures are also extremely heterogeneous. Therefore, a characterization of the slags is only successful by a combination of chemical,

Table 12.2 Phase composition of slags from waste combustion plants

Very often	Frequent	Existent
Glass phase	Feldspar $K[AlSi_3O_8]$ $Na[AlSi_3O_8]$ $Ca[Al_2Si_2O_8]$	Chromite $FeCr_2O_4$
Magnetite Fe_3O_4		Eskolaite Cr_2O_3
Quartz SiO_2		Fayalite $Fe_2[SiO_4]$
Melilite $(Ca,Na)_2(Al,Mg)[(Si,Al)_2O_7]$		Monticellite $CaMg[SiO_4]$
		Maghemite Fe_2O_3
		Corundum Al_2O_3
		Portlandite $Ca(OH)_2$
		Talc $Mg_3[(OH)_2Si_4O_{10}]$
		Clinochlor $Mg_6FeAl[(OH)_8/AlSi_4O_{10}]$
		Anhydrite $CaSO_4$
		Hedenbergite $Ca(Mg,Fe)[Si_2O_6]$
		Augite $Ca(Mg,Fe,Al)[(Si,Al)_2O_6]$

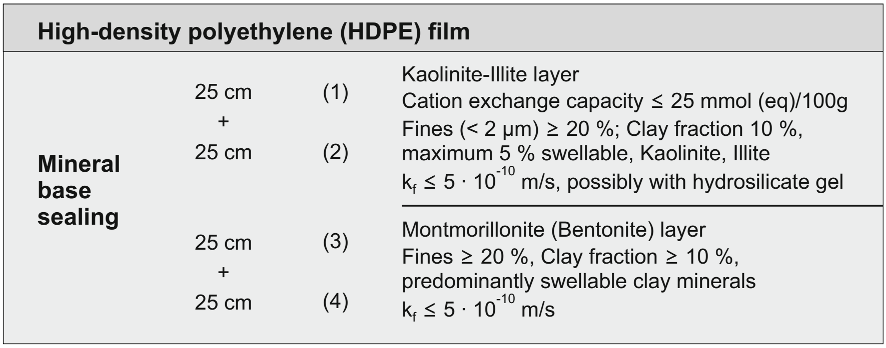


Fig. 12.6 Example of a multimineral base sealing of a landfill site

optical and phase analytical investigation methods. Besides a predominant X-ray amorphous glass phase (SiO_2 44–51, Al_2O_3 14–16, CaO 12–15, Na_2O 4–6, Fe_2O_3 4–14, MgO ~3, K_2O ~ 1.5 wt%), various crystalline mineral phases may occur in such slags depending on the waste material thermally treated such as e.g., anhydrite, Ca-phosphates, Fe-oxides, melilite, or various spinel phases (Jamieson et al. 2015; Table 12.2). Thus, the phase composition is very similar to that of lignite fly ashes (Fig. 11.4 as well as Table 11.1).

Various clay minerals play a major role in modern environmental and landfill technology. Due to their extremely low permeability to liquids and high adsorption capacity for various pollutants, clays and bentonites are used for mineral sealing of landfills (Fig. 12.6). Clays are also preferred for encapsulating and securing contaminated sites or for stabilizing liquid and pasty wastes.

A further development of pollutant immobilization is the "inner barrier system", which is based on the crystallochemical fixation of pollutant ions in storage minerals (Pöllmann 1994). Through a two-stage process

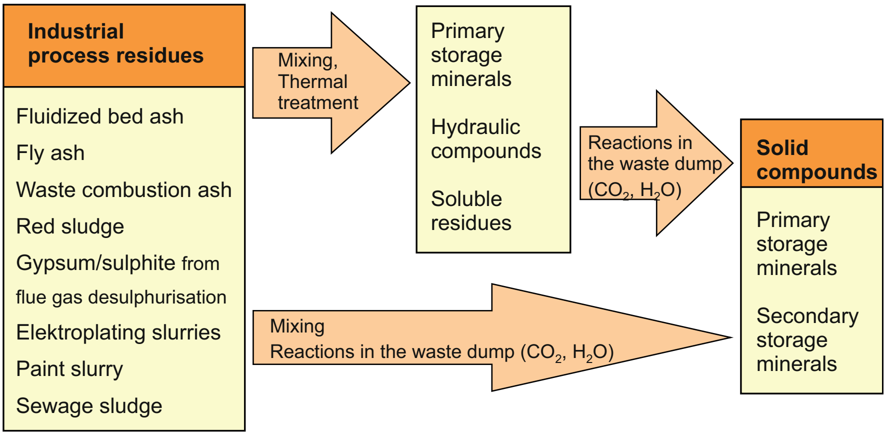


Fig. 12.7 Process diagram for the production of storage minerals from industrial residues. (Modified after Pöllmann 1994)

- Formation of anhydrous minerals by thermal reaction and
- Formation of hydrous minerals by hydration reaction

the phase composition of the waste products is modified and converted by the hydraulic reaction into a mixture of storage minerals that is as leach-proof as possible (Fig. 12.7).

Due to the interlocking of the storage minerals during the hydraulic process, a consolidation and stabilization of the landfill is also achieved and the permeability is reduced. Prerequisites for an optimal effect of the storage minerals are the complete formation of the minerals from the industrial residues, the crystal-chemical variability for the incorporation of different cations and anions as well as the prevention of pollutant leaching through a dense structure and geochemical stability in the application area.

Various storage compounds can be prepared in the following chemical systems:

- $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}CaSO_4$
- $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}CaCl_2$
- $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}CaCl_2\text{-}MgO$
- $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}CaSO_4\text{-}CaCl_2$

It is obvious that the $CaO\text{-}SiO_2\text{-}Al_2O_3$ ternary system again plays a central role. Figure 12.8 lists some important examples of storage minerals.

▪ Immobilization of chlorides/sulphates, heavy metals:	***Ellestadite*** $Me_{10}[Cl_2/SiO_4)_3(SO_4)_3]$
▪ Immobilization of oxoanions/hydraulic reaction:	***Sodalite*** $Me_8[Al_{12}O_{24}] \cdot (XO_4)_2$
▪ Immobilization of oxoanions:	***Ettringite*** $[Ca_6Al_2(OH)_{12} \cdot 24H_2O]^{6+}[(SO_4)_3 \cdot 2H_2O]^{6-}$
▪ Immobilization of heavy metals:	***Metal-Metal-Hydroxysalt*** $[Me_6Al_2(OH)_{16}]^{2+}[(CO_3 \cdot nH_2O]^{2-}$
▪ Immobilization of organic anions:	***Calcium-Aluminium-Hydroxysalt*** $[Ca_4Al_2(OH)_{12}]^{2+}[(OH)_2 \cdot nH_2O]^{2-}$

Fig. 12.8 Examples of storage minerals (*Me* = suitable metal ion). (Data from Pöllmann 1994)

12.2 Mineralogy and Geochemistry of the Atmosphere

Although our atmosphere consists predominantly of gases (approx. 78% nitrogen, 21% oxygen, 1% noble gases, 0.03% carbon dioxide), mineral particles do not play an insignificant role. The mixture of gases, liquids and solids present in the atmosphere, with particle sizes generally <10 µm, is called an aerosol. The specific composition of aerosols depends on many regional, climatic and seasonal factors. Aerosols can be classified in the dynamic cycle of emission (element and substance input into the atmosphere), transmission (transport associated with various processes of substance transformation and redistribution) and immission (element discharge from the atmosphere). As a result, the chemical and phase composition of aerosols is subject to constant change over time.

The ratio of natural (geogenic) to man-made (anthropogenic) substance input into the atmosphere has also changed over time. Since the beginning of the industrial revolution, the atmosphere has been increasingly polluted by energy production, traffic, industrial exhaust gases, etc. Air pollution does not only have local effects, but can lead to regional and even global atmospheric influence. In comparison to the natural dust input, many toxic metal compounds are enriched in the aerosols by industrial processes. This results in great significance for the environment, ecology and medicine. In the investigation of aerosols, the interconnection of substance input, dispersion, discharge from the atmosphere and dissolution and accumulation processes in soils and waters up to direct uptake via the respiratory organs or indirectly via accumulation in the food chain of plants, animals and humans must always be taken into account. In the following, some fundamental aspects of these complex processes will be presented.

12.2.1 Sources of Aerosols (Emission)

The input of substances into the atmosphere is very diverse. A distinction is made between the two large groups of natural (geogenic) and anthropogenic (technogenic) sources of substances. The natural substance production originates mainly from continental dust movements, volcanic activities, forest fire, sea aerosols and the activities of plants. The technogenic sources include mainly various industrial processes, power generation, transportation, and small-scale consumers such as domestic heating and trade. To estimate the contribution of each emission source to total aerosol production, the shares of natural and anthropogenic sources are compared in Table 12.3.

Although natural sources account for the largest amount of total material inputs, anthropogenic sources are of decisive importance, especially for many pollutants. Many toxic elements (e.g. lead, cadmium, arsenic) are present in anthropogenic aerosols in concentrations several times higher than in natural ones (Table 12.4).

In addition to the dust input itself, emissions of sulphur dioxide (SO_2), nitrogen oxides (NO_x), carbon dioxide (CO_2) and hydrocarbons also play a significant role, as apart from the direct environmental impact (e.g. greenhouse effect), they also lead to

Table 12.3 Contributions of natural and anthropogenic sources to total aerosol production in the atmosphere

Source	Natural		Anthropogenic	
	$\times \cdot 10^6$ t a^{-1}	%	$\times \cdot 10^6$ t a^{-1}	%
Primary particle production				
Coal fly ash			39.7	1.4
Iron/steel industry			9.9	0.34
Non-fossil fuels			8.8	0.30
Oil exploitation			2.2	0.08
Waste combustion			4.4	0.15
Cement industry			7.7	0.27
Agriculture			11.0	0.35
Miscellaneous			17.6	0.61
Sea salts	1102	38.3		
Soil dust	220	7.7		
Volcanic material	4.4	0.15		
Forest fire	3.3	0.12		
Gas-solid conversions				
Sulphates from H_2S	225	7.8		
Sulphates from SO_2			162	5.6
Nitrates from NO_3	476	16.6	33	1.1
Ammonium from NH_3	297	10.3		
Organic aerosols	220	7.7	30	1.1
Total	**2548**	**88.7**	**326**	**11.3**

Data from Natusch (1982)

Table 12.4 Major anthropogenic emission sources of selected chemical elements

Emission source	Chemical elements
Power plants (gas, oil, hard coal)	As, Pb, Cr, Cd, Hg, Ni, Se, Tl, V, Zn
Power plants (lignite)	Ca, S, Al, Fe, Mg, Ti
Steel and foundry industry	Cu, Ni, S, Fe, Pb, Zn, As
Glass industry	As
Cement industry	Tl, Cd, Sb
Car and traffic	Pb, Pt, Cl, Br
Fertilizer, sewage sludge	Cd, P

Table 12.5 Mean residence time (in days) of suspended particulate metals and ions under Central European conditions

Total suspended particulate matter	Fe	Si	Cu	Mn	Pb	As	Cd	NO_3^-	SO_4^{2-}
2.2	1.6	1.7	1.8	2.0	2.5	2.5	2.8	2.6	2.9

Data from Müller (1982)

the formation of various solid phases (sulphates, organic compounds, etc.) in the atmosphere.

12.2.2 Transformation Processes and Residence Time of Aerosols in the Atmosphere

The residence time of a substance in the atmosphere is an important criterion for its assessment. This is understood to be the residence time of a substance emitted into the atmosphere, i.e. how quickly the atmosphere is able to remove this substance. The average residence time for many aerosol particles under Central European conditions is in the range of several days (Table 12.5).

Since high-temperature processes are responsible for the formation of many aerosol particles, the volatility point, i.e. the mean value of the melting and evaporation temperatures of the phases, plays an essential role. Chemical elements with low volatility temperatures can be mobilized more easily and remain in the atmosphere longer, so that they accumulate in aerosols (Fig. 12.9). This behaviour can be observed in both technical and geogenic processes (e.g. volcanic eruptions).

Aerosols can be modified in the atmosphere by various processes. Many gaseous substances are converted into solids (condensation) or accumulate on the surface of solid particles (e.g. dust particles). In addition, coagulation of particles of different origin and size and dissolution processes in raindrops can occur.

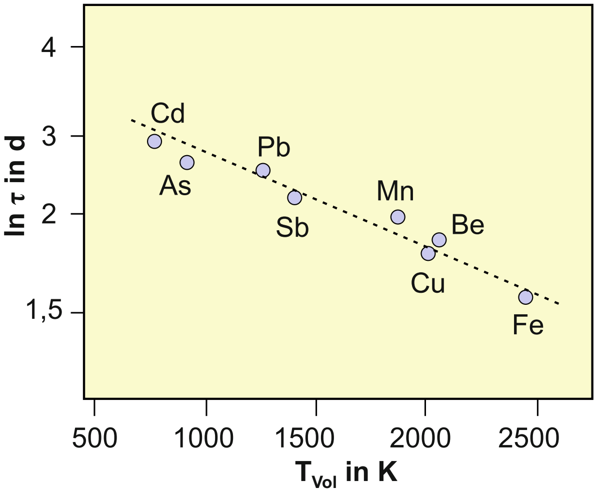


Fig. 12.9 Relationship between volatility temperature T_{Vol} (average of melting and boiling temperatures) of selected elements and their residence time τ in the atmosphere. (Data from Müller 1982)

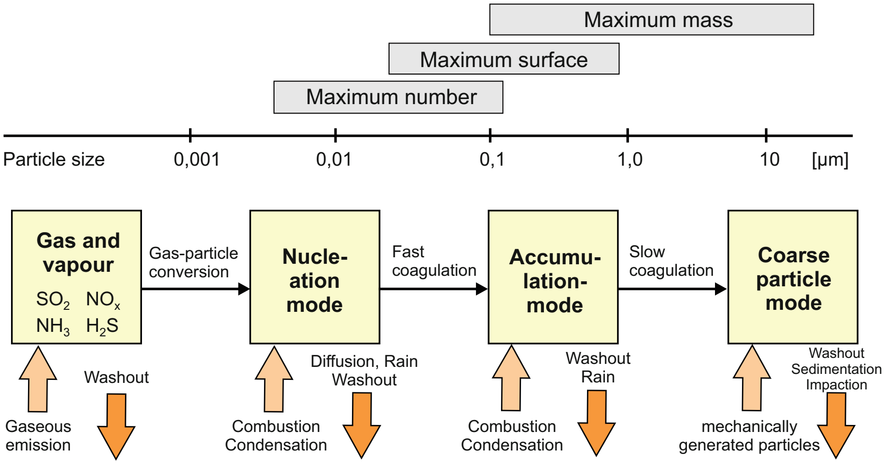


Fig. 12.10 Material cycle of aerosols in the atmosphere. (Modified after Hinds 1999)

12.2.3 Discharge of Dust from the Air (Immission)

Transport and deposition processes of aerosols are essentially determined by the behaviour of particles in flowing gases. Therefore, particle size is particularly important for the discharge of aerosols from the atmosphere (Fig. 12.10). In general, four forms of discharge are distinguished: wet discharge (by rain or snowfall), sedimentation (gravitational sinking), thermal diffusion (deposition by molecular self-motion) and so-called impaction.

Dust particles with a diameter between 0.1 and 2.0 μm are particularly long-lived in the air (approx. 3.5 days in Central Europe), as they are too inactive for thermal diffusion and too light for sedimentation. These particles are mainly removed from the atmosphere by wet discharge. For this reason, the dust content in the air drops dramatically after rainfall events. Very small particles (<0.1 μm) are degraded within a few hours due to violent thermal diffusion, with the rate increasing as the particle radius decreases. Aerosols with larger diameters (>2 μm) are also deposited by sedimentation over a period of hours, with the sedimentation velocity increasing with increasing particle size (up to 2.2 cm s^{-1}). These particles therefore also achieve little dispersion from the emission source. Atmospheric trace gases such as SO_2 and NO_x and their transformation products are removed from the atmosphere by rainfall and dry deposition.

12.2.4 Mineralogy and Geochemistry of Aerosols

For the characterization of aerosols, three parametres are essential: the particle size distribution of the particles, the phase composition and the chemical composition. These parameters determine all the properties and thus the behaviour of the aerosols in the environment.

The particle size distribution of the aerosols is not only decisive for the atmospheric residence time, but also for the toxicological assessment with regard to uptake by the lungs as well as solubility. In general, the particles are divided into three particle size classes, with the upper particle size of the aerosols being specified as 10 μm. From a medical point of view, 10 μm also represent an important limit, since particles >10 μm are relatively harmless from a medical point of view. In particular, the particle-size range 0.1–3 μm comprises the respirable particle size, of which up to 40% can be deposited in the lungs (Fig. 12.11). Depending on their consistency, these particles can cause short-term respiratory diseases or lead to long-term impairment of the respiratory organs.

The smallest particles cover the range smaller than 0.08 μm. These are mostly particles from high-temperature condensation processes and secondary reaction products of organic and inorganic air pollutants. Due to their low mass and residence time in the atmosphere, these particles do not play a significant role.

In the so-called accumulation mode of 0.08–2 μm, substances are enriched which are produced, for example, by condensation after combustion processes and therefore contain large amounts of heavy metals. Therefore, they represent above all the anthropogenic dust fraction. Their great importance is based on the fact that they have the largest specific surface area and, due to their high residence time in the atmosphere, also account for the major proportion of the total particle mass.

The third particle size fraction (coarse particles >2 μm) is mainly composed of particles from natural weathering processes, mechanical abrasion, volcanic ash and substances of marine and plant origin. This fraction thus represents the main part of the natural substance input into the atmosphere.

The phase composition of airborne dusts is extremely diverse and complicated, since it documents the totality of chemical and anthropogenic processes and can also be influenced in part by local emission sources. Despite the complex composition, it is evident that a few characteristic phases occur, particularly in industrial areas (Fig. 12.12). The main part (75–90 mass-%) is formed by silicate and oxide glass

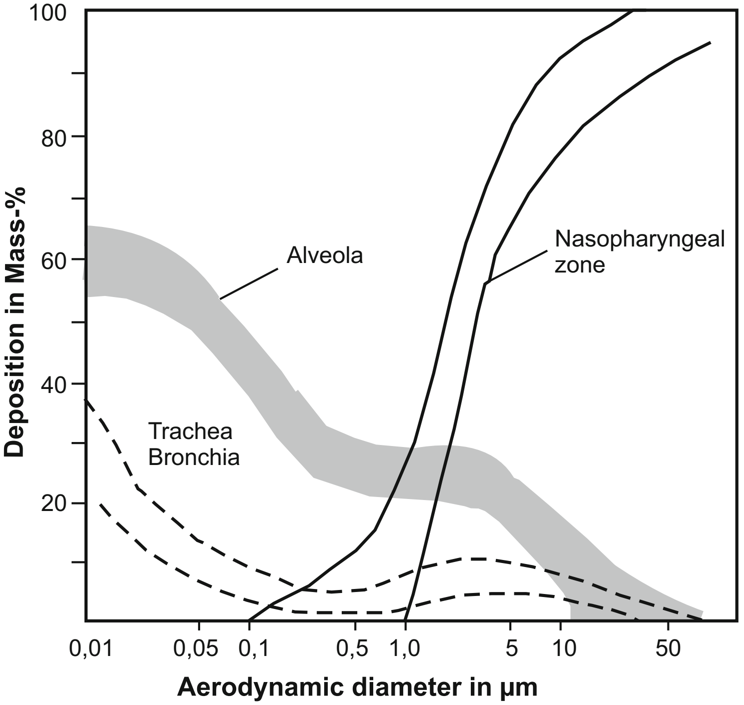


Fig. 12.11 Aerosol deposition in the respiratory tract in dependence on particle size. (Modified after Naumann 1983)

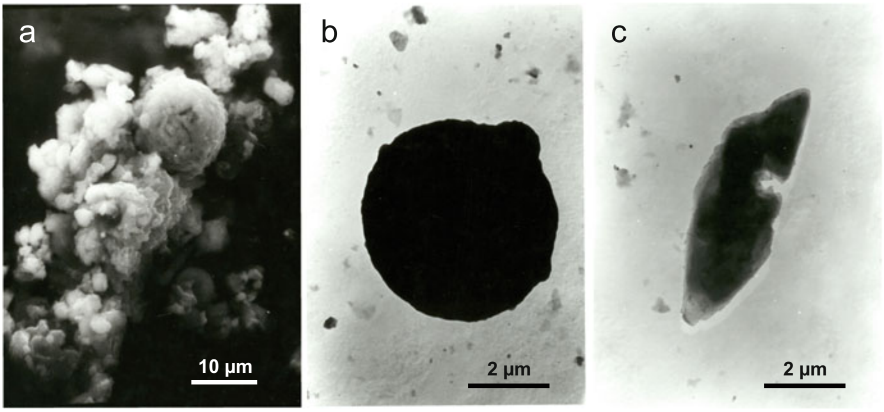


Fig. 12.12 Electron micrographs of characteristic phases in aerosols. (**a**) Agglomerate of dust particles (SEM); (**b**) slag globules (TEM); (**c**) gypsum crystal (TEM)

phases and a large proportion of organic matter. The main crystalline mineral phases in aerosols are quartz (SiO_2), gypsum ($CaSO_4 \cdot 2\ H_2O$), calcite ($CaCO_3$), and aluminosilicates (mullite). In addition, anglesite ($PbSO_4$), zincite (ZnO) or barite ($BaSO_4$) occur accessory.

The occurrence of inorganic components results from the mechanism of their formation. Particles of geogenic origin are transported as mineral dust in the aerosols. The phases emitted from technogenic sources mostly originate from high-temperature processes. Therefore, the volatilization-condensation process plays a major role and higher proportions of glass phases occur. For example, no crystalline phases could be detected for common chemical elements such as Fe, K, Na or Mg. Consequently, these elements are bound in the glass phase, e.g. as slag globules (Fig. 12.12b). The proportion of the glass phase in aerosols is on average approx. 60%. Crystalline mineral phases can usually only be detected with the electron microscope due to the small grain size (Fig. 12.12).

A large proportion of the solid substances contained in aerosols are organic substances. According to König (1982), the content of solid organic carbon in the atmosphere reaches 23–150 million tons per year. In addition, up to 60 million tons per year are introduced into the atmosphere by condensation of organic gases. The nature of the chemical compounds is extremely diverse due to the large number of different emission sources. In addition to substances emitted by anthropogenic processes, they include products of volcanic activity, plant activities (pollen, spores, etc.) and residues of dead organic matter (insect wings, plant debris, etc.). König (1982) gives the proportion of the organic fraction in the total dust as 25–40%, with more than 400 solid organic compounds known to date. As a rule, the organic matter content shows a seasonal pattern, with the highest values above all in spring and summer.

The geochemistry of aerosols is very complex too, whereby all chemical elements of the periodic table can be contained in aerosols. The strong variations in the content of chemical elements can be explained primarily by different sources. Depending on the proportion of natural and anthropogenic element input, the element composition and concentration ranges of the elements in aerosols differ. At least three different areas can be distinguished: areas strongly influenced by industry, areas with strong natural input (e.g. deserts) and areas with very low levels of air pollution (e.g. polar regions; Fig. 12.13).

For the characterization of relatively unaffected aerosols, the polar regions are ideal. Especially in the summer months, this region is separated from other areas by the polar front and shows hardly any anthropogenic influences. The almost complete covering of the earth’s surface with snow and ice also prevents the input of geogenic material. As a result, the aerosols are characterised by low absolute dust contents and only elevated concentrations of the marine elements Cl, K, Na and Ca in their chemical composition. Only in areas of human settlements or during certain weather conditions do the contents of anthropogenic indicator elements such as S, Ni, Cu, Zn or Pb increase. In general, the aerosols of the polar region can thus serve as guide values for clean and unaffected aerosols.

Element	Arctic summer aerosol	Desert (Beer-Sheva, Israel)	Industrial region (average content)
Si	k.A.	**0,58**	0,32
Ca	k.A.	**5,4**	1,49
K	0,05	**0,52**	0,40
Rb	k.A.	**0,73**	0,28
Fe	0,01	0,49	0,91
Ti	0,02	0,51	0,6
Ni	< 0,5	1,07	**3,6**
Se	k.A.	18,0	**860**
Zn	0,85	17,8	**91**
Pb	4,4	18,8	**265**
Cl	**2820**	58,8	**288**
	↑ marine (“sea spray“)	↑ lithophilic	↑ anthropogenic

Fig. 12.13 Chemical composition of aerosols from different regions (given as Clarke concentration = content in the aerosol in relation to the mean content in the Earth's crust) (Data from Voland and Götze 1988)

In geogenically dominated regions with little industrialization, it is above all the natural input of elements into the atmosphere that plays a major role. This becomes clear when one considers the aerosols of semi-arid regions, which are strongly enriched with material from the earth's surface due to desert dust. Especially during sandstorms, the dust content in the air is more than an order of magnitude higher than the average content in common areas. Typical lithophilic elements of the earth's crust (Ca, Si, Sc, Rb, etc.) are enriched in the aerosols, while characteristic technogenic elements such as Pb, S, Ni or Zn show lower concentrations.

In areas of strong industrialization, anthropogenic element input from technical processes plays a decisive role. In particular, elements that volatilize easily in high-temperature processes (low volatility temperature) are strongly enriched in aerosols of industrial regions. These are, for example, the elements As, Br, Cd, Cl, Cr, Cu, Pb, S and others. This is of particular importance as these are many toxic elements. As Fig. 12.13 shows, certain elements can be assigned to specific emission sources. The specific chemical composition of aerosols in industrial areas is therefore strongly related to local emission sources.

12.2.5 Environmental Problems of Aerosols and Aspects of Dust Measurement

Since aerosols have a complex composition, possible harmful properties cannot generally be described by one parameter such as the content of a particular toxic element. Rather, it is necessary to analyse the particle sizes of pollutants and their possible mobility in the biosphere. For example, the direct exposure of the human respiratory tract to aerosols depends primarily on the size distribution of the

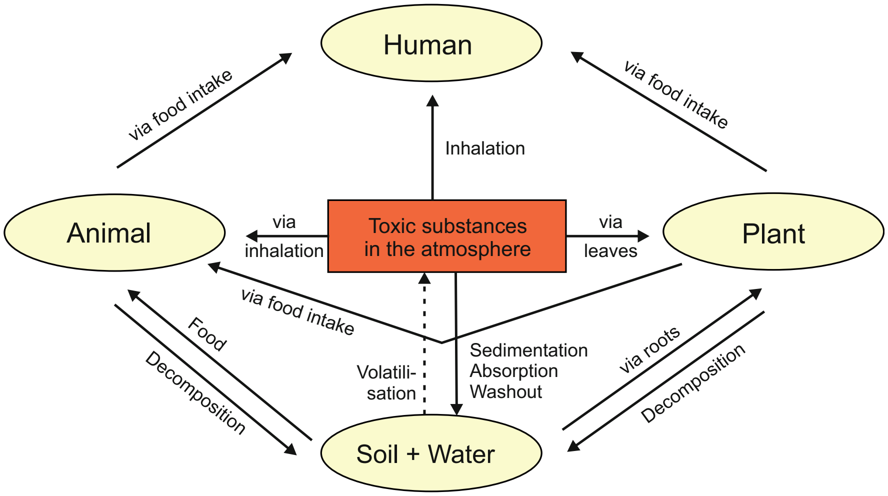


Fig. 12.14 Schematic cycle of the air-soil-plant-animal-human ecosystem. (Modified after Naumann 1983)

particles. The dust fraction of 0.1–3 μm, which is decisive for toxicological assessment, is deposited in the lungs to the extent of approx. 35–40%. In the case of fibrous particles in aerosols (e.g. asbestos), the particle shape may also be important.

However, atmospheric contamination with toxic substances also influences the overall cycle of the air-soil-plant-animal-human ecosystem (Fig. 12.14). Thus, toxic elements or organic compounds are repeatedly mobilized and enriched within this cycle. Heavy metals can thus affect humans not only directly through respiration, but also indirectly through the food chain. In addition to the direct impact on humans, aerosols can also have other far-reaching effects on the ecosystem (e.g. forest dieback) and climate (greenhouse effect).

For the protection of human health, various legal guidelines have been created for parameters such as total dust pollution, fine dust pollution (PM_{10} = dust with a particle size ≤10 μm) or for the chemical composition of aerosols. For the implementation of these environmentally relevant measures, a continuous mineralogical-geochemical characterization of aerosols is necessary. A prerequisite for these investigations is an appropriate representative sampling of the airborne solid particles, which can be very complex due to the specificity of the material. Particle concentrations range from 1 ng m^{-3} to several mg m^{-3}, depending on the exposure situation, and particle sizes range from a few nanometers to about 100 μm. Sample collection can be realized by simple sedimentation techniques, filtration (usually glass fiber or cellulose filters) or so-called impaction techniques (separation in a cascade impactor). The results are evaluated as individual data or summarized in regional immision maps.

12.3 Asbestos

Asbestos has a very long and varied history and has evolved over time from a sought-after mineral raw material to an extremely hazardous substance. More than 2000 years ago, asbestos wicks were used for the eternal flame of the Acropolis in Athens, and since the nineteenth century, asbestos fibres have been processed for fireproof protective clothing for firefighters and many other industrial applications. Most notable was the development of asbestos cement (Eternit) by the Austrian Hatschek in 1900. Over 170 million tonnes of asbestos were mined worldwide during the twentieth century, but the enormous health risks associated with asbestos use were also recognised. For this reason, an EU-wide ban on asbestos has been in force since 2005. So what are the special properties of asbestos that caused its transformation from a valuable material to a hazardous substance, and how are the consequences of decades of industrial asbestos use being dealt with today?

Important for the characterization of asbestos is the fact that it is not a single mineral. The term asbestos refers to long-fibre to hair-shaped variants of natural silicate minerals. The term fiber here describes materials with a very large length to thickness ratio. According to ASTM (American Society for Testing Materials), a ratio of $L{:}D \geq 10{:}1$ is assumed for a diameter < 0.25 mm and a cross-sectional area $< 0.05\ \text{mm}^2$.

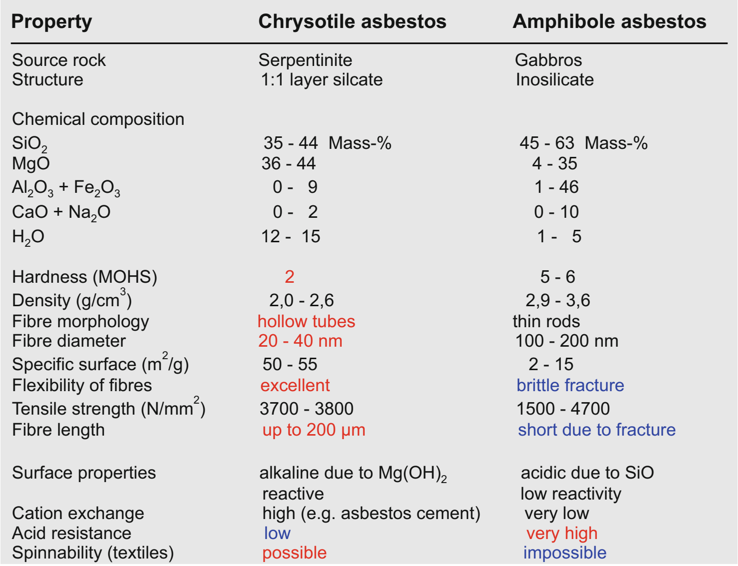
Asbestos (ancient Greek *asbestos:* indestructible, imperishable, indelible) is thus a collective term for two groups of naturally occurring, fibrous silicate minerals. The serpentine group includes chrysotile, also called white asbestos (white fiber), the fiber that is by far the most widely used technically. The amphibole group includes crocidolite (blue asbestos = blue fibre), amosite (brown asbestos), tremolite, anthophyllite and actinolite. Important properties of these two groups are summarized in Fig. 12.15.

The different properties of the various asbestos minerals can be explained by structural features. Serpentine ($Mg_3(OH)_4[Si_2O_5]$) is a 1:1 layer silicate in which the Mg hydroxide octahedra, which are slightly larger than the SiO_4-tetrahedra, cause curvature of the layer packets (Fig. 12.16). In the case of chrisotile, this leads to the curling of several layer packets and thus to the formation of flexible asbestos fibres, whereas in the case of antigorite and lizardite a change in orientation of the layer packets leads to corrugated sheet-like structures (no asbestos!).

Amphibole asbestos (Inosilicate) has a “stack of boards” structure (Fig. 12.17), which results in stiffening of the asbestos fibres. As a result, the hard and brittle amphibole asbestos fibres break easily and are much more difficult to work with. The medical effects are much more critical due to the physical properties.

The differences in properties between chrysotile and amhibole asbestos have resulted in over 90% of industrial use being based on chrysotile asbestos fibres. The main application-oriented properties of asbestos include:

- good mechanical properties, high stability in the direction of the longitudinal axis
- spinnability (chrysotile asbestos)
- low dead weight



Property	Chrysotile asbestos	Amphibole asbestos
Source rock	Serpentinite	Gabbros
Structure	1:1 layer silcate	Inosilicate
Chemical composition		
SiO_2	35 - 44 Mass-%	45 - 63 Mass-%
MgO	36 - 44	4 - 35
$Al_2O_3 + Fe_2O_3$	0 - 9	1 - 46
$CaO + Na_2O$	0 - 2	0 - 10
H_2O	12 - 15	1 - 5
Hardness (MOHS)	2	5 - 6
Density (g/cm^3)	2,0 - 2,6	2,9 - 3,6
Fibre morphology	hollow tubes	thin rods
Fibre diameter	20 - 40 nm	100 - 200 nm
Specific surface (m^2/g)	50 - 55	2 - 15
Flexibility of fibres	excellent	brittle fracture
Tensile strength (N/mm^2)	3700 - 3800	1500 - 4700
Fibre length	up to 200 µm	short due to fracture
Surface properties	alkaline due to $Mg(OH)_2$ reactive	acidic due to SiO low reactivity
Cation exchange	high (e.g. asbestos cement)	very low
Acid resistance	low	very high
Spinnability (textiles)	possible	impossible

Fig. 12.15 Properties of chrysotile asbestos and amphibole asbestos. (red – good properties, blue – poor properties)

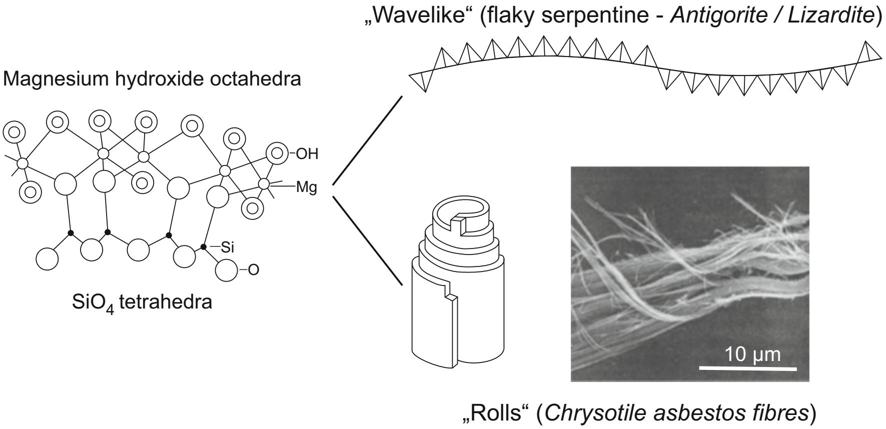
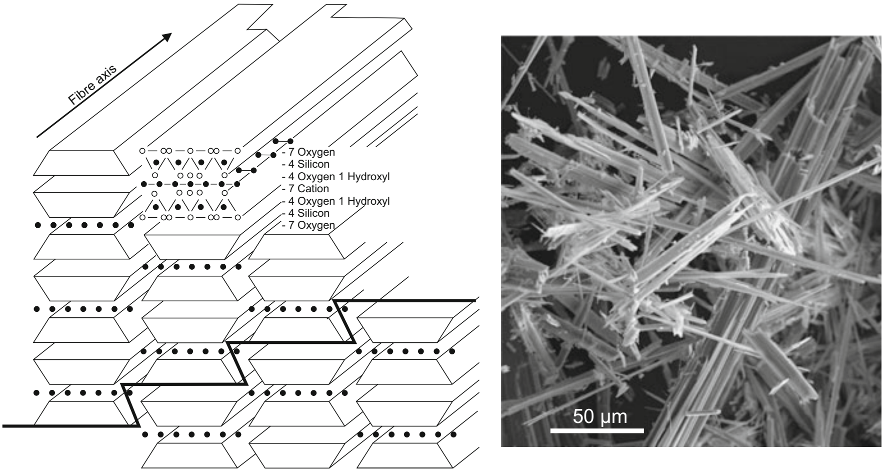


Fig. 12.16 Structure of serpentine with curling of layers (chrysotile asbestos) or alternating orientation (foliated serpentine). (Modified after Rösler 1981)

- chemical resistance (blue asbestos > white asbestos)
- thermal resistance, non-combustibility
- electrical insulator
- high adsorption and absorption capacity.



„Stack of boards“ structure (Amphibole asbestos)

Fig. 12.17 Schematic structure of amphibole asbestos and scanning electron micrograph of the hard and brittle fibres

Table 12.6 Relationship between properties and technical use of asbestos

Property		Technical use
Parallel elementary fibrils	Slidable	Spinnability Friction lining
Large surface	Adsorption	Filter
Cavities Low weight	Fluid intake	Seals Lubricant Insulating material
Stability in longitudinal direction Splicing in tufts	Reinforcing fibres	Asbestos boards (Unsupported)
Melting point >1100 °C	Incombustible	Refractory Friction linings
Chemically resistant	Cement binder	Asbestos cement Insulating material

These specific properties led to a wide range of industrial applications (Table 12.6). Particularly noteworthy is the use in asbestos cement (firmly bound asbestos product) and in asbestos boards (weakly bound asbestos product with 40–97% asbestos). As mentioned at the beginning, the health hazards of asbestos have been known for some time, especially when asbestos fibres are inhaled via the respiratory tract. Asbestos acts biologically in the human organism in two different ways. Firstly, fibrogenic action results in the formation of scar tissue. This disease is known as asbestosis and is now recognised as an occupational disease. In addition, however, a carcinogenic (cancer-causing) effect is also known, which can lead to bronchial carcinoma (lung cancer) or mesothelioma (cancer of the ribs and peritoneum). Because of the different physicochemical properties, the pathogenic potential of amphibole asbestos is much higher than that of crysotile asbestos (Selinus et al. 2013).

The problem in detecting asbestos diseases is that there is a long latency period of 10–40 years between the cause, i.e. inhalation of the asbestos fibres, and the effect in the form of asbestosis or cancer. As a result, it is often difficult to reconstruct the relationships. Although there was a marked decrease in the use of asbestos as early as the 1980s, there are still several 1000 registered deaths every year (Centeno et al. 2010).

The technical implications of the asbestos ban are asbestos substitution and corresponding asbestos remediation measures. A major challenge is the provision of suitable alternative materials that have analogous properties to asbestos fibres. There is a whole range of inorganic and organic, natural and synthetic fibres that have been tested with regard to the substitution of asbestos. Non-fibrous fillers (mica, talc, diatomaceous earth, calcium silicate hydrates) have also been investigated for their suitability.

The basic problem of all organic fibrous materials is their combustibility and low temperature stability. For use in building materials, the decomposition of most substitute materials at pH values above 12 as well as the price and quantity of the required material prevent their use. It has also not yet been clarified whether inorganic fibrous materials in principle have a carcinogenic effect. Nevertheless, there are a number of successful asbestos substitutes. Examples include the construction industry (synthetic fibres), heat protection clothing (SiO_2-ceramic fibres with metallised surface) or friction linings (brake and clutch linings with metal, polyamide, glass, textile or ceramic fibres).

Despite these extensive measures, environmental pollution by asbestos fibres continues to exist due to numerous asbestos emission sources from industry, commerce and end users. For this reason, there are strict legal requirements regarding the monitoring of asbestos contamination and remediation measures. Monitoring measurements can be carried out by air sampling (conimeter, filter method) or directly on corresponding material samples. Due to the complex characteristics of asbestos in terms of size, shape and chemical composition, clear identification can only be achieved by coupling optical and local chemical analysis using a scanning electron microscope.

Asbestos abatement measures are also subject to strict guidelines and must, above all, prevent or minimize the emission of asbestos fibers during reconstruction activities. Basically, there are three possibilities for remedial actions:

- Removal of the asbestos product from the component
- Solidification or coating of the asbestos product
- Spatial separation.

In the case of removal of asbestos parts, these must be collected and transported under controlled conditions. In order to ensure safe disposal or, if necessary, further recycling (e.g. aggregate in road construction), the asbestos product must be processed with the aim of destroying the fibre structure. Various processes are commonly used for this purpose:

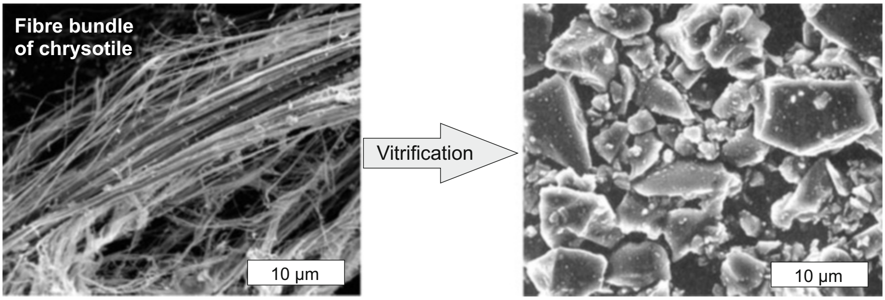


Fig. 12.18 Scanning electron micrographs documenting the destruction of the fibrous structure of asbestos by vitrification

- mechanical comminution processes
- thermal processes (vitrification, Fig. 12.18)
- chemical processes (cracking with hydrofluoric acid)
- bonding in cement and binders.

The consequences of decades of industrial use of asbestos will continue to require intensive efforts and technical developments in the renovation sector in the years to come.

12.4 Natural Stone Weathering and Restoration of Structural Damage

Natural stone is one of the most important mineral raw materials and is quarried and processed annually in quantities of several billion tonnes (Sect. 3.1). In addition to the use of fresh natural stone, the problem of natural stone weathering and the conservation of building fabric encompasses another important field of modern industrial society. Due to a whole range of natural (geogenic) and anthropogenic influences, natural stones are subjected to constant weathering and decomposition (Fig. 12.19). The detection, diagnosis, prevention and repair of this damage are the subject of natural stone weathering and stone conservation (Snethlage 2013).

12.4.1 Weathering and Stone Decay

Natural weathering is a major factor affecting the properties and stability of natural stone material. Both in the raw material in the deposit/quarry and in the installed material, different forms of physical and/or chemical weathering act depending on the specific climatic conditions.

Physical weathering includes all processes that generate stress in the rock structure resulting in fractures and stone decay such as temperature weathering, frost weathering, salt blasting (Fig. 12.20) or physical-biological weathering (e.g. by plant

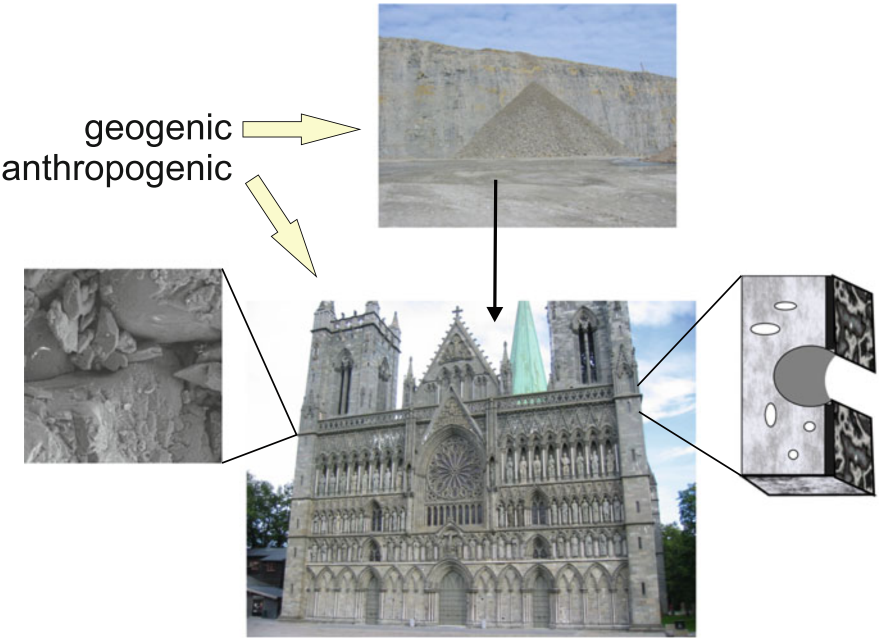


Fig. 12.19 Scheme of natural and anthropogenic influences on natural stone as well as their effects and diagnostics

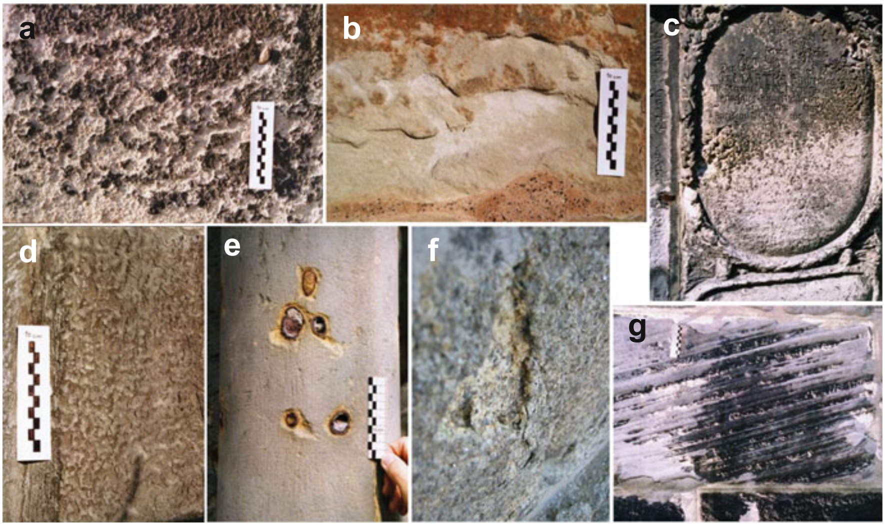


Fig. 12.20 Examples of common structural damage to sandstones and granites. (**a**) Patina sanding; (**b**) Salt formation, scaling; (**c**) Patina/salt formation; (**d**) Crust formation; (**e**) Fe oxidation; (**f**) Salt blasting; (**g**) Weathering parallel to strata

roots). The degree of weathering is decisively influenced by the mineral content and structure of the natural stones. In particular, rocks containing minerals with high volume expansion (e.g. quartz SiO_2) or directional parameters (calcite $CaCO_3$) are susceptible to temperature fluctuations. So, volume expansion of quartz produces a pressure of 54.5 MN m^{-2} when heated by 40°. The effects can be observed, for example, in the phenomenon of onionskin weathering.

In chemical weathering, various factors cause chemical reactions between rock and circulating solutions and gases. These include processes such as solution weathering, oxidation, hydration/hydrolysis, carbonic acid weathering or chemical-biological weathering (Fig. 12.20). Primary components of natural stones such as fine-grained components (e.g. clay minerals), organic matter, sulphur compounds (sulphides, sulphates), salt compounds (e.g. chlorides), oxidic ores or amorphous silica often react very strongly and are therefore harmful components. In addition, chemical weathering is very strongly influenced by climatic conditions (temperature, humidity, biological activity) and environmental pollution. In many cases, physical and chemical weathering overlap.

In addition to external, natural sources of weathering and damage such as moisture, temperature variations and biological activities, anthropogenic factors play an increasing role in stone decay. Such factors include air pollution, changes in groundwater levels, fertilization, fire damage, use of incompatible materials or introduction of harmful substances, and restoration errors. Mineral transformations in the building stone itself or reactions in or with mortar and cement can also cause damage to building materials.

Some of the main factors causing structural damage are summarised below (see also Figs. 12.20 and 12.21):

- Air pollutants – input of particles such as soluble salts (salt input) and soot particles (black crusts and catalytic effect) and gaseous pollutants such as SO_2 and nitrogen oxides (oxidation to sulphuric and nitric acid and destruction of carbonate binders) or hydrocarbons (substrate for microorganisms).
- Chemical dissolution from the surface (especially sulphates, carbonates, salts)
- Crust formation of mainly gypsum + $C_{org.}$ (so-called patina) on carbonate and sulphate rocks by industrial gases and acid rainwater.
- Efflorescence of easily soluble salts
- Sanding on the surface of sedimentary rocks (sandstone), but also granites, due to temperature fluctuations, frost and salt weathering.
- Crumbling decay (sandstones and limestones with irregular clay mineral intercalations) mainly due to frost weathering (cracking and disintegration into blocks)
- Bursting (especially quartz-rich rocks) by frost and temperature weathering but also salt blasting
- Discoloration of the surface due to oxidation processes (especially Fe)
- Rock blasting by biological material (plant roots)
- Cracking due to improper machining or rusting of anchorages.

Fig. 12.21 Example of progressive stone decay at the Trondheim Cathedral, Norway (soapstone)

12.4.2 Damage Analysis

The recording and analysis of damage to natural stones is a complex process (Fig. 12.22). The building fabric must be examined in detail in terms of physical properties, phase analysis and geochemistry in order to assess the state of damage and design the necessary restoration work. In some cases, a regular building stone mapping is carried out on historic buildings in order to record the entirety of the building fabric.

An important factor for the mineralogical-geochemical analysis of building materials is the coupling of phase-analytical and chemical methods. This is to be explained by way of example on the basis of the composition of salt crusts on building materials. According to chemical analyses, the most common salt compounds by far are sulfates and nitrates of Na, K and Ca. Important for the effects on the building substance is the existence of salts of the same cation and anion composition with different water contents. Thus, the change from moist to dry environment leads to the change from hydrous to anhydrous minerals and vice versa. During the formation of hydrous mirabilite ($Na_2SO_4 \cdot 10\ H_2O$) from

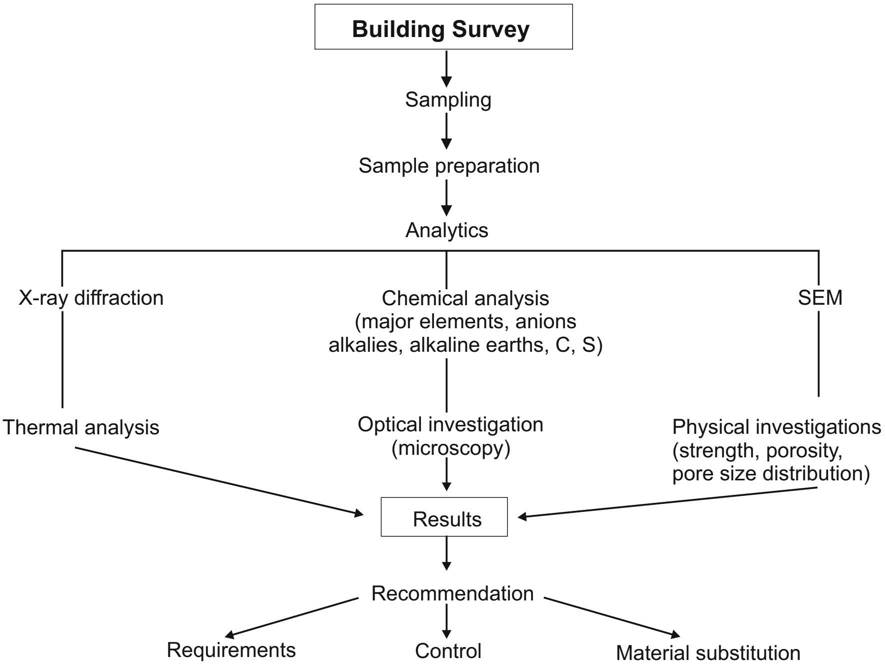


Fig. 12.22 Examination scheme for the evaluation and characterisation of structural damage

anhydrous thenardite (Na_2SO_4), a volume increase of more than four times takes place, resulting in the loosening of the microstructure and thus in rock destruction during continuous recrystallization due to the crystallization pressure:

$$\begin{array}{ccc} Na_2SO_4 & & Na_2SO_4 \cdot 10\,H_2O \\ \textit{Thenardite} & \leftrightarrow & \textit{Mirabilite} \\ 53\ \text{cm}^3 & \text{4.18-fold (pressure)} & 220\ \text{cm}^3 \end{array}$$

For this reason, chemical analyses alone are not sufficient for the characterization of damage states.

12.4.3 Procedures for the Repair of Structural Damage

An important prerequisite for the successful restoration of damage to natural stone materials is the diagnosis of the source(s) of the damage. This knowledge is required to implement appropriate conservation or replacement measures. Some frequently used procedural steps are:

- Preventing the circulation of water, interrupting the capillary action of the plaster.
- Washing out of salts with water, cellulose extraction, “sacrificial plaster”.

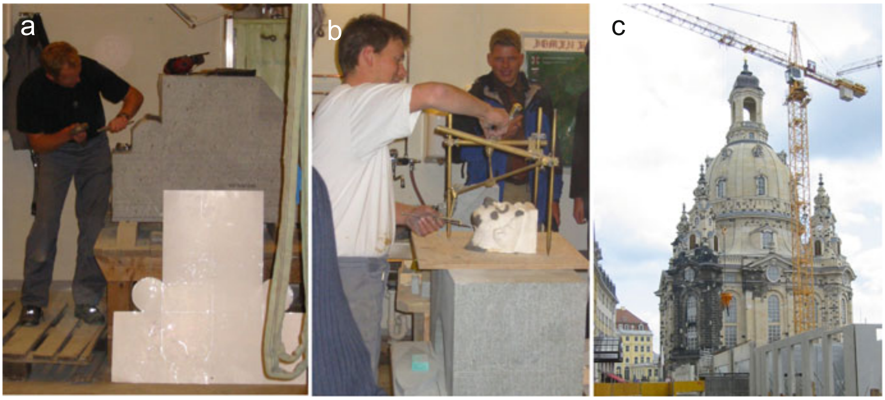


Fig. 12.23 Preparations of natural stone during stone replacement using various templates (**a, b**); optical effects when replacing the original material (Church of our Lady, Dresden/Germany) (**c**)

- Water sprinkling to remove patina (gypsum + $C_{org.}$)
- Prevention of ettringite formation through the use of low-Al cements
- Increased resistance to weathering through hydrophobic treatment (stone conservation)
  - Organics (oils, glues, paraffin, gels)
  - Synthetic resins (epoxy, acrylic), silicone resins
  - Fluates, water glass, silicic acid esters
- Mechanical removal and/or stone replacement (Fig. 12.23)

When replacing natural stone material or replacing missing parts, the aim is to use original material as a replacement. This is to ensure that both the physical (strength) and optical properties of the replacement material correspond to the original natural stone. Particularly in the case of old buildings, this often requires detailed research into the historical natural stone sources.

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Biomineralogy: Biomaterials

13

The subject of biomineralogy is the *in vivo* formation of inorganic minerals by living organisms. Biomineralogy thus acts as a link between mineralogy, biology, palaeontology, medicine, physics and chemistry (Fig. 13.1).

Based on the definition of biomineralogy, biominerals include all mineral components that are formed by the activity of various life forms (Lowenstam and Weiner 1989). Biomineralization has been known for about 2 billion years, when in vivo formation of minerals began with the appearance of living organisms on Earth. Early witnesses of biomineralization are considered to be terrestrial magnetofossils, which dominated these mineralization processes from this time until about 550 million years ago (Cambrian), mainly by the crystallization of magnetite (Fe_3O_4). Due to the explosive spread of various life forms from the Cambrian onwards, the formation of calcium-bearing biominerals such as carbonates and phosphates subsequently came to the fore (Dove et al. 2003).

The best way to understand the basic features of biomineralization is to compare the vital chemical elements with the main elements in biomineralization processes:

- vital chemical elements: C, O, H, **N,** S, Mg, **K,** P, Ca, Fe
- chemical elements in biominerals: C, O, H, **Si,** S, Mg, **Mn,** P, Ca, Fe

From this comparison it is obvious that, with the exception of Si and Mn, the main elements in biominerals are also essential elements of life forms. In general, biominerals occur in all mineral classes and can be classified according to their chemical composition. In quantitative comparison, Ca^{2+} represents the most important cation in biominerals with about 50%. The compounds are dominated by carbonates and phosphates, besides silicates ($SiO_2 \cdot n\ H_2O$) and oxides (Fe-oxides) as well as sulfides and sulfates in surficial environments (Kohnhauser 2007).

The biochemical processes leading to mineral formation are usually very complex and depend very much on the geochemical environment. Thus, the chemical environment, age of the organisms or trace elements can modify the structure and/or

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https://doi.org/10.1007/978-3-662-64867-4_13

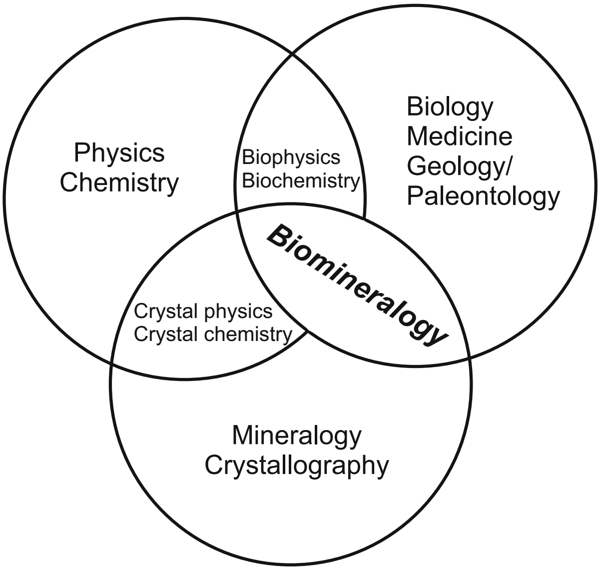


Fig. 13.1 Position of biomineralogy in the natural sciences

morphology of the biominerals. A remarkable feature of many biomineralization processes is also the co-occurrence of oxidizing and reducing organisms.

The importance of biomineralization for organisms becomes clear when the various functions are listed:

- Mechanical strength
- Stabilization of the structure (skeleton)
- Protective function
- Shredding tool
- Magnetic, optical and gravity sensors
- Storage medium

13.1 Principles of Biomineralization

In general, biomineralization occurs in "isolated" sites where biological activity occurs. In terms of the organism, mineral formation can occur epicellularly (on the cell wall), intercellularly (in intercellular spaces), intracellularly (in specific areas within the cell) or extracellularly (on/in a macromolecular matrix).

A prerequisite for mineral formation is mass transport, which ultimately leads to the supersaturation of a component and thus to mineralization. In general, a distinction can be made between biologically induced and biologically controlled mineralization (Fig. 13.2).

While biologically controlled mineralization involves control and regulation of mineral deposition (Fig. 13.3), in the case of biologically induced mineralization,

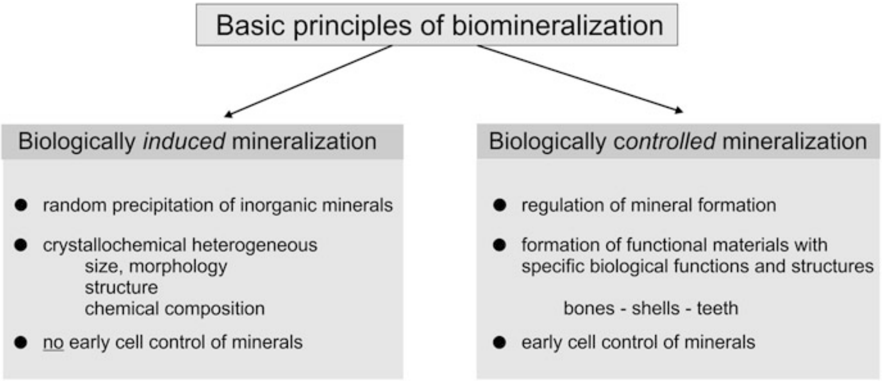


Fig. 13.2 Basic principles of biomineralization

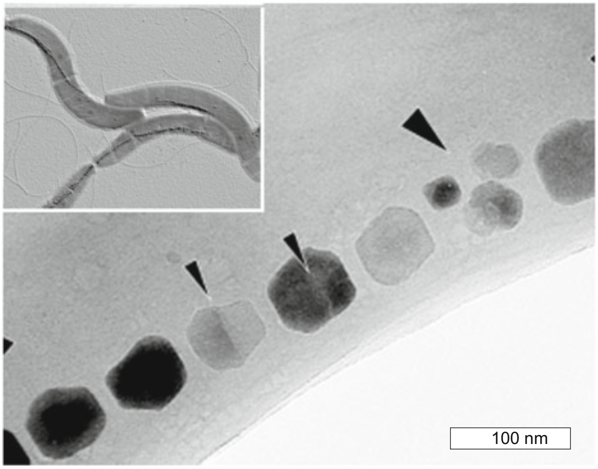


Fig. 13.3 Biologically controlled (intracellular) mineralization of magnetite crystals in the magnetosome of a bacterium. (Modified after Mann 2001)

inorganic mineral deposition is only triggered by organic processes (e.g. sulfate-reducing bacteria in sulfide deposits).

In biologically controlled mineralization, a complex of control mechanisms ensures the regulation of the crystallization processes:

- Chemistry: solubility, supersaturation, nucleation and growth, regulation of ion transport, molecular inhibitors/promoters
- Space: supramolecular preorganization of organic molecules, the biological environment determines positions for controlled chemistry
- Structure: nucleation of crystal faces by molecular recognition on the surface of an organic matrix (template)
- Morphology: pattern recognition, vectorial growth, minerals with life-like forms *(morphogenesis)*

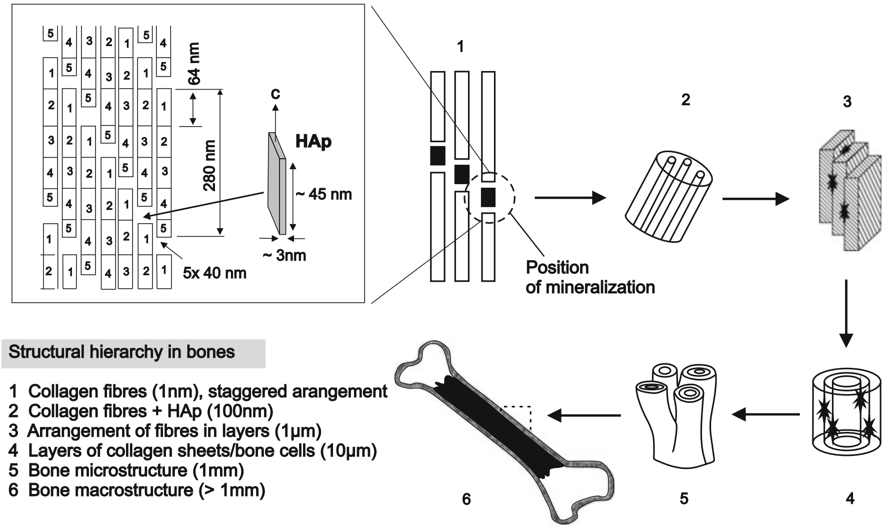


Fig. 13.4 Example of structural hierarchy in *biomineral tectonics* for bones. (Modified after Mann 2001)

- Construction: process sequence on several length scales (fractals) *(biomineral tectonics)*

The mechanisms of biomineralization are controlled by biopolymers as matrix, which influence the hierarchical structure of the organic-inorganic composite structure of the biomaterial. The resulting complex structures exhibit a high degree of order over several orders of magnitude. Figure 13.4 illustrates the complex linkage of organic and inorganic structures exemplarily for the mineralization of hydroxyapatite in bone.

13.2 Natural Biomineral Systems

13.2.1 Bacterial Formation of Fe/Mn Minerals

Iron, is the fourth most abundant chemical element in the Earth's crust (5 mass-%) and is also a very important element for all organisms. Iron-processing microorganisms are among the oldest forms of life realizing a number of mineralization and demineralization processes. These processes in particular include sulfate reduction and oxidation of sulfide minerals and associated Fe/Mn oxidation and reduction, as well as biologically induced mineralization and dissolution of magnetite. Typical for the bacterial formation of Fe/Mn minerals is especially the co-occurrence of reducing and oxidizing bacteria.

Table 13.1 Compilation of some biologically induced iron and manganese minerals

Chemical formula	Mineral name
$Fe(OH)_3$	Iron hydroxide
α-FeO(OH)	Goethite
γ-FeO(OH)	Lepidocrocite
$5\ Fe_2O_3 \cdot 9\ H_2O$	Ferrihydrite
Fe_3O_4	Magnetite
γ-Fe_2O_3	Maghemite
$FeCO_3$	Siderite
$Fe_3(PO_4)_2 \cdot 2\ H_2O$	Vivianite
FeS (tetragonal)	Mackinawite
Fe_3S_4	Greigite
$Fe_{1-x}S$	Pyrrhotine
FeS_2	Pyrite
$KFe_3(SO_4)_2(OH)_6$	Jarosite
$Fe_8O_8SO_4(OH)_6$	Schwertmannite
$FeSO_4 \cdot 7\ H_2O$	Melanterite
$MnCO_3$	Rodochrosite
$Mn_4O_7 \cdot H_2O$	Todorocite
$Na_4Mn_{14}O_{27} \cdot 9\ H_2O$	Birnessite

Because of the large number of processes occurring in different geochemical environments, it is not surprising that there is a large number of Fe and Mn biominerals (Table 13.1).

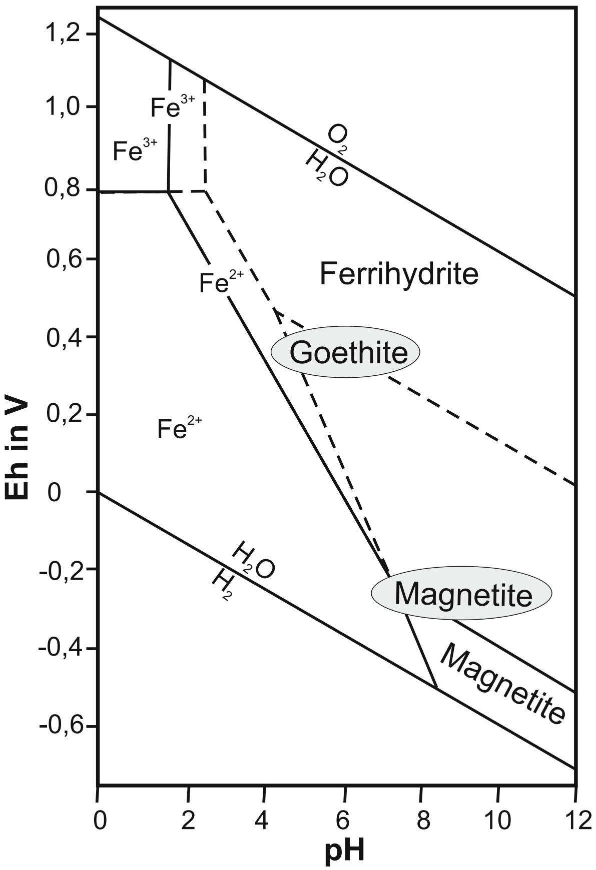
Due to the prevailing Eh/pH conditions in the surface region, goethite and magnetite in particular occur as Fe biominerals (Fig. 13.5). Under anaerobic conditions, no oxidation of iron is possible without bacterial processes.

An example of biologically controlled intracellular Fe mineralization is the formation of magnetic minerals such as magnetite $Fe^{II}\ Fe_2^{III}\ O_4$ or greigite $Fe^{II}\ Fe_2^{III}\ S_4$ at the nanoscale (35–120 nm) by magnetotactic bacteria. These bacteria form different morphologies depending on species and conditions and are mainly active in the transitional oxidizing/reducing zone in marine, brackish and fresh water. The magnetic nanominerals are arranged in chains to generate a dipole moment. By aligning with the earth's magnetic field, orientation is thus possible.

Extracellular Fe biomineralization occurs much more frequently in nature. Thus, the formation of the giant Precambrian iron ore deposits (*banded iron formation* – BIF) occurred through bacterial-triggered sedimentary accumulation. Biomineral precipitation is initiated by the formation of hydrocarbon/protein biofilms. Various chemolithoautotrophic microorganisms (e.g. *Geobacter metalloreducens*) extract nutrients such as iron using C or CO_2 as energy and carbon sources. Such activities are detectable both recently and from fossil biosignatures in older geological formations (Fig. 13.6).

The formation of extremely fine-grained (<0.1–100 nm) amorphous Fe oxihydroxides in rust is also controlled by organic-inorganic processes. The fineness

Fig. 13.5 Eh/pH diagram for the Fe-O-OH system at 25 °C. (Modified after Skinner and Fitzpatrick 1992)



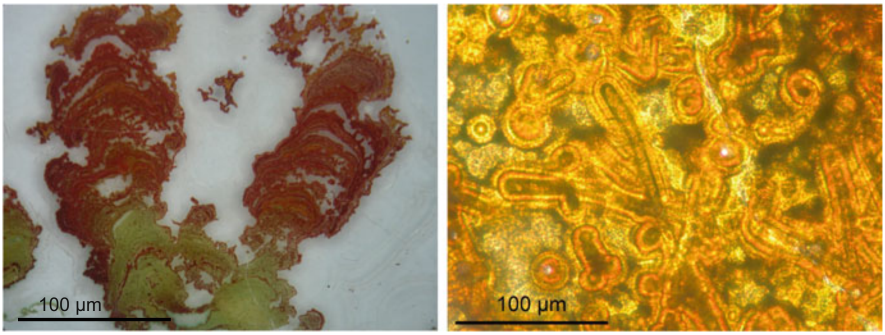


Fig. 13.6 Stromatolitic accumulated hematite biofilms (*left*) and filamentous biopseudomorphs after Fe-oxidizing bacteria in a cryptocrystalline SiO_2 matrix (*right*) from biomineralizations (Matra Mountains, Hungary)

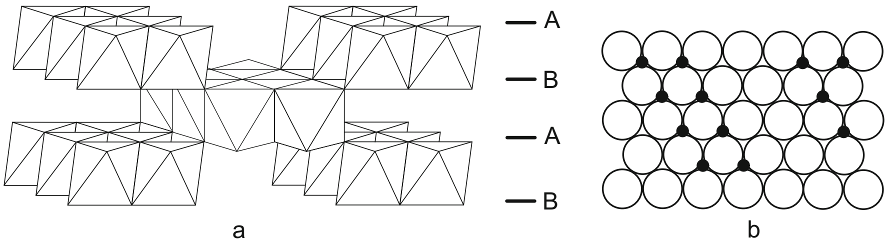


Fig. 13.7 (**a**) Schematic structure of goethite (α-FeOOH) with arrangement of octahedra; (**b**) incorporation of foreign ions (small circles) on interstitial sites. (Modified after Rösler 1981)

and microstructure with interstitial positions (Fig. 13.7) cause an extremely large surface area, which results in very good adsorption properties and the incorporation of foreign elements. This makes the material suitable as a filter material for ions and substances in nature and technology. Further industrial applications of bioactivities arise from the processing ("deferrization") of certain raw materials by microbial treatment. Iron crusts on quartz grains in high-purity quartz sands, for example, can be removed by the use of *Thiobacillus ferrooxydans*.

13.2.2 Carbonate Biominerals

Main minerals of biological carbonate formation are trigonal $CaCO_3$ (calcite) and rhombic $CaCO_3$ (aragonite). In addition, hexagonal $CaCO_3$ (vaterite) and amorphous $CaCO_3 \cdot n\ H_2O$ also exist. Although the calcium carbonates often contain small amounts of magnesium (Mg-calcite) and/or strotium, no magnesite or dolomite is primarily formed.

Carbonate biomineralizations have been occurring for about 550 million years and are mainly found in aqueous environments at pH 7–8 and an appropriate supply of calcium, magnesium and CO_2/HCO_3^-. Several hundred different biological forms are known in oceans, sediments and lakes that form extracellular, intracellular and intercellular $CaCO_3$. It is interesting to note that, on the one hand, different $CaCO_3$ modifications occur in different organs or growth periods and, on the other hand, milieu-dependent factors (*pTx* – pressure - temperature – chemical supply) can influence growth and morphology. In part, there is also the possibility of remineralization of destructed areas.

The greatest diversity of carbonate biomineralization is found in the sea. Biocarbonate is produced in various organs of multicellular organisms such as molluscs, oysters and gastropods. In addition, hard parts such as carapaces, shells or skeletons in reef-building corals, gastropods and bivalves are formed from calcite or aragonite. Also thousands of species of foraminifera form hard parts of calcite, aragonite (and opal) for brace and protection.

However, oceanic carbonate sedimentation and global limestone deposition are mainly regulated by algae or cyanobacteria. These processes can lead to large-scale

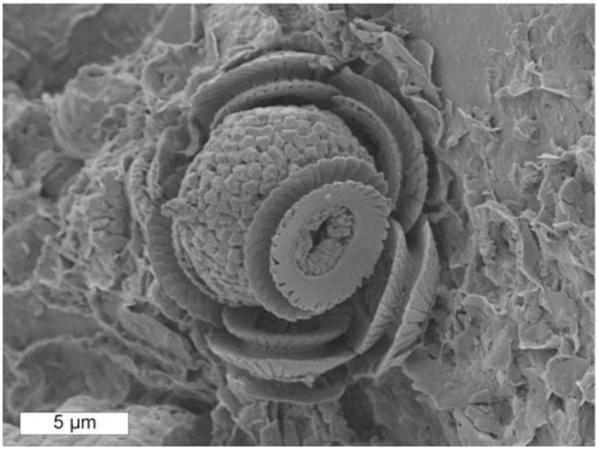


Fig. 13.8 Scanning electron micrograph of coccoliths from the Neogene of Sardinia. (Photo: O. Elicki, TU Bergakademie Freiberg with kind permission)

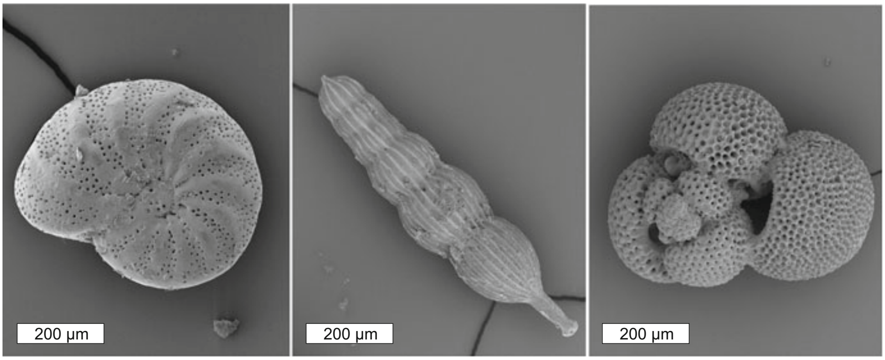


Fig. 13.9 Scanning electron micrographs of foraminifera from the Neogene of Sardinia. (Photos: O. Elicki, TU Bergakademie Freiberg with kind permission)

biogenic rock formation. For example, coccoliths, which are calcite platelets of max. 10 µm in size that form the shells of calcareous algae, have existed for many millions of years (Fig. 13.8). The carbonate rock formed from mass deposits of these shells is the eponym for the geological period of the Cretaceous. The hard parts of foraminifera can also result in massive calcareous deposits (Fig. 13.9).

$CaCO_3$ biominerals also play a major role in terrestrial organisms and mammals. Eggshells, for example, are made of calcium carbonate (Fig. 13.10), with eggshells of birds and crocodiles being predominantly calcite, while turtle eggs or the shells of snails are primarily aragonite.

$CaCO_3$ crystals play a certain special role in the organ of equilibrium of various living beings. On sensory cells in the human inner ear, for example, calcite single crystals of approx. 0.01 mm in size are arranged in a gelatinous layer, whose orientation changes with movement and triggers a corresponding signal to the brain. A similar mode of operation is found in the organs of equilibrium of various

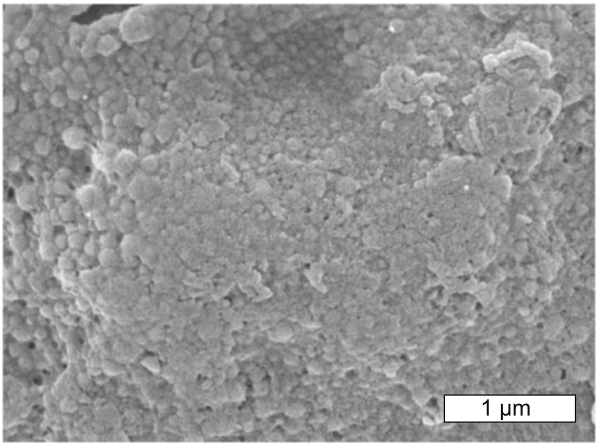


Fig. 13.10 Scanning electron micrographs of the shell of a chicken egg with oriented calcite crystals

animals, which are equipped with crystals of calcite, aragonite, vaterite, monohydrocalcite ($CaCO_3 \cdot H_2O$) or apatite.

13.2.3 Phosphates as Biominerals

In the system $CaO\text{-}P_2O_5\text{-}H_2O$ a number of compounds occur, of which in particular the hydroxyapatite $Ca_5\ [OH/(PO_4)_{3]}$, the octacalcium phosphate $Ca_8H_2[PO_4]_6 \cdot 5\ H_2O$ and amorphous calcium phosphate compounds occur as biominerals (Kohn et al. 2002). The main mineral is biogenically formed hydroxyapatite, which has a very complex composition compared to geogenic hydroxyapatite and shows variable substitution possibilities depending on its position in the biosystem (Elliot 1994):

$$\text{Bioapatite}\ (\mathbf{Ca}, \text{Na}, \text{Mg}, \text{Sr}, \text{Pb}, \ldots)_{10}(\mathbf{PO_4}, \text{CO}_3, \text{SO}_4, \ldots)_6(\mathbf{OH}, \text{F}, \text{Cl}, \text{CO}_3)_2$$

The biogenic hydroxyapatite is usually very fine-grained (<100 nm) and crystallizes mostly hexagonal, sometimes also monoclinic. A special feature is also the incorporation of the CO_3-group on two structural positions.

In nature, various apatite-mineralized tissues occur in vertebrates with variations in mineral content and composition. Tooth enamel is the most highly mineralized tissue in vertebrates, containing virtually no living cells in adult organisms. Rodents are an exception, where there is constant “regrowth”. Sharks also have several rows of teeth that can quickly replace themselves when destroyed or worn.

Bones, on the other hand, represent a complicated tissue biomineralization system. They can constantly reform and change depending on age, nutrition, stress, environment, etc.. There is a complex interplay between bone-forming (osteoblasts) and bone-resorbing (osteoclasts) cells. The more than 200 bones in humans vary strongly depending on age (from fetus to death) and position in the skeleton. Each bone is more or less its own variable organ (Sect. 13.3).

13.2.4 SiO_2 Formation by Organisms

The geochemical cycles of carbon and silicon are closely linked in the geological time frame, and there are immense biogenic material movements and accumulations of Si. Silicification is found across the entire biological system in bacteria, protozoa, invertebrates, vertebrates and plants. Amorphous SiO_2 almost exclusively occurs as a biomineralization product (Fig. 13.11, Table 13.2). In some cases, sedimentation and diagenesis of SiO_2 constituents of dead marine organisms such as radiolarians or diatoms can lead to the formation of massive deposits of chert.

The mineralization processes occur intracellularly and extracellularly in different biochemical environments together with lipids, proteins and hydrocarbons. The decisive factors are complex cellular processes that have not yet been fully elucidated in detail. The formation usually occurs from undersaturated solutions at more or less neutral pH and temperatures in the range between 4 and 40 °C. The starting point is usually monomeric silicic acid ($Si(OH)_4$), which is stable for long periods at concentrations below 100 ppm in water at 25 °C. The polymerization of monomers

$$Si(OH)_4 + Si(OH)_4 \leftrightarrow (HO)_3Si–O–Si(OH)_3 + H_2O$$

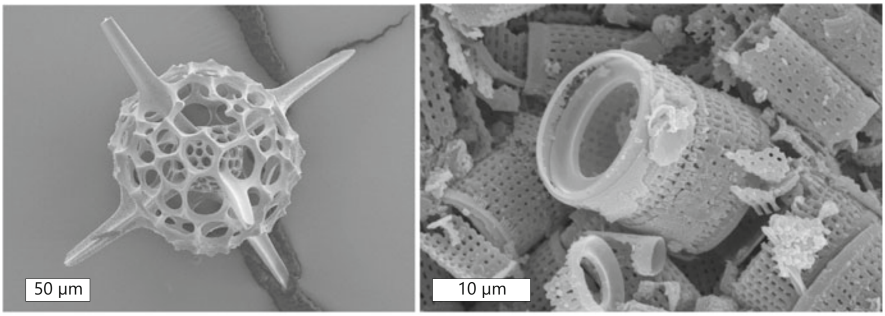


Fig. 13.11 SEM micrographs of SiO_2-biomineralization (opal) in (**a**) radiolarians (Eocene of Barbados) and (**b**) diatoms (Oligocene of Baruther Maar). (Photos: O. Elicki, TU Bergakademie Freiberg with kind permission)

Table 13.2 Important SiO_2-biomineralizations and their functions

Mineralization	Organism	Location	Function
Amorphous $SiO_2 \cdot n\ H_2O$	Diatoms	Cell wall	Exoskeleton
	Radiolaria	Cellular	Microskeleton
	Flagellates – Choanomonada	Cellular	Protection
	Chrysophytes – Golden-brown algae	Cell wall	Protection
	Limpets	Teeth	Shredding
	Plants	Leaves	Stabilization

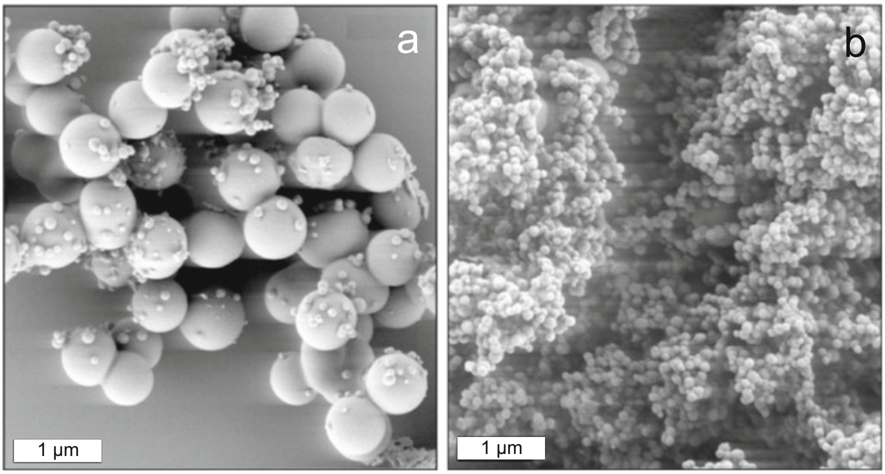


Fig. 13.12 Formation of different SiO_2 structures in the presence of low molecular weight (left) or higher molecular weight (right) polyamines. (From Kröger et al. (2000) with kind permission)

results in stable nuclei of critical size, which can form spherical particles by further growth.

The aggregation of the particles via organic compounds as matrix finally results in the formation of chains and three-dimensional structures. The influence of the organic matrix on the structure of SiO_2-mineralization can be seen in Fig. 13.12.

The interaction of organic and inorganic components can also be clearly demonstrated in SiO_2 accumulation in various plants. Here, silification occurs intracellularly and extracellularly in different plant parts and serves mainly to increase supporting and stabilizing functions. Si uptake occurs via nutrient solutions from the soil, and transport can be realized passively with the transpiration current or bound to organic compounds. The deposited amorphous SiO_2 (so-called phytoliths) is found on cell walls and cell membranes or in intracellular spaces of plant root and shoot walls. The most silicified outer side of the epidermis can reach Mohs hardness up to 4.

The strongest silicon accumulators in the plant world are the horsetails, which can reach up to 70 mass-% SiO_2 in the ash. In addition, various ferns and orchids accumulate significant amounts of SiO_2 in the organic matrix. Of particular interest are the high SiO_2 contents (up to 19%) in rice husks. Rice husks are a sought-after raw material for the thermal production of fine-grained SiC powder for the ceramics industry (Chap. 9).

Completely different biomineralization processes occur at high temperatures in hydrothermal processes. Modern investigations of fossil and active hydrothermal systems have provided evidence that microorganisms colonize hydrothermal vents in both terrestrial and deep-sea environments. These findings also led to new theories regarding the origin of life on Earth. Under such extreme conditions, there is a close

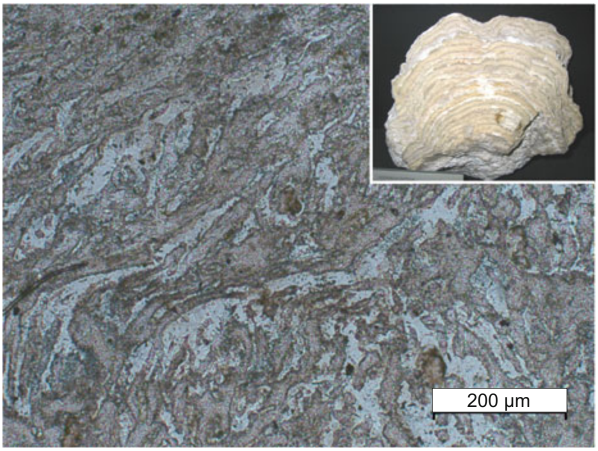


Fig. 13.13 Biogenic-abiogenic formed siliceous sinter, Yellowstone National Park (USA)

interplay of microbial and geochemical activities that create basic building blocks for the synthesis of organic molecules and fundamental metabolic processes. On the other hand, complex microbial surface formations can also support the precipitation of SiO_2, iron oxides or calcite.

Nearly all microfossils found in hydrothermal systems are filamentous. These microorganisms are thermophilic (i.e. the organisms grow best at temperatures >45 °C) and derive their energy from the oxidation of inorganic components (chemolithoautotrophic). Biogenic silicification in thermal springs of the Kenya Rift has been shown to occur at temperatures above 90 °C. Hyperthermophilic and/or thermoacidophilic bacteria (e.g. cyanobacteria of *Calothrix* and *Fischerella* sp.) or thermophilic algae (e.g. *Cyanidium caldarium*) survive under these extreme conditions and accumulate silica. Biosignatures of such microbial activities are already detectable in very old rocks such as the Warrawoona Formation in Western Australia (3.0–3.5 billion years), but can also be observed in recent hydrothermal systems of the Yellowstone National Park (USA), in New Zealand, Japan, Iceland, or at the ocean floor (Fig. 13.13).

In general, each occurrence can produce different biostructures (e.g. geyserite, needles, stalky or layered microstromatolites or microbial coatings) depending on the microbial association and varying hydrodynamic, geochemical and temperature conditions. The occurrence of geyserite demonstrates that microscopic biofilms and microbial layers can be involved in the formation of centimeter-thick siliceous sinter structures (Fig. 13.13). A network of bacterial cells is thought to promote the precipitation of silica by acting as nuclei for crystallite formation.

Cyclic layer sequences of biogenic and abiogenic SiO_2 can be explained by changing microbial activities. In general, the main part of silicification is thought to occur very rapidly (about 0.45–0.9 mm a^{-1}), probably while the cells are still alive. A possible process for the formation of silica can be attributed to the direct interaction of dissolved silicate anions with positively charged groups on the peptide chains (e.g. amino groups) (Belton et al. 2004).

13.3 Minerals in the Human Body

Inorganic (and organic) mineral formation is essential for human life. In particular, the bones of the skeleton and the teeth are indispensable components of the human body. The range of biominerals and pathological crystalline compounds is enormous (Table 13.3).

The most important compounds are various calcium phosphates, in particular bioapatite (Sect. 13.2.3). The basic substance of human bones consists of two thirds of fine-grained apatite ($Ca_{10-x}H_x(PO_4,CO_3)_6(OH,CO_3)_{2-x}$), octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5\ H_2O$) and brushite ($CaHPO_4 \cdot 2\ H_2O$). The remainder is made up of about one-third organic collagen. Bone formation itself occurs from dissolved phosphate in the blood serum by osteoblasts.

Two basic types of bone occur in the human body. Compact cortical bone tissue is densely mineralized with bioapatite. In contrast, trabecular bone tissue has a relatively open, porous structure with collagen and blood cells in the cavities.

Human teeth are also essentially composed of fine-grained hydroxyapatite, with enamel being the most mineralized (Fig. 13.14). Dental cementum has a similar

Table 13.3 Biominerals and pathological crystalline compounds in the human body

Chemical formula	Name
$Ca_5(PO_4)_3(OH)$	Hydroxyapatite
$Ca_5(PO_4)_3F$	Fluorapatite
$Ca_{10-y}Na_y(PO_4)_{6-x}(CO_3)_x(OH)_{2-x}$	Bioapatite
$CaHPO_4$	Monetit
$CaHPO_4–2\ H_2O$	Brushite
$Ca_8H_2(PO_4)_6 \cdot 5\ H_2O$	Octacalcium phosphate
$Ca_3(PO_4)_2$	Tricalcium phosphate
$Ca_9(PO_4)_6\ Mg(PO_3OH)$	Whitlockite
$Mg_3(PO_4)_2 \cdot 8\ H_2O$	Bobierrite (magnesium phosphate octahydrate)
$MgHPO_4$	Magnesium hydrogen phosphate
$Mg_2(NH_4)_2(PO_4)_2 \cdot 6\ H_2O$	Magnesium ammonium phosphate hexahydrate
$MgNH_4(PO_4) \cdot 6\ H_2O$	Struvite
$Ca_2P_2O_7 \cdot 2\ H_2O$	Calcium diphosphate dihydrate
$CaCO_3$	Calcite
$CaCO_3 \cdot H_2O$	Monohydrocalcite
$CaC_5H_3N_4O_3 \cdot H_2O$	Monosodium urate monohydrate
$CaC_2O_4 \cdot H_2O$	Whewellite
$CaC_2O_4 \cdot 2\ H_2O$	Weddellite
$C_5H_4N_4O_3$	Uricite
$C_4H_6(NH_2)_2S_2(COOH)_2$	Cystine

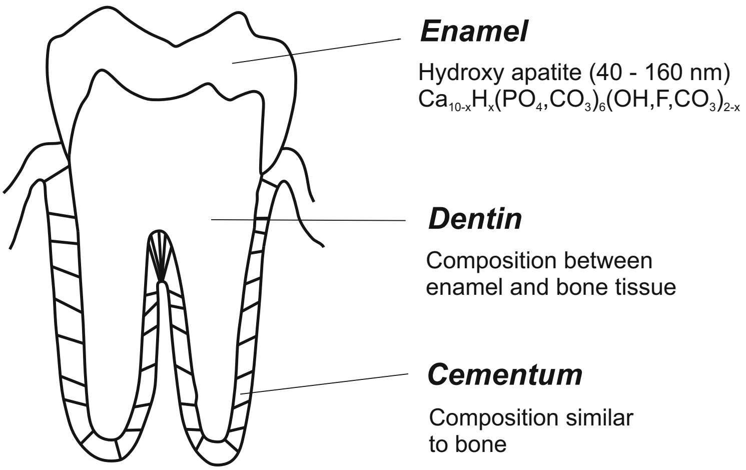


Fig. 13.14 Schematic structure of the human tooth

composition to bone substance, while the composition of dentin lies between those of enamel and dental cementum.

Carbonates also play an important role in the human body. The human ear, for example, is not only a complex hearing organ, but also responsible for the control of balance. In the sensory cells in the inner ear, calcite single crystals *(Otoconia* or *Statoconia) of* approx. 0.01 mm in size are stored in a gelatinous layer in an oriented manner. When movement occurs, the orientation of these crystals changes and a signal is sent to the brain.

Minerals formed by disease in various organs can significantly restrict vital functions and cause painful changes. Urinary stones, bladder stones and kidney stones are deposits that are formed mainly by an excess of certain substances or malfunctions. The most important mineral components are oxalates (whewellite, weddelite), phosphates (hydroxyapatite, brushite, struvite) and organic compounds (uric acid, see Table 13.3). The symptoms of gout are caused by deposits of sharp-edged uric acid crystals in the joints. Gallstones are essentially composed of a mixture of cholesterol and $CaCO_3$.

13.4 Technical Biomaterials

Based on natural biominerals, biomaterials are now used in many areas of medicine and medical technology. A biomaterial is understood to be a non-viable material that is used as a medical assembly for interaction with/in biological systems (Williams 1987).

The most important prerequisite for the use of technical biomaterials is the compatibility between the technical and the biological system, so-called biocompatibility. This means that the material must not be toxic, must not cause rejection

Table 13.4 Examples of biomaterials and their applications

Biocompatibility	Material	Application examples
Biotolerant	Stainless steel	Bone screws and plates
Biotolerant	Bone cement PMMA (polyethyl methacrylate)	Fixation of implants
Bioinert	Pure titanium (cp titanium)	Acetabular cup for hip prostheses
Bioinert	Titanium alloys (Ti_6Al_4V)	Shanks for hip endoprostheses Knee endoprostheses
Bioinert	Cobalt alloys (CoCrMo, CoNiCrMo)	Ball heads for hip prostheses Knee endoprostheses, screws, plates
Bioinert	Alumina ceramic	Ball heads/cups of hip prostheses
Bioinert	Zirconium oxide ceramic	Ball heads for hip prostheses
Bioinert	Polyethylene	Articular sockets of knee/hip prostheses
Bioactive	Hydroxyapatite (HAp)	Bone replacement, implant coating
Bioactive	Tetracalcium phosphate (TTCP)	Dental cement
Bioactive	Tricalcium phosphate (TCP)	Bone substitute, non-load bearing
Bioactive	Bioglass	Bone substitute, non-load bearing

Data according to Willmann (1999)

reactions and/or allergies, and must not cause inflammations or the development of cancer cells in the long term (Yaszemski et al. 2004).

In the context of biocompatibility, different classes of materials are distinguished:

- Biotolerant: release of substances in non-toxic concentrations that can lead to encapsulation in connective tissue or weak foreign body reactions (distance osteogenesis)
- Bioinert: no release of toxic substances, no positive interaction with the tissue. No formation of connective tissue; the bone tissue is formed in the immediate vicinity of the implant (contact osteogenesis).
- Bioactive: positive interaction with tissue and, as a consequence, bonding or adhesion of bone along the interface between implant and recipient tissue (composite osteogenesis)

Biomaterials used today (e.g. bone replacement implants) come from different material classes (polymers, ceramics, metals; Table 13.4). However, the structure of these materials often does not reflect the structure of natural biominerals.

Hip endoprostheses play a dominant role among implant materials. Approximately one million hip implants are surgically implanted worldwide each year. The prosthesis essentially consists of the shank, the acetabular cup and the ball head (Fig. 13.15).

Due to their mechanical properties, titanium alloys (e.g. Ti_6Al_4V) are mainly used as the material for the shank. In addition to a high mechanical load capacity, the acetabular cup and ball head must also have very good sliding properties. For this reason, Al_2O_3- or Al_2O_3/ZrO_2 mixed ceramics with up to 10% Y-stabilized zirconium oxide are preferred. Additions of strontium aluminate improve the elastic

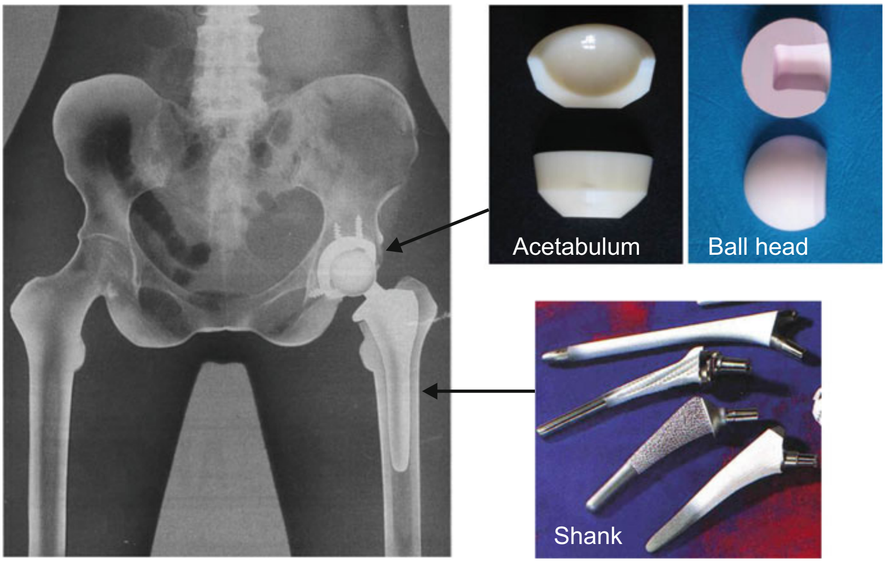
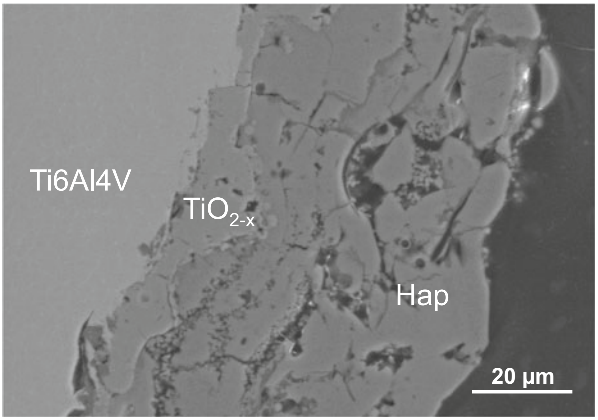


Fig. 13.15 Overview of the use of hip endoprostheses

Fig. 13.16 SEM image of the cross-section through a hip implant with titanium alloy (shank), TiO_2-adhesion promoter layer and hydroxyapatite layer (Hap)



modulus and crack resistance. To improve the bond between the implant and the bone tissue, the surfaces of the titanium shanks can be coated with hydroxyapatite, which is very similar in composition to the bone material (Fig. 13.16).

In order to improve the functionality of biomaterials, modern materials research is constantly developing new biomaterials with better medical compatibility and optimal usage properties. Knowledge of the natural processes of biomineralization is a decisive prerequisite for these developments.

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From Ore to Steel

14

The basic principle of a smelting process is the reduction of ores or starting materials to metal. The aim is to form two immiscible melts – the slag melt and the metal melt. Due to density and viscosity, the slag melt floats on the molten metal. Most of the components that are undesirable in the molten metal collect in the slag melt. Therefore, it is essential not only to adjust the reduction to the metal by means of temperature and redox state, but also to pay special attention to the slag composition.
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Due to the reduction of the iron ores by means of carbon, about 4.5 mass-% of carbon dissolves in the molten pig iron. This leads to the crystallization of iron carbide next to the metallic iron during the solidification of this metal melt, which causes a high brittleness of this so-called cast iron. It is not forgeable. Therefore, in the steelmaking process, the carbon content is significantly reduced to about 2 mass-% and the desired alloying elements are added to the iron to eliminate the brittleness and achieve the desired steel properties.

14.1 From Ore to Pig Iron

14.1.1 Iron Ores and Precursor Products

Three groups of materials are needed to smelt ore into iron:

- Iron carriers such as iron ores or scrap metal
- Fuels and reducing agents such as coke, coal, oil and gas
- Aggregates (slag formers) such as sand, lime and dolomite.

Iron ores are the most important iron carriers, and these must be reduced to metallic iron in the blast furnace process. In nature, native iron occurs in only two cases: on the one hand, as iron or stony iron meteorites, and on the other hand, in the rare case

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that a magmatic melt clearly containing iron penetrates a coal seam in the course of volcanic activity and the iron is partially reduced as a result. Both cases are extremely rare and irrelevant in practice because of the small amount of iron present. The occurrence of metallic iron in the Earth's core is also of more academic interest. The iron ores are divided into four groups:

- oxidic or hydroxidic ores, e.g. magnetite, hematite, limonite
- sulphide ores, e.g. pyrite
- carbonatic ores, e.g. siderite
- siliceous ores, e.g. olivine, pyroxenes

The silicate iron ores are negligible and of no economic interest in iron smelting. Only olivine is used in small quantities as a sintering aid in the production of iron ore pellets. Carbonate ores such as siderite or concretions such as earth iron were historically important as iron ores due to their near-surface occurrence (smelting in smelting furnaces since the Iron Age), but are no longer used now as raw materials due to the low occurrence compared to oxide ores. Sulphide ores are also no longer used directly; they are used in the chemical industry, e.g. for the production of sulphuric acid. The resulting tailings, which consist of fine-grained iron oxides, are then used as raw material for the production of iron ore sinter. The main obstacle to the use of sulphidic ores is their high S content, which has a negative impact on the quality of steel.

The main iron ores are magnetite, hematite and limonite. Since these are often intergrown with different proportions of gangue and the iron content of limonite is quite low, processing is carried out after mining from the respective deposit. In the process, pellets are produced which are easier and cheaper to transport due to the separation of the gangue and the increase in iron content, and which have advantages for use in the blast furnace.

All products fed into the blast furnace must be lumpy so that the reduction gases can flow relatively freely upwards from the lower area of the blast furnace. It is therefore necessary to pre-treat fine ores into "lumpy material". This is done, on the one hand, at the deposit after mining during the production of pellets and before transport to the blast furnace, and, on the other hand, in the smelter in sintering plants.

For the production of iron ore pellets, the already rich iron ore is pre-processed. Crushing and coarse grinding of the ore enables sorting into ore and gangue. This fine ore is rolled with clay, sand, lime and olivine in a moist state on a pelletizing machine to form pellets, which are then fired in large shaft, grate or rotary kilns at approx. 1100–1200 °C. Depending on the degree of reduction, magnetite, hematite, spinels, olivine and glass phase are formed. At first glance, the formation of hematite on the production route to metallic iron is counterproductive, but the small amount of hematite formed and the energy and economic savings in transporting these highly ferrous precursors of the blast furnace process far compensate for this. The pellets are about the size of a hazelnut.

For the production of iron ore sinter, fine ores, fine sinter, smelter recyclables, coke, lime, possibly dolomite and sand are mixed in suitable proportions and piled up about 20 cm high on approx. 4 m wide perforated steel conveyor belts. This passes through a burner section which ignites the mixture due to the coke content and starts the sintering process. Magnetite, various calcium ferrite phases, hematite and glass phase are formed. At the end of the downward circulating sintering belt, the sinter cake breaks off and is broken into pieces the size of a hazelnut to a walnut. Sinter particles that are too fine are returned to the process. Smelter recirculating materials are all dusts, fine particles, etc. that accumulate in a smelter and contain iron. These are returned to the production cycle via the sinter.

The chemical composition of the ore, the pellets and the iron ore sinter are important parameters which must be known and taken into account when lining the blast furnace in order to be able to carry out an energy-optimised reduction process with targeted slag guidance in a controlled manner.

14.1.2 The Blast Furnace Process

Based on thermodynamic processes, one can deduce why iron oxides can be reduced to metallic iron with carbon (coke). No excursion into thermodynamics is to be undertaken here. The rough relationships are only explained in principle. Let us consider the Ellingham diagram (Fig. 14.1). It shows the temperature dependence of the stability of compounds. The Gibbs free energy ($\Delta G°$) is plotted against temperature. Since the oxygen partial pressure is also thermodynamically related to the Gibbs free energy, it can also be derived from the diagram.

Two examples are qualitatively plotted, the oxidation of Fe^0 to FeO and of C to CO (or the reduction of FeO to Fe^0 and CO to C). Above the curves the oxides are stable, below the curves the elements. One can also give the reaction equation above the curve, in which case the oxides above the curve are stable, the elements below. The slope of the stability curves can be different in the course, possibly even bend. Both example curves intersect, i.e. both reactions directly influence each other. At temperatures above approx. 993 K (approx. 720 °C), carbon can reduce iron oxides to metallic iron by oxidation to CO. The corresponding oxygen partial pressure is about $10^{-14.4}$ atm or lower.

In the blast furnace process, the iron ore or the precursors are reduced to metallic iron in a controlled manner. This takes place in the so-called blast furnace (Fig. 14.2).

The blast furnace is an oversized, up to 35 m high, continuously operated shaft furnace used for iron reduction. It consists of a steel body lined with refractory materials for thermal and chemical insulation. It operates according to the counter-current principle, in which the hot blast passes into the blast furnace gases in the course of reactions, rises to the top and the charge materials such as ore, coke and aggregates sink to the bottom in a reacting and reducing manner. The different areas of the blast furnace have special designations (Fig. 14.2). From top to bottom, these are the throat top, the furnace shaft, the belly, the bosh and the hearth. In the throat

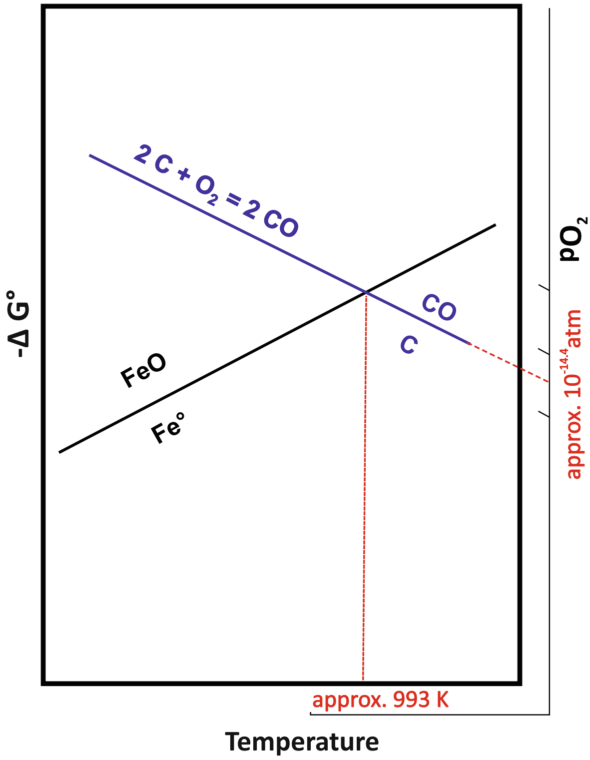

Fig. 14.1 Principle of the Ellingham diagram illustrated by the example of C-CO and Fe^0-FeO

top, on the one hand, the blast furnace gases escape in a controlled manner, and on the other hand, the charge materials such as ore, coke and aggregates (e.g. lime) are fed in to build up the burden. The charge of the blast furnace above the hearth is referred to as the burden.

In the blast furnace and the upper area of the shaft, the burden is heated up by the rising blast furnace gases and the first reactions take place. Residual moisture is expelled and possible siderite and magnesite components are decalcined. In the shaft different decalcinations of lime and dolomite and reduction stages of the iron in the iron carriers take place depending on the temperature. In the belly, coke and distinct melt components are present, which begin to separate in the rest. Only melt is found in the bosh, the heavier iron melt segregating under the floating slag melt. Hot air (approx. 1300 °C, 4 bar) is injected through several burner nozzles arranged in a circle and mixed with fuel (gas, heavy oil or coal dust) in the blow mould level in the lower area of the bosh. This creates a vortex zone in the blast furnace, in which local temperatures of up to 2200 °C prevail due to the combustion of the carbon. These turbulently rising gas flows and the burden, which sinks from above in countercurrent, lead to complex flow conditions, which result in the formation of the "dead man zone" in the centre of the blast furnace in the area of the coal sack and the rest. It is round and conical in shape, "guides" the material flows, is formed when the blast

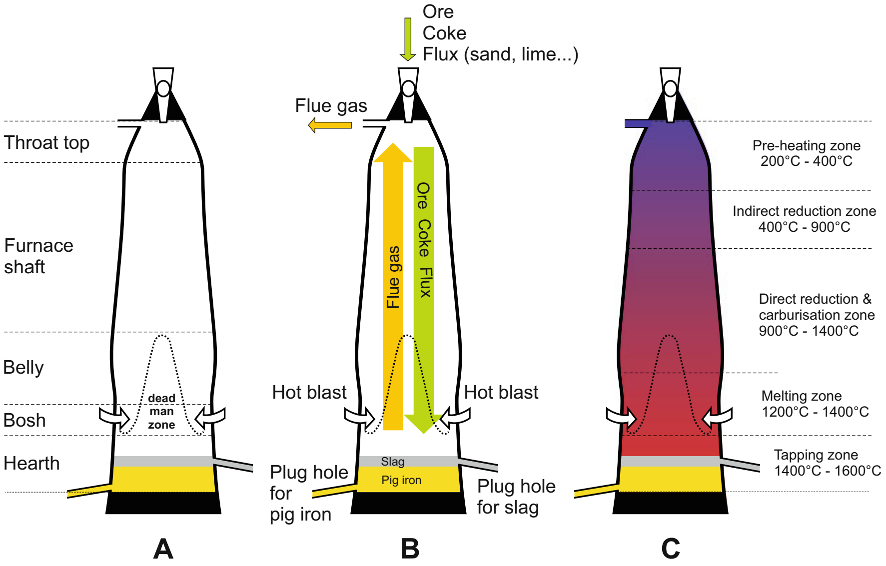

Fig. 14.2 Schematic layout of the blast furnace. (**a**) Designation of the areas, (**b**) Material flows, (**c**) Temperature distribution

furnace is started up and remains there unchanged as a core until the blast furnace is shut down after about 15–25 years.

In addition to these traditional designations of the blast furnace, there is also a chemistry-based designation of the reaction zones (Fig. 14.2), in which the reduction reactions to metallic iron take place according to the temperature.

- Drying and preheating zone
  - approx. 200–400 °C
- Indirect reduction zone
  - approx. 400–900 °C
  - $3\ Fe_2O_3 + CO = 2\ Fe_3O_4 + CO_2$
  - $Fe_3O_4 + CO = 3\ FeO + CO_2$
- Direct reduction and carburisation Zone
  - approx. 900–1200 °C
  - $C + CO_2 = 2\ CO$
- Melting Zone
  - approx. 1200–1400 °C
  - $FeO + CO = Fe^0 + CO_2$
- Tapping Zone
  - approx. 1400–1600 °C
  - Adjustment of the segregated melts slag and pig iron

When sufficient metallic iron and slag have formed, the blast furnace is tapped. For this purpose, a discharge hole of approx. 20 cm diameter is drilled at predetermined points in the lower frame, through which pig iron or slag can flow out. The pig iron flows through sand-lined channels into so-called torpedo ladles or other transport vessels in which it can be transported to the steelworks. The slag flows into slag troughs and is partially solidified to a glassy consistency. The pig iron contains up to 4.8% carbon. It is therefore brittle and not forgeable.
Significant amounts of slag are produced during the blast furnace process. Up to 300 kg of slag is formed for 1000 kg of pig iron. This is used as a latent hydraulic binder (aggregate) for low-quality cements. In addition to iron reduction in the blast furnace process, it is also essential to chemically adjust the slag for this recycling application.

The material balance of the blast furnace looks quantitatively on 1 t of produced pig iron as follows (Stahlfibel 2002):

- Feed

Ore & Surcharges	1.60 t
Coke	0.36 t
Coal	0.12
Hot blast	1.36 t (1050 m^3)
Oxygen	0.05 t (34 m^3)

- Retrieved

Pig iron	1.00 t
Slag	0.26 t
Blast furnace gas	2.10 t (1550 m^3)
Dust and mud	0.011 t

- Exhaust air hall dedusting 2000–3000 m^3
- Cooling water 20 m^3

14.2 The Iron-Carbon System

All processes in the iron and steel industry are based on the iron-carbon phase diagram. Figure 14.3 shows the iron-rich part of this system.

Metallic iron can incorporate significant amounts of carbon into the crystal lattice. At 911 °C, α-iron (ferrite) transforms into the γ-modification (austenite), at 1392 °C the δ-modification forms, and the melting point is 1536 °C. Ferrite and δ-Fe° can incorporate only small amounts of carbon (<0.5 mass-%), whereas austenite can incorporate up to 2.06 mass-% at the eutectic temperature of 1147 °C. Incorporation of 0.8 mass-% carbon lowers the stability of austenite to 723 °C. This phase relationship is called eutectoid because it resembles an eutectic system but is in the

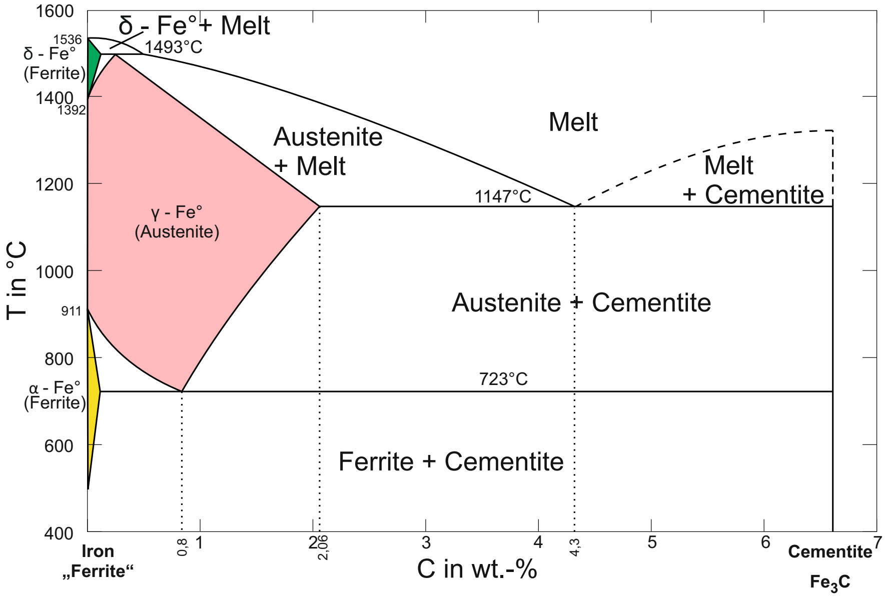

Fig. 14.3 The phase diagram F-C. (Modified according to Stahlfibel 2002, Fig. 9 p. 8)

sub-solidus. 723 °C is thus the eutectoid temperature. Cementite Fe_3C is the next stable phase in the diagram towards higher carbon contents.

In ferrous metallurgy, in addition to the phase and phase field designations shown in Fig. 14.3, special terms are used which can be traced back to appearances of metastable solidified microstructures (Fig. 14.4). The growth microstructures occurring in this case would change during thermal post-treatment for equilibrium adjustment.

Above the eutectoid temperature of 723 °C, austenite has a carbon content of 0.8 mass-%. Below 723 °C it is no longer stable and segregates into ferrite and cementite according to the quantity ratios given by the phase rule. This specific metastable crystallization structure is called perlite. The metastable crystallization structure of solidified melts of the eutectic composition between austenite and cementite is called ledeburite. These metastable microstructures behave like stable phases and do not react with the coexisting other phases during cooling.

Compositions between ferrite and 0.8 mass-% carbon form ferrite and metastable austenite of perlitic composition at the eutectoid temperature on cooling. Since below 723 °C this austenite is not stable, it segregates accordingly in the microstructure of perlite. Thus, perlite is present next to the ferrite.

Compositions between 0.8 and 4.3 mass-% carbon crystallize below the eutectic temperature of 1147 °C and above the eutectoid temperature of 723 °C as austenite next to the eutectic segregation structure of ledeburite. Below 723 °C austenite is no longer stable and segregates to form perlite. The ledeburite intergrowth structure is not affected by this.

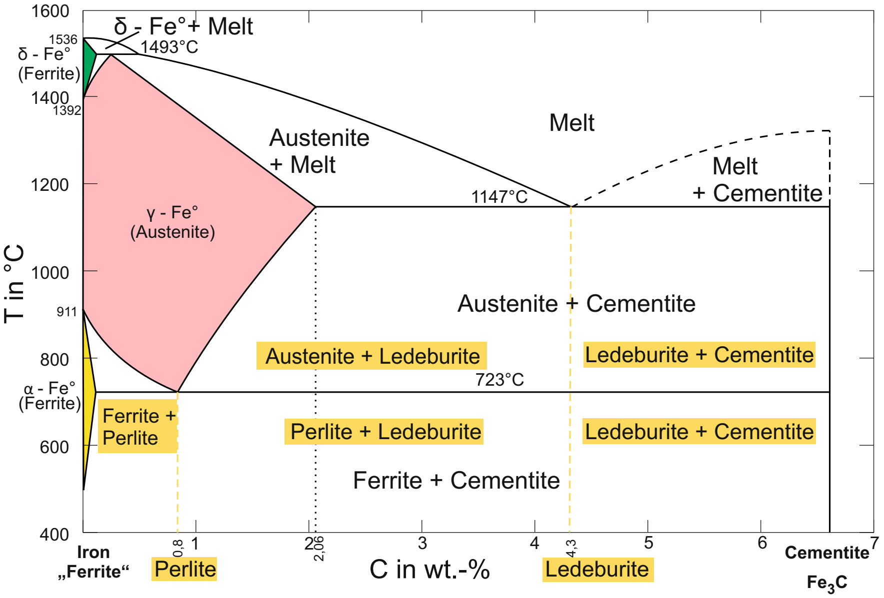

Fig. 14.4 The phase diagram Fe-C, with entry of special designations of metastable microstructures of ferrous metallurgy. (Modified from Stahlfibel 2002, Fig. 9 p. 8)

Between the eutectic composition of 4.3 mass-% carbon and the cementite phase, a microstructure of ledeburite and cementite is formed below 1147 °C. The cementite phase is the most important phase of the eutectic composition. At 723 °C nothing changes here in principle in the microstructure.

14.3 From Pig Iron to Steel

After the blast furnace tapping the pig iron has a temperature of 1500–1550 °C.

Compared to pig iron, steel has a significantly lower carbon content. Furthermore, silicon, sulphur and phosphorus have to be removed. This is done in the steel plant in the so-called converter. Figure 14.5 shows a comparison of the carbon content of pig iron and steel in the iron-carbon diagram.

Pig iron has a carbon content of 4–4.8 mass-% carbon, in addition to contents of Si, P and S and possibly transition metals such as Mn, etc. Due to the carbon content, more than 50 mass-% of cementite is present in the structure in the solidified state. Cementite as iron carbide is a brittle phase in terms of its fracture behaviour. Therefore, cast iron solidified from untreated pig iron is not malleable and cannot be forged. The pig iron must therefore be depleted of unwanted elements in the steelmaking process and, depending on the steel specification, alloyed with desired elements in a controlled manner.

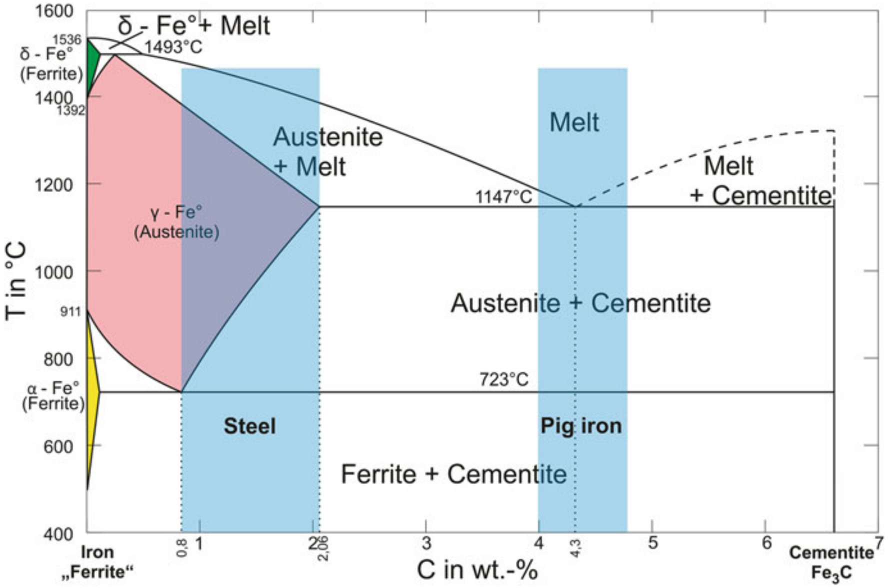

Fig. 14.5 The Fe-C phase diagram, showing the composition ranges of pig iron and steel. (Modified according to Stahlfibel 2002, Fig. 9 p. 8)

When tapping the blast furnace, the pig iron is filled into transport vessels, e.g. torpedo ladles, via channels made of sand. This is used for transport to the steelworks, where the pig iron is transferred to the converter. The main processes for reducing the unwanted element contents then take place in the converter. This in turn produces a slag, the so-called steelworks slag or converter slag. In contrast to blast furnace slag, its composition is not optimized for further use, since steel production plays the dominant role; on the other hand, converter slag is significantly smaller in terms of quantity. Depending on its composition, it is used as an aggregate for cement or as road gravel.

In the steel process, a distinction is made between primary and secondary metallurgy. The primary metallurgy takes place in the converter, the secondary metallurgy in a transport vessel after decanting. The most important step is the so-called decarburization of the pig iron. In this process, oxygen is blown onto or into the pig iron in the converter (Fig. 14.6). This process is called “refining”.

Oxygen exothermically oxidizes carbon to carbon monoxide, which escapes as a gas. By checking the partial pressure of oxygen in the molten iron, it is possible to detect the moment at which the carbon content has been reduced to the desired value, which is desirable for the steel grade to be produced. Further “blowing” would result in undesirable oxidation of the iron. The other undesirable contents of silicon, phosphorus and sulphur cannot be removed by the refining process. This is done by adding lime.

The following processes are assigned to primary metallurgy:

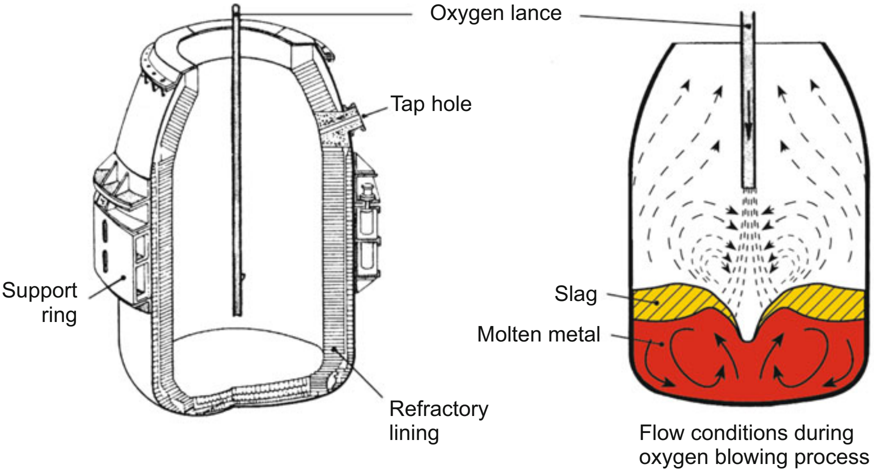

Fig. 14.6 Schematic representation of the refining process in the converter. (From Stahlfibel 2002, Fig. 43 p. 54)

- Freshening process (freshen = burn, oxidize)
- Reduction of the C-content
- Removal of unwanted admixtures
- Setting the desired alloy composition
- Reactions: ([. . .] dissolved in pig iron, (. . .) contained in slag)
  - Decarburization: $[C] + \frac{1}{2}\,[O_2] \rightarrow CO$ (exhaust gas)
  - Slagging of the accompanying elements
  - Desilication: $[Si] + [O_2] + 2\,[CaO] \rightarrow (2\,CaO - SiO_2)$
  - Manganese reaction: $[Mn] + [O] \rightarrow (MnO)$
  - Dephosphorization: $2\,[P] + 2.5\,[O_2] + 3\,(CaO) \rightarrow (3\,CaO - P_2O_5)$
  - Desulfurization: $[S] + [CaO] \rightarrow (CaS) + [O]$

The decarburization process causes an exothermic oxidation of carbon to carbon monoxide. This would cause the molten steel to heat up extremely. In order to absorb this heat generation, steel scrap of a defined composition is added to the pig iron in the converter.

The process at the steel mill is:

- Filling steel scrap into the empty hot converter
- Pouring the pig iron into the converter
- Carrying out the refining process, decarburisation and possibly manganese reaction, through the exothermic reactions melting up and melting down of the scrap added
- Addition of limestone and, if necessary, fluorite for desilication, dephosphorisation and desulphurisation
- Pouring the steel into a transport vessel

The steel in the transport vessel is now transported to secondary metallurgy, the post-treatment of the steel. This is necessary in order to meet the high requirements for the different steel qualities. Secondary metallurgy is in part quite complex. It is therefore only briefly touched on here.
The following processes can be carried out in secondary metallurgy:

- Alloy setting
- Homogenization of the temperature, in order to promote chemical homogeneity as well
- additional decarburization
- Deoxidation to remove dissolved oxygen from the steel due to the refining process
- Vacuum treatment to remove the last gas residues in the form of bubbles from the molten steel

14.4 Refractory Materials

The blast furnace is a steel shaft furnace lined with suitable refractory materials in order to be able to carry out the high temperatures and the process sequences in a controlled manner. In this process, the erosive factors change from top to bottom according to the increasing temperature and change of the burden up to the melting zone with the two immiscible melts slag and metal. In the upper area, the abrasive aspect of corrosion is in the foreground; as the temperature increases, the chemical-corrosive aspect becomes more and more important.

With a height of up to 75 m and correspondingly a diameter of about 12 m at the top and of about 15 m in the frame, there are varying thicknesses of the refractory lining inside. This varies in the upper area from a few decimeters up to 1 m in the frame. In the upper area there are combinations of thinner refractory lining and gunning mixes, transitioning to a pure refractory lining up to the frame. This lining is composed of fireclay or high quality bricks rich in alumina (Chap. 7). The rest is often lined with fused cast bricks (e.g. mullite or corundum), whereas the frame is lined with carbon bricks of the highest purity.

On the outside, the blast furnace is cooled by means of cooling water pipes, cooling boxes and plate coolers to protect the steel shell and refractory materials. Further to the outer area, insulation materials of high porosity are found for thermal insulation. Torpedo ladles, transport vessels and converters consist of steel vessels which are usually lined with basic refractory bricks. They have no external insulation.

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