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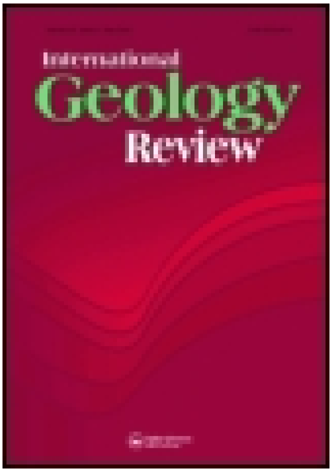

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Origin of stratiform lead-zinc deposits

D.I. Gorzhevskiy and V.N. Kozerenko

The stratiform deposits make up a special group of lead-zinc deposits possessing many common features in which they differ from the similar deposits of other industrial-genetic types.

They are characterized by ores confined to strata of carbonate rocks, most frequently dolomites, by ore bodies of predominantly stratal form represented by impregnation ores of simple mineral composition, within which galena usually predominates over sphalerite (rarely the reverse), by the absence of magmatic rocks of similar age to the ore in the vicinity of the deposits, by the substantial proportion of carbonates, barite and fluorite among the vein minerals, and often by increased contents of germanium and thallium.

The deposits of this type include those of the Tri-state area, and the states of Kentucky, Illinois and others in the USA, the Pine Point deposit in Canada, the Upper Silesian deposits in Poland, and the Mirgalimsay, Achisay, Sumsar, Uch-Kulach and other deposits in the Soviet Union. This type of lead-zinc deposits is of great economic importance: about 30% of all the lead-zinc ores extracted in the capitalist countries comes from stratiform deposits.

The genesis of these deposits is highly controversial. Some investigators (5, 10, 34, etc.) regard them as low-temperature hydrothermal deposits far from the ore-containing magma chambers (telethermal deposits, according to L. Greyton). They explain the predominance of conformable ore bodies by the effect of the lithologic factor; the ores are either considered epigenetic relative to the host rocks, or else their localization is controlled, these investigators believe, by tectonic factors. The usual absence of any visible connection with igenous rocks is explained by their great distance from the intrusives to which they are genetically (or paragenetically) related.

According to the other hypothesis (3, 11, 15, 23, etc.), the ore material of stratiform lead-zinc deposits was formed at the same time as the host rocks in the course of sedimentation, and its subsequent redeposition was due to the processes of diagenesis, epigenesis and weak metamorphism. This idea, which in the Soviet Union was first advanced forcefully by M. M. Konstantinov and later by V. M. Popov, was perfected in the writings of N. M. Strakhov (21, 22). Strakhov emphasized that the stratigraphic control of the ore mineralization characteristic of these deposits cannot be explained by the special properties of the rocks containing the ores. Deposits of this type are confined not only to definite lithologic complexes, but also to a particular facies group, the monoclimatic ore triad (Cu-Pb-Zn) of the arid zones, in which they occupy a regular place.

But the conclusion drawn by many adherents of the hypothesis of the sedimentary origin of these deposits, to the effect that the distribution of the ore bodies does not depend on the character of the folded structures or ruptures and that therefore such deposits show no signs of alteration around the ores, can hardly be accepted. The materials obtained in recent years, and especially the detailed investigations made in mines and within ore fields, indicate just the opposite. Thus we encounter what seems to be an insuperable contradiction.

However, the two views mentioned above are actually not mutually exclusive. As the discussion of the genesis of stratiform lead-zinc-barite-fluorite deposits at the international symposium in 1966 showed, the views of the adherents of the sedimentary and hydrothermal genesis of these deposits have recently converged.

V. I. Smirnov (19) notes that those who believe in the sedimentary formation of these ores "... consider the present structure and composition of stratiform deposits to be the consequence of a prolonged process of sedimentation, diagenesis and epigenesis, as a result of which the primary ore-containing sedimentary deposits have undergone both initial diagenetic and later alterations, up to the reorganization of the ores by aggressive solutions that caused the regrouping of the ore-forming material and transformation of its chemical and mineral composition, and its local redeposition along the stratal and intersecting elements of the geologic structure. The idea has been advanced that, depending on the depth and intensity of these transformations, one can see all the transitions from only slightly altered ore bodies showing all the signs of sedimentary genesis to intensively altered ore bodies that have lost all traces of their initial origin and resemble the products of energetic hydrothermal activity" (p. 9).

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On the other hand, as Smirnov says, many adherents of the hypothesis of hydrothermal ore formation no longer regard magma chambers as the exclusive source of the fluids and metals. They also acknowledge the formation of stratiform deposits by circulating ground waters that become heated at depth, taking on the properties of chemically active thermal solutions capable of mobilizing and redepositing ore-forming substances, including metals, from the host rocks that contain them in dispersed state.

It can also be supposed, as Smirnov quite properly emphasizes, that stratiform deposits belong to the category of convergent deposits — that is, they may include both sedimentary syngenetic and hydrothermal epigenetic ores. It is of great interest from this standpoint to examine the results of P. Zuffardi's study (35) of the stratiform deposits of Sardinia, where according to that investigator one can distinguish epigenetic lead deposits distributed zonally around Hercynian granite plutons, epigenetic deposits without zonal distribution around granite plutons, syngenetic deposits in Cambrian and Gotlandian rocks, and complex or dialogenetic (according to T. Lovering) deposits produced by epigenetic redeposition of ore-forming material of primary syngenetic character.

Considerable material has been accumulated in recent years in the Soviet Union that in large measure suggests a complex history of the formation and subsequent transformation of the lead-zinc ores in stratiform deposits. This material indicates that the initial deposition of the lead and zinc sulfides was sedimentary and synchronous with the formation of the surrounding host rocks. Thus arose the extended zones of dispersed sulfide mineralization, as a rule with lean contents of lead and zinc. Subsequently, as a result of the renewal of tectonic movements, old deep-seated faults were reactivated and new ones formed. Along these faults circulated heated waters of juvenile and mixed origin, and in some cases predominantly primary-vadose waters or waters of the metamorphic type, which dissolved and partly transported the lead and zinc, redepositing them as galena, sphalerite and the accompanying minerals. It was these processes that gave rise to the rich concentrations of sulfides, forming ore bodies of industrial value.

Below we shall present some proofs of the primary sedimentary origin of the lead-zinc mineralization of stratiform deposits and of the redeposition of this material.

Source areas. The question of the sources of the lead and zinc compounds in a marine basin is one of the most complex problems in the study of the origin of stratiform deposits. The writings of P. Laffitte (23, 33) are among the most interesting on this subject. According to that investigator, around the old Hercynian massifs in France (the Armorican massif and that of central France), the Triassic, Jurassic and Lower Cretaceous rocks contain stratiform deposits of lead, zinc, barite and fluorite. The ore bodies of these deposits consist of stratal bodies confined to horizons of lagoonal dolomites, and more rarely limestone and arkoses, and lie close to normal faults of regional extent.

Within the Armorican massif and the massifs of central France, which are composed of Precambrian and Paleozoic rocks, are numerous veins of galena, sphalerite, fluorite and barite. These are associated with zones of "post-kinematic" granites, and also with later normal faults of Carboniferous, Permian and even Triassic age.

Ore mineralization of this type is characterized by regional zonality, which Laffitte thinks is determined by the system of regional faults breaking up the massifs into blocks. The main features of this zonality are the following: the amount of galena increases in the western part of the massif of central France, and by contrast decreases in the veins situated in its eastern part; the higher concentrations of sphalerite are confined to its southern margin; the content of chalcopyrite is slight in the center but increases in the southern and northeastern parts; fluorite is abundant in the western part of the massif and close to the "Great Coal Basin"; barite is abundant in the central but scanty in the marginal zone.

Laffitte notes that the composition of the ores in the stratiform deposits occurring in Mesozoic stratified sedimentary rocks shows a definite relationship to the above distribution of the minerals in the vein bodies of the old massifs: the abundance of fluorite in the northern continuation of the "Great Coal Basin," the increased concentrations of sphalerite in the ores of deposits south of the massif of central France; the limited distribution of stratal barite deposits in the marginal zone of Brittany, and the increased concentrations of chalcopyrite and sphalerite in the northern part of the Vosges. On the basis of these observations, he concludes that the source of the ore materials in the Mesozoic stratiform deposits were the veins that are contained in the rocks of the old massifs.

H. Schneiderhöhn (26) has arrived at similar conclusions as to the genesis of the lead deposits in the Eifel and Oberpfalz regions of East Germany.

U. Asanaliyev (1) states that most of the stratiform lead-zinc deposits of the Tien Shan region are confined to bodies of Upper Devonian and Lower Carboniferous carbonate rocks and lie along the structural line connecting the Caledonian uplift of the northern Tien Shan with the Hercynian Karatau-Naryn marginal basin. The ore-bearing dolomites here occur directly in the northern part of this basin and are replaced in its central and southern parts by barren limestones.

Hence the area of the Caledonian uplift must have been the source of material for the stratiform nearby deposits.

In Asanaliyev's opinion sources of lead that entered the marine basin were the products of the erosion of Lower and Middle Devonian volcanogenic rocks containing increased amounts of this metal and occurring at the base of the producing carbonate layers.

But not only old ore deposits and occurrences can be the sources of lead and zinc in the sea water. The lead in magmatic rocks is known to accumulate primarily in the potassic feldspars and the micas, where it isomorphously replaces potassium. Zinc is accumulated mainly in the biotites and amphiboles, replacing bivalent iron, which has a similar ionic radius.

The lead content differs in the feldspars of the various rocks. Thus according to A. V. Rabinovich and Z. A. Baskova (17), the granitoids developed in the lead-zinc ore belt of eastern Transbaykal are characterized by relatively high contents of lead in the feldspars. On the other hand, the feldspars of the granitoids in the adjacent metallogenic zone contain far less lead, and here it is not lead-zinc, but tin-ore deposits that are commonly developed.

According to A. V. Kopeliovich (12), as a result of the dissolution of the rock-forming minerals of magmatic rocks, lead and zinc go into solution, thus becoming mobile and occurring in places where hydrogen sulfide is concentrated. As Kopeliovich stresses, sulfide occurrences of lead, zinc and copper can be seen as fillings in the cavities of phosphorite concretions, stratal and intersecting veinlets and also impregnations, showing both a spatial and a genetic relation to the epigenetically altered rocks.

Simple calculations show that the role of acidic magmatic rocks as sources of the lead in a marine basin may be no smaller than that of old vein deposits. Thus if one takes an old ore occurrence, represented by a quartz or quartz-carbonate vein with a lead content of 2%, a thickness of 1 m and a length of 1000 m, the erosion of such a vein to the depth of 500 m will release a total 28,000 metric tons of lead. Thus for 1 million tons of lead to be carried into a marine basin, 36 such veins must have been eroded. Assuming the average content of lead in acidic magmatic rocks to be 20 g/ton (4), one can readily see that such an amount of lead (1 million metric tons) will be formed as a result of the erosion of a pluton of granitoids or body of acidic vulcanites to the depth of 500 m over an area of 40 km^2.

The forms of transportation. Considerable success has been achieved in the past few years in studying the forms in which lead and zinc compounds are transported by surface and ground waters; this progress has been due to hydrochemical investigations associated with explorations for ore deposits. Physicochemical calculations by G. A. Goleva (6) of the forms in which zinc migrates in various types of natural waters have shown that in acidic sulfate waters with pH < 4 most of the zinc is in the form of the bivalent cation Zn^{2+}. In slightly acidic sulfate waters with pH > 5, according to Goleva's calculations, sulfate complexes of zinc ($ZnSO_4$) should predominate, whereas neutral and chemically positive zinc chloride complexes – $(ZnCl)^+$, $ZnCl_2$ – should prevail in chloride-sulfate and slightly alkalic chloride waters; in carbon dioxide waters containing increased amounts of fluorine, the zinc may form stable compounds with the fluorine.

Approximate calculations of the inorganic forms in which lead occurs in various types of natural waters (6) show that in acidic sulfate waters with pH < 4 the lead is predominantly in the form of the cation Pb^{2+}. In slightly acidic (pH> 6.5) and alkalic hydrocarbonate waters there is probably a predominance of the complex ions $Pb(OH)^+$ and $[Pb(HCO_3)_2]^-$. Carbonate compounds of lead and zinc are quite stable in natural waters and usually migrate in regions where carbonate rocks are developed. In slightly alkalic chloride-sulfate waters with increased mineral contents, most of the lead, in Goleva's opinion, probably migrates in the form of the $(PbCl)^+$ and $(PbCl_3)^-$ ions.

Konstantinov (11) believes that lead, like zinc, may also be transported in the form of soluble organic compounds. In surface waters with high rates of movement, part of the lead migrates in colloidal and suspended forms.

All this indicates that lead and zinc compounds can be transported under specific conditions both by surface (stream and sea) waters and by ground waters, in the form of various soluble compounds, and in all probability also as fine mechanical suspended particles and colloidal compounds. Under arid conditions the ground waters are often considerably enriched in chlorides and sulfates; if these then circulate through salt-bearing bodies of rock, conditions favorable to the solution and transportation of lead and zinc compounds will be created.

Means of deposition. The ways in which sulfides are precipitated from marine waters – that is, the transformation of soluble compounds of lead and zinc into insoluble compounds, have been thoroughly studied as a result of the work of Ye. V. Rozhkova, O. V. Shcherbak, Z. G. Vasil'yeva and others (18). These investigations have shown that the rocks to which accumulations of lead and zinc sulfides are usually confined as a rule have the greatest sorption capacity. Among such sorbents are dolomite, brown coal, bentonite and calcium phosphate. From observations of sulfate-reducing bacteria, it has been possible to determine the physicochemical parameters of the biogenic sulfate-reducing process, which played an important role in forming the accumulations of lead, zinc, selenium, molybdenum, vanadium and uranium in sedimentary rocks.

The essential conclusions of the above-mentioned investigators, as confirmed by their own experimental observations and by modeling of the process of accumulation of sulfides in sedimentary rocks, may be stated briefly as follows. The soluble lead and zinc compounds present in sea water even in very small concentrations are sorbed by dolomites. The sorption ions are transformed into sulfides probably in the stage of diagenesis, as a result of the action of sulfate-reducing bacteria, which develop in rapid abundance on the substrate of organic matter contained in the carbonate rocks, leading to still more highly reducing conditions in the environment. The hydrogen sulfide thus given off, reacting with the lead and zinc compounds, transforms them into sulfides. The formation of the sulfides increased the sorption capacity of the carbonate oozes, promoting the further accumulation by sorption of new portions of the metals from the sea water. Thus, as Rozhkova, Shcherbak and Vasil'yeva emphasize, the accumulation of lead and zinc is a multistage process. In the first stage it is controlled by the sorption capacity of the dolomite, but in subsequent stages by sulfate reduction, which transforms the sorbed elements in them into sulfides, the sorbent thereby acquiring the capacity for absorbing new portions of the elements from the solutions.

The sorption accumulation of lead and zinc in the sorbents under dynamic conditions goes on continuously from solutions even with extremely small contents of these elements. Their contents in the rocks depend on the sorption capacity of the latter and are determined by the amount of the element contained in the entire volume of the solution passing through the sorbent, and not by its concentration in the solution.

The experiments carried out by Rozhkova, Shcherbak and Vasil'yeva were concerned not only with sorbents, but also with rocks that have minimal sorption capacities. Thus, for example, experiments were made with quartz sand, to which an accumulative culture of sulfate-reducing bacteria had been added, in the deposition of lead and zinc sulfides from solutions close in composition to natural ground waters containing zinc and lead in the amounts of 5×10^{-4} and 2×10^{-4} g/lit, respectively. These investigations showed that there is no precipitation of the sulfides of these metals under such conditions.

Lithologic control. The conclusions of the above investigators are fully confirmed by geologic observations. It is well known, for example, that stratiform lead-zinc deposits are localized predominantly in dolomites. According to Ye. Ye. Zakharov (9), more than 50% of the ore occurrences of the Karatau range are contained in dolomites, 20% in bodies of interbedded dolomites and limestones, and 30% in limestones; there is no ore mineralization in the carbonate rocks containing a considerable admixture of clay material.

In the Chatkal range, according to Asanaliyev, more than 80% of the ore occurrences are confined to sedimentary dolomites rich in organic matter. These dolomites are characterized by almost complete absence (less than 5-6%) of terrigenous admixtures.

The ore occurrences of the Kalkan-Ata mountains are confined to a horizon of black dolomites interlayered with marls and limy-clayey dolomites. In the Moldatau zone of the Tien Shan region, according to V. M. Popov (15), the lead-zinc mineralization in all three horizons of Lower Carboniferous deposits is confined to dark dolomites rich in organic matter. The lead-zinc mineralization of the Upper Silesian deposits also occurs in dolomites enriched in organic matter (5, 30).

According to Ye. S. Zorin, who has studied the Mirgalimsay deposit, the composition of the rocks making up the ore-containing horizon (the thickness of this horizon ranges from 2-4 m to 24-28 m) varies both along the section and horizontally in plan. Pure dolomites are most common in the lower part of the horizon; in the upper part the area of development of the dolomites diminishes, the dolomites gradually retreating toward the center of the ore field and being replaced by more limy varieties of carbonates. The change in the composition of the carbonate rocks here is accompanied by changes in the concentrations of the ore elements distributed in them. Thus, for example, the highest contents of lead are confined to the limy dolomites, but drop in the more limy and more dolomitic varieties. The zinc content in the dolomite-limestone series gradually increases, whereas the amounts of barite, on the other hand, diminish in the same direction.

All these materials indicate that the galena and sphalerite are probably of primary sedimentary origin; it is hard to understand them in the light of the hypothesis of primary hydrothermal origin. It is interesting to note that, according to Asanaliyev (1), the porosity of both the ore-bearing and oreless dolomites is very low (1-1.5%); the oreless limestones usually are more porous than the dolomites. Nor do the ore-containing dolomites differ from the oreless dolomites and limestones in their degree of fracturing.

Asanaliyev emphasizes that the ore-bearing bodies containing stratiform lead-zinc deposits usually consist of three cyclic suites (macrocycles): a lower suite composed of terrigenous

TABLE 1. Background concentrations of lead, zinc, copper, and silver in different horizons of Sumsar ore deposit.

Horizon and Designation	Content, n · 10^{-3}%				Remarks
	Pb	Zn	Cu	Ag (n · 10^{-5})	
1st D_2gv^B	10	5	30	7	Dolomitized limestones and dolomites, 15-18 m thick
2nd D_2gv^G	25	21	10	6	Black ("sparkling") dolomites, 25-35 m
3rd D_3fr^A	8	10	8	4	Dolomites, dolomitic limestones, limestones, about 800 m thick
D_3fm	4	8	5	4	Limestones, more rarely dolomites, 600 m
C_1	1	5	1	2	Light-colored limestones, about 2000 m
Intermediate terrigenous rocks	0.9	4	1	0.8	Red polymictic sandstones
Abundance ratios of carbonate rocks	0.7	5	2	2	

or terrigenous-carbonate rocks, with which deposits of cupriferous sandstones or cupriferous shales are often associated; a second suite represented by dolomites and limestones, indicating maximum transgression, with which lead-zinc mineralization is associated; and a third suite consisting of marls, clayey limestones, gypsums, anhydrites and various salts, reflecting the regressive stage of development of the basin.

Considerable material has now been accumulated on the distribution of the concentrations of metals within the ore-containing horizons. Extremely interesting data from this standpoint have been obtained by V. I. Zlobinskiy on the area of the Sumsar ore deposit in the Chatkal range. He states that in this region one finds very extended (up to 10 km long), relatively thin horizons of dolomites and dolomitized limestones with a rich primary sulfide mineralization (table 1).

Zlobinskiy notes that although the entire body of Givetian and Frasnian deposits is enriched in sulfides, the richest in sulfides are the D_2gv^B, D_2gv^G and D_3fr^A horizons. It was found, moreover, that the various horizons are characterized by a geochemical specialization that is directional in time, manifested in the fact that the first horizon (D_2gv^B) is richer than the others in copper and silver, whereas the second (D_2gv^G), within which the Sumsar deposit lies, contains more lead and zinc, but less copper than the first. In the younger horizons and bodies of rocks, the amounts of copper and lead diminish and zinc begins to predominate. Zlobinskiy thinks this is due to the deepening of the sedimentation basin, to the appearance of communication with the open sea, etc. He calls attention to the fact that the observed zonality in the distribution of metals over the course of time resembles the horizontal distribution of these elements relative to the basin's shoreline, where copper is precipitated in the near-shore zone,

TABLE 2. Distributions of lead concentrations (%) in lithological varieties of rocks in middle Tien Shan, from U. Asanaliyev (1).

Age of Rocks	Composition of Rocks	Structural-formational Subzone			
		Kuraminskaya	Chatkal	Naryn	Karatau
Givetian	Sandstones	0.002			
	Siltstones	0.0018			
	Argillites	0.003			
	Limestones	0.008			
	Dolomites	0.028			
Frasnian	Sandstones	0.0008	0.0008	0.002	0.0001
	Limestones	-	0.001		
	Dolomites	-	0.016		
Famennian	Limestones	0.001	0.001	0.007	0.0015
	Dolomites				0.02*
Lower Tournaisian	Limestones		0.001	0.004	
	Dolomites	0.001	0.001	0.015	0.01-0.1

*Kyzyl-Ata facies of Famennian stage.

the main mass of lead is precipitated farther from the shore and zinc, finally, in the center of the basin.

Asanaliyev (1) presents some interesting data on the distribution of lead in the Givetian, Frasnian and Famennian deposits of the central Tien Shan region (table 2). Examination of Table 2 leads to two conclusions: first, that the highest concentrations of lead are confined to the dolomites (3-20 times exceeding its concentrations in the limestones of the same suites); second, that the lead contents in the limestones and dolomites are different in the different structural-formational zones of the central Tien Shan region.

Thus in the Lower Tournaisian dolomites of the Naryn and Karatau zones, for example, the lead contents are 10 to 100 times higher than in the dolomites of the Kuraminskaya and Chatkal zones. Most of the lead-zinc ore occurrences are confined to just those areas in which the dolomites have increased contents of lead. Thus in the central Tien Shan only the Famennian carbonate deposits of the Kyzyl-Ata facies in the Karatau range are characterized by increased concentrations of lead — and it is to these rocks that all the lead-zinc ore occurrences known here are confined. The same can be said of Lower Tournaisian deposits, in which the occurrences of lead and zinc ores are distributed mainly in the areas (the Naryn and Karatau structural-formational zones) where the dolomites have increased concentrations of lead.

It is known that the abundance ratio of lead in sedimentary rocks increases from carbonates to sandy and clayey deposits (4). But, as Asanaliyev emphasizes, the distribution of lead concentrations in the sedimentary rocks of the central Tien Shan region shows just the reverse: these concentrations are higher in the limestones and especially the dolomites than in the sandstones and siltstones. Thus we probably see the effects of different laws governing the accumulation of lead.

Mineral composition of the syngenetic ore mineralization. Study of the mineral composition, textures and structures of the lead-zinc ores of stratiform deposits also indicates their primary sedimentary genesis. According to S. A. Yushko (28), who has made a detailed study of the lead-zinc deposits in southern Kazakhstan, the earlier mineral association of the lead-zinc ores in the Karatau stratiform deposits, represented by pyrite, sphalerite and galena, is syngenetic with the ore-containing dolomites. This is proved by the oolitic, pseudo-oolitic and layered structures characteristic of both the ores and the host rocks. The minerals of this association form a layer-by-layer impregnation in particular stratigraphic horizons of the carbonate rocks, which can be traced for many kilometers along the strike.

M. D. Troyanov has similarly concluded that the lead-zinc ores of the Uch-Kulach deposit in southern Uzbekistan are also of primary sedimentary origin. According to his data the lead-zinc mineralization of the first stage is syngenetic with the ore-containing carbonate rocks, as proved by the following: a) the complete absence of alterations of the host rock; b) the presence of fragments of ore minerals in the cemented breccias; c) the confinement of the ore mineralization to the bedding, with the formation of characteristic banded structures; d) the isotope composition of the lead, which indicates that the galena is of Devonian age.

All the facts cited above confirm the primary sedimentary origin of the lead-zinc mineralization of stratiform deposits. But the concentrations of lead and zinc here are low, and as a rule of no industrial interest. Such ores of these deposits as are suitable for practical exploitation usually show signs of epigenetic origin and were formed as a result of redeposition of the syngenetic mineral associations.

Geochemical conditions for solution of initially deposited sulfides of lead and zinc. As a result of experimental investigations, much new material has recently been obtained on the conditions governing the solution of a number of sulfides, including sphalerite and galena. H. L. Barnes and G. K. Chamanskiy in a recently published paper (2) showed that the solubility of sphalerite in pure water at temperatures up to 350° is very small, as in liquid H_2S. But in the region of stability of HS^-, Barnes obtained values for the solubility of sphalerite of up to 2700 mg/lit (25° C, P = 7 atm H_2S, pH = 8.2). In this case, apparently, the following complex-forming reaction takes place:

$$ZnS + H_2S + HS \rightleftarrows Zn(HS)_3^-.$$

As for the role of chlorine, according to these authors complexes simultaneously containing HS^- and NH_4^+ or Cl^- are not favorable to the solution of sphalerite.

Barnes and Chamanskiy further concluded that galena is insufficiently soluble in slightly acidic, H_2S-enriched solutions at low temperatures, but forms a bisulfide complex somewhat more stable than ZnS. The solution of galena may perhaps be substantially affected by chloride complexes with Pb^{++}, which in contrast to the Zn^{++} complexes are stable and are the optimal transporting agents of lead. H. Helgeson (25) has shown that the formation of lead chloride complexes may be the reason for its high solubility at temperatures of around 300°.

These geochemical data in our opinion show that the initially deposited sulfides of lead and zinc are soluble and that their different relationships to the chloride complexes are the reason for separation of the sphalerite and galena ores during redeposition of these minerals.

Mineral associations of redeposited ores. According to Yushko (28), the second mineral association of the lead-zinc ores in the Karatau deposits, represented by calcite, dolomite, galena, sphalerite and pyrite, is later than the first. The minerals of the second association occur in the form of veinlets, amygdaloids and impregnations in the ore minerals of the first association and in the carbonate rocks. It is important to note that the number of dolomite segregations in the veinlets increases sharply if they are contained in dolomite strata; on the other hand, if the host rock is limestone, the amount of calcite in the veinlets increases. As Yushko emphasizes, the metals in this stage of mineralization are localized in diagenetic fissures and desiccation cracks in the carbonate rocks containing the ore of the first stage of mineralization. Some of the difference in the mineral composition and paragenesis of the chemical elements may be due to their having been removed from the carbonate rocks in the course of the latter's diagenesis and metamorphism.

In his study of the ores of the Mirgalimsay deposit, Zorin called attention to the fact that the most common of the structural-mineralogical varieties of carbonates of the ore-containing horizon are dolmicrite and micrite (fine-grained pelitomorphic dolomite and calcite, respectively), and also dolspar and spar (recrystallized dolomite and calcite with grain sizes more than 0.01 mm), formed as a result of recrystallization of the pelitomorphic components.

According to Zorin, it can be clearly seen that the syngenetic impregnations of the lead and zinc minerals are directly related to the pelitomorphic structural components of the rock (dolmicrite) and inversely related to the dolspar — that is, with an increase in the amount of dolspar, the number of minute impregnations and fine veinlets of sulfides (0.02-0.2 mm) diminishes and the number and size of the galena aggregates increases.

Some interesting data on the Sumsar stratiform deposit are cited by V. I. Zlobinskiy, who distinguishes two types of ore mineralization: syngenetic-sedimentary and redistributed. In his opinion, the two types of mineralization have both common and different features. The features they have in common are the following:

a) the ore mineralization does not extend beyond the contact surfaces of the ore-containing horizon — that is, the redistribution of the ore mineral occurred mainly within the horizon;

b) the composition of the redistributed ore is similar to that of the primary ore; both types of ore mineralization lack the elements characteristic of the hydrothermal deposits of this region, such as tin, bismuth, tungsten, molybdenum, etc.;

c) if one component, such as the copper in the lower horizon, predominates in the syngenetic mineralization, it will also predominate in the ore after redistribution — that is, the geochemical specialization is inherited.

The distinctive features in which the syngenetic-sedimentary concentrations of lead and zinc differ from the redistributed in the Sumsar ore deposit may be presented as follows (after V. I. Zlobinskiy):

Syngenetic-Sedimentary	Redistributed
1. Universally increased concentrations of Pb, Zn and Cu	1. High dispersion of contents of metals, from very high values to very low
2. Even distribution of ore mineralization and low dispersion of contents	2. Appearance of zonality close to that of endogenic deposits
3. Existence of stratigraphic and geochemical specialization	3. Appearance of areas of concentration (ore bodies) and areas of lean ores
4. Existence of correlation between contents of lead and silver (silver present as isomorphous admixture in composition of galena).	4. Disruption of correlation between contents of lead and silver, appearance of relationship of silver to copper and arsenic (silver forms independent minerals — freibergite).

Thus the above data indicate redeposition of the ore and vein minerals of initially sedimentary formation. Moreover, the areas of favorable structures are often enriched in lead and zinc minerals, sometimes leading to the formation of ores with industrial contents of these metals. The redeposited ore bodies in many respects resemble hydrothermal formations of magmatic origin.

Approximate calculations show that the amount of lead and zinc of primary sedimentary origin redistributed in the ore-containing horizons is sufficient for the formation of relatively large ore deposits. Thus, for example, the average content of lead in the ore-bearing horizon of the Sumsar deposit is 0.25% — that is, 1 m^3 of dolomites contains 62.5 kg of lead; the thickness of this horizon is 30 m. Consequently the total quantity of lead distributed over an area of 1 km^2 will be

2,875,000 metric tons, enough to form a very large ore deposit.

In the second lenticular horizon of Famennian deposits in the Karatau region (the Kyzyl-Ata facies), the lead content is 0.02%, corresponding to the presence of 50 kg of lead in every 1 m^3 of dolomites; the average thickness of this horizon is 15 m. Hence the total amount of lead within an area of 1 km^2 will be 750,000 metric tons.

Data are still insufficient on the temperature of the solutions determining redeposition. According to E. Roedder (34), the redeposited ores of the Pine Point deposit in Canada were formed at temperatures of 50-100°. As T. Galkevich points out (5), according to N. P. Yermakov's investigations the ore minerals in certain lead-zinc deposits of Upper Silesia were formed at temperatures of 50-120°. According to G. A. Gorbatov, the first-generation galena in the deposits of the Karatau range has an electromotive force corresponding to a temperature of formation of 45-60°, whereas the galena of the fourth generation corresponds to temperatures on the order of 200-300° (28).

Thermosound analysis of the quartz, sphalerite and galena from the sulfide occurrences in the epigenetically altered sandstones of the Dnestr region showed that the temperature at which they were formed did not exceed 50-60° (12).

There are still fewer data on the chemical composition of the solutions determining the redeposition of the primary-sedimentary mineral associations. Roedder (34) states that the sphalerite in the ores of the Pine Point deposit was precipitated from solutions with a very high concentration of salts, the dolomite from solutions with lower concentrations and the calcite from solutions with still lower contents of salts. Roedder believes that the ore minerals in the Pine Point deposit were leached out by hot solutions seeping through the sedimentary rocks or the crystalline basement, whereas the sulfides were deposited under conditions in which these solutions became mixed with a comparatively small amount of relatively fresh, cold surface waters.

Many investigators have remarked that stratiform deposits often lie close to regional faults (5, 7, 33). This fact probably has two explanations. On the one hand, the regional faults often form the boundaries between areas of sedimentation and uplifts that were the source areas of various compounds, including lead and zinc. On the other hand, tectonic movements have occurred along the zones of regional faults even in recent times; such movements created paths for the hydrotherms that moved up from the deeper zones of the earth's crust and redeposited minerals of initial sedimentary formation. These solutions most often appear to be of magmatic origin. In Yushko's opinion (28), such may be the origin of the solutions that precipitated the minerals of the fourth stage of formation of the ores in the lead-zinc deposits of the Karatau region. The mineral associations of this stage differ sharply from those of the preceding stages: the fourth stage here is characterized by the appearance of sulfides of copper and silver and also magnetite, hematite, ankerite and fluorite and by the presence of a large number of elements as admixtures (cadmium, germanium, gallium, indium, etc.).

However, under specific conditions already mentioned above, these thermal waters were not necessarily of magmatic origin; the syngenetic complex of minerals, including lead and zinc, can also be dissolved in heated ground waters or in waters of metamorphic origin arising in the course of epigenesis and metamorphism of clay and sandy rocks containing hydroxide minerals.

For confirmation of the last proposition let us turn to the experiments of B. N. Robinson (36), who heated a mixture of pyrite and rock (pyroxenite, limestone and coaly shale) at the temperature of 600° and pressures of 1 to 2.5 kbar for 10 to 12 days, adding HCl, NH_4Cl, NaCl and H_2O as mineralizing agents. After the pyrite was removed from the mixture it was found to be enriched in cobalt (6 times), nickel (3.7 times), copper (1.7 times) and to a lesser degree in lead and zinc, which do not enter the pyrite crystal lattice.

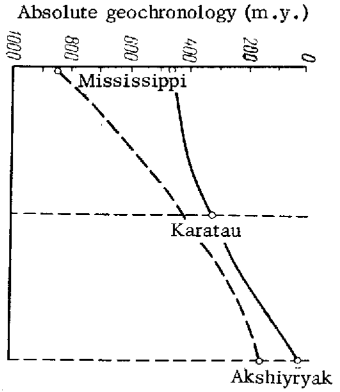
On the basis of his experiments Robinson concluded that the mineralizing solutions were formed in the dehydration of the rocks undergoing metamorphism at high temperatures and pressures and were enriched in metals from the surrounding rocks. In his opinion the concentration of metals in sulfide bodies will depend on the thermodynamic conditions of metamorphism, the initial contents of the dispersed elements in the pyrite and the host rocks, the duration of the reaction, and other factors. Impregnation deposits may arise at exceedingly high temperatures and pressures.

A. D. Shcheglov (27) has established that stratiform lead-zinc deposits are localized in areas and zones around the peripheries of reactivated regions within sedimentary complexes only slightly affected by the tectonic movements synchronous with the reactivation (such as the ore deposits of Upper Silesia and the Rhine zone in the northern frame of the activated region of the Czech massif, the Lozère zone in the south of the massif of central France, and elsewhere). A similar tectonic position probably characterizes the ore deposits of the Karatau area, in the immediate vicinity of the northern Tien Shan median massif, the stratiform ore deposits of the Lake Baykal region, which are confined to the boundary between the Siberian Platform and the Baykalian zone of folding, and others.

The activation processes lead to the renewal of tectonic movements along regional faults, to the ascent of hydrotherms from the depths and also to a change in the geothermal gradient in that particular area of the earth's crust, thus raising the temperature of the ground waters and increasing their solvent capacity.

The likelihood that stratiform lead-zinc deposits are of primary sedimentary origin is also confirmed by isotope analysis of the lead. The very important materials data on this matter are summarized by V. I. Smirnov (20), who notes that according to the isotope ratios of the lead from the galenas of many stratiform deposits, this lead is older than the host rocks containing the ore bodies. This is hard to explain from the standpoint of the usual hydrothermal origin of the stratiform ores. According to the age of the galena, the ores of the deposits in the Mississippi-Missouri region contained in Lower Paleozoic rocks turn out to be Precambrian, the ores of the Karatau deposits in Middle Paleozoic rocks are Early Paleozoic and the ores of the Akshiyryak deposits of the Tien Shan region, which lie in Paleogene rocks, are Upper Paleozoic (see figure). Smirnov believes that this has caused many geologists to speak of the mobilization of older lead on the paths of ascending solutions circulating through the underlying rocks and its redeposition in the galenas.

L. N. Grinenko and V. A. Grinenko (8) distinguish two types of deposits, according to the isotope ratios of the sulfur in the sulfides. In the first of these, to which the copper-pyrite deposits of the Urals and the northern Caucasus belong, as well as the copper-pyrite and pyrite-polymetallic deposits of Japan, the composition of the sulfur differs very little from that of the sulfur in meteorites (S^{34} is from -0.15 to +0.4%). On this basis we believe that the sulfide sulfur here is of mantle origin — that is, it may be derived both from the mantle and from the basaltic layer of the earth's crust.



Age of telethermal deposits of lead ores by geological data (solid line) and by the isotopic ratios of the metal (dotted line), from V.I. Smirnov.

The deposits of the second type, to which the Grinenkos assign the stratiform lead-zinc deposits of the Mississippi-Missouri region and the southwestern part of Sardinia, and also the cupriferous sandstones of Rhodesia and the uranium deposits of the Colorado plateau, are characterized by substantially different isotope ratios of the sulfur (S^{32}/S^{34}) in the sulfides and by a wide range of fluctuation in isotope composition. In their opinion the sulfide sulfur here was formed from different crustal sources (probably from the sialic layer), and the solutions that deposited the sulfides were not homogeneous. As one reason for the wide dispersion of the sulfur's isotope composition, the Grinenkos mention the possible formation of sulfides from biogenic hydrogen sulfide. American investigators (31) have shown that sulfate sulfur predominates in the composition of the sulfides of stratiform lead-zinc deposits.

A. I. Tugarinov (24), in studying the isotope composition of the lead from the galenas of the deposits of the Kuraminskiy and Chatkal ranges in Central Asia, called attention to the fact that a distinctive feature common to these deposits, despite the great distances between them, is the constant isotope composition of the lead of their impregnation ores, which are confined to carbonate rocks of Devonian (Sumsar deposit and others) and Carboniferous (Gavasayskoye ore occurrence) ages. The lead of the skarn deposits confined to the contact of the carbonate rocks with Hercynian intrusives and of the vein deposits contained in intrusives or volcanogenic rocks of Permian age is distinguished by its far more variable isotope composition and greater content of radiogenic isotopes. From these facts Tugarinov concludes that in the selective assimilation of the Middle Paleozoic limestones by the Hercynian intrusives, the older lead previously existing in them was removed. He believes that the Hercynian magmatism promoted mainly the redeposition of ore material and the formation of ore deposits in their present form, whereas the primary accumulation of the lead in the rocks of this region occurred in Devonian and Early Carboniferous times.

Thus there appears to be a long interval between the rise of the syngenetic lead-zinc mineralization and the formation of the redeposited ores. In the case of the Sumsar deposit this interval lasted from the Givetian age of the Devonian to the Middle or Late Carboniferous, when the granitoid batholiths were injected in the Chatkal-Kuraminskaya zone of the Tien Shan (14). For the ore deposits of Upper Silesia this interval was from the Middle Triassic to the Paleogene, when the basalt plutons were intruded into the adjacent zone of Alpine structures of the Carpathians (5).

Thus the lead and zinc contained in the rock-forming minerals of magmatic rocks or in the ore bodies of old deposits are dissolved as a result of weathering and subsequent solution by surface or ground waters, and transported into marine basins and under favorable circumstances redeposited in particular areas of these basins. In this case lean accumulations of sulfides are usually formed, although one cannot exclude the possibility that concentrations of metals of industrial significance may also be formed in this manner. Then, as a result of tectonic activation along old or newly formed faults, heated waters enter the area and again dissolve and redeposit the metals of syngenetic origin. In the areas of redeposition, ore bodies are formed that are no different in many features from the usual hydrothermal magmatogenic ore bodies.

Investigators generally use the term "genesis of deposits" to refer to the combination of conditions corresponding to some short-lived period in which the ores are deposited. The example of the stratiform lead and zinc deposits shows that the concentration of these elements is a process occupying a considerably longer segment of time, characterized by several stages of formation and redeposition of the material. These examples also show that the complex and prolonged history of the deposits often does not fall within the rigid framework of the existing genetic classifications. In this concrete instance one might use the seemingly paradoxical term sedimentary-hydrothermal deposits. We believe the question they have considered is part of a larger problem, inasmuch as such processes of redeposition of a relatively lean ore, which are in many cases typical of sedimentary bodies, are quite widespread.

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