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# Problems of Siderite Formation and Iron Ore Epochs: Communication 1. Types of Siderite-Bearing Iron Ore Deposits

**V. N. Kholodov and G. Yu. Butuzova**

*Geological Institute, Russian Academy of Sciences, Pyzhevskii per. 7, Moscow, 119017 Russia*

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**Abstract**—It is shown that siderite is unstable during sedimentation, diagenesis, and metamorphism of sedimentary and volcanosedimentary rocks. Regularities in the distribution of siderite in Precambrian jaspilites (iron formations), metasomatic ores of the Bakal type, continental–marine coaliferous formations, and oolitic iron ores are discussed. The genesis of the Precambrian iron formations and Riphean–Lower Paleozoic elisional–hydrothermal deposits is considered. The genetic relation of nodular siderites from coaliferous formations and oolitic iron ores with lowmoor coal-forming peat deposits is noted.

Strakhov (1947) was first to show that the iron ore formation was intermittent in time. During the Precambrian and Phanerozoic, one can distinctly recognize two types of epochs: (1) epochs characterized by the formation of numerous and often different-type iron ore deposits and (2) epochs characterized by the attenuation, reduction or even termination of the iron ore process.

In terms of mineralogy, iron ore deposits represent concentrations of carbonates, silicates, sulfides, and iron hydroxides. Sometimes, these deposits are monomineral, but usually they include ore bodies composed of variable mineral assemblages.

Carbonate minerals in iron ores are mainly present as siderite $FeCO_3$ represented by different varieties (Mn-bearing oligonites and Mg-bearing sideroplesites) and ankerite $Ca(Mg, Fe^{+2}, Mn)(CO_3)_2$.

Siderite is most widespread in sedimentary iron ores. Moreover, there are grounds to believe that precisely siderite is the primary mineral, the formation of which governed the ore-forming process. Therefore, our conception of the iron ore process turns out to be far from being complete without the reconstruction of siderite formation conditions.

The important feature of siderite is its extreme instability. Under the influence of oxygen, it is easily oxidized in accordance with the reaction $4FeCO_3 + O_2 \longrightarrow 2Fe_2O_3 + 4CO_2$. The product includes amorphous phase, goethite, hydrogoethite, hematite, and other iron hydroxides.

According to experimental data (Kissin and Pakhomov, 1967, 1969), heating of siderite with water at 75°C results in the formation of unstable hydroxide $Fe(OH)_2$ and carbon oxide. The bivalent Fe is easily dissolved in water in this process.

As was shown in (Schmidt, 1963; French, 1968; Morey; 1972; Klein, 1975), metamorphism of siderite within a wide temperature range can produce secondary silicate minerals, such as minnesotaite $Fe_3Si_4O_{10}(OH)_2$, greenalite $(Fe, Mg)_6Si_4O_{10}(OH)_8$, stilpnomelane $K_{0.6}(Mg, Fe^{+2}, Fe^{+3})_6(Si, Al)_6(O,OH)_{22}$, grunerite $(Fe^{+2}, Mg)[Si_8O_{12}](OH)_2$ in line with the following schemes:

$$\text{siderite} + \text{quartz} + H_2O = \text{minnesotaite} + CO_2;$$

$$\text{minnesotaite} = \text{grunerite} + \text{quartz} + H_2O;$$

$$\text{siderite} + \text{quartz} + H_2O = \text{grunerite} + CO_2;$$

$$\text{minnesotaite} + \text{magnetite} = \text{grunerite} + \text{quartz} + H_2O + CO_2; \text{ and}$$

$$\text{stilpnomelane} = \text{grunerite} + \text{Fe-hornblende} + \text{quartz} + H_2O\ (+\ K_2O).$$

It is clear that all secondary transformations of siderite deposits, including the hypergene weathering and oxidation of ores by atmospheric oxygen, the subsidence to elision systems and hydrolysis, or more intense metamorphic alterations at high temperatures and pressures, equally result in the destruction of siderite deposits and the replacement of siderites by other minerals.

Because of the ephemeral character of siderite deposits, regularities in their spatial distribution require special reconstructions and will remain vague for a long time.

The purpose of this work is to summarize all the available data on the genesis and temporal distribution of siderite deposits and adequately interpret their patterns.

## PRECAMBRIAN IRON FORMATIONS AND SIDERITE FACIES

Iron formations mainly developed in the Precambrian represent iron ores composed of alternating layers of quartz or jasper material and ore minerals (magnetite, martite, hematite, iron silicates and carbonates, pyrite, manganese minerals) from 0.1 to 20 mm thick. Locally, the layers are grouped into cycles. The largest

Comparative characteristics of Precambrian iron formations and associated iron ore deposits

| Specific features of defined iron formations | Type of iron formations | |
|---|---|---|
| | Algoma type | Lake Superior type |
| Stratigraphic distribution | Prevalent in the Archean but distributed in a wide stratigraphic interval from the Archean (Michipicoten, Ontario in Canada) to Cambrian (Dzhetymtau, Kyrgyz Republic), Ordovician (Bathurst, England), and Carboniferous (Tynagh, England) | Form almost coeval large basins in the stratigraphic interval of 2.0 to 2.5 Ga at the Archean–Proterozoic boundary (Lake Superior, Canada; Minas Gerais, Brazil; Transvaal, South Africa; Krivoi Rog, Ukraine; KMA, Russia; and Hamersley, Australia) |
| Structural position | Greenstone belts of cratons and riftogenic depressions | Pericratonic basins and synclinoria complicated by longitudinal faults |
| Relationships with volcanics | Iron formations are replaced by various volcanic sequences along the strike | Usually subsynchronous volcanics are absent, although they occur in adjacent stratigraphic intervals |
| Facies–mineralogical features | Major sulfide (pyrite and pyrrhotite) and carbonate (siderite and ankerite) facies; subordinate iron oxides (magnetite, martite, and hematite) and silicates | Major oxides (magnetite, martite, and hematite), carbonates (siderite and ankerite), and silicates; sulfide facies is reduced or even absent |
| Geochemical characteristics | Ores of iron formations are very similar in the contents of main components and accessory elements. In Eu/Sm ratio and Nd isotope composition, iron formations (2.3–3.8 Ga) are similar, but differ from their younger counterparts | |

iron ore deposits are associated with iron formations (Strakhov, 1947; James, 1983; Kholodov and Butuzova, 1999, 2001).

Following Gross (1965, 1980), most of researchers distinguish nowadays two (Algoma and Lake Superior) types of iron formations. Their comparison is given in Table 1.

Based on the mineralogical–paleogeographic studies, James (1954, 1983) defined four facies groups among iron formations: oxide group (magnetite, martite, and hematite), carbonate (siderite and ankerite), silicate (greenalite, stilpnomelane, and minnesotaite), and sulfide (pyrite and less common pyrrhotite). They are observed in iron formations of both the Algoma and Lake Superior types, although the sulfide and carbonate facies usually prevail in iron formations of the first type, while the oxide, carbonate, and, to a lesser extent, silicate facies dominate in deposits of the second type (Table 1).

The study of iron formation (Algoma type) in the Michipicoten area of the Ontario Province, Canada allowed Goodwin (1973) to demonstrate that the oxide facies are successively replaced in deeper zones by the carbonate and sulfide facies (Fig. 1a). Menard (1981) summarized the data reported by D.A. White, V.M. French, R.W. Mersden, and G.B. Morey who studied the Lake Superior-type Biwabik–Gunflint iron formation in Minnesota (the United States) and established that the shallow-water facies of granular quartzites are separated from the deeper banded facies by several transitional mineralogical–geochemical associations ranging from the hematite–magnetite variety to the silicate (minnesotaite, grunerite, and stilpnomelane) and carbonate (siderite and ankerite) varieties. This succession corresponds to the transition from the shallow- to deep-water settings (Fig. 1b).

Because of difficulties in defining the prevalent indicative minerals in the intricately alternating laminated polymineral rocks, the recognition of mineralogical–geochemical facies in iron formations is an arduous task.

Therefore, some researchers (Plaksenko, 1959, 1966; Strakhov, 1960, 1963; Plaksenko *et al.*, 1972) described a somewhat different (reversed, according to Strakhov) type of the mineralogical–geochemical zoning in the Kursk Magnetic Anomaly (KMA) iron ore basin in Russia (Fig. 2a).

Tracing transitions of the iron formation into coastal facies, Plaksenko (1959, 1966) established that its analogues in the shallow-water zone are represented by terrigenous sediments (sands, siltstones, and clays altered to quartzites and schists). He identified the following facies succession within the iron formation along the profile between Yastrebovka in the southeast to Tim in the northwest: silicate–carbonate facies, magnetite facies, and hematite facies that mark the transition to the deepest-water settings.

The indicator-minerals behave in accordance with the increase of oxidizing potential in deep-water sediments of the paleobasin and make up the following succession: pyrite–siderite–magnetite–hematite (Fig. 2b).

It is still unclear which of the two defined mineralogical–geochemical zonings is typical of the Precambrian iron formations. This debatable issue needs special mineralogical–geochemical studies of iron formations.

Nevertheless, it is evident that the siderite facies is a universal and widespread constituent of the facies succession in the Precambrian iron formations.

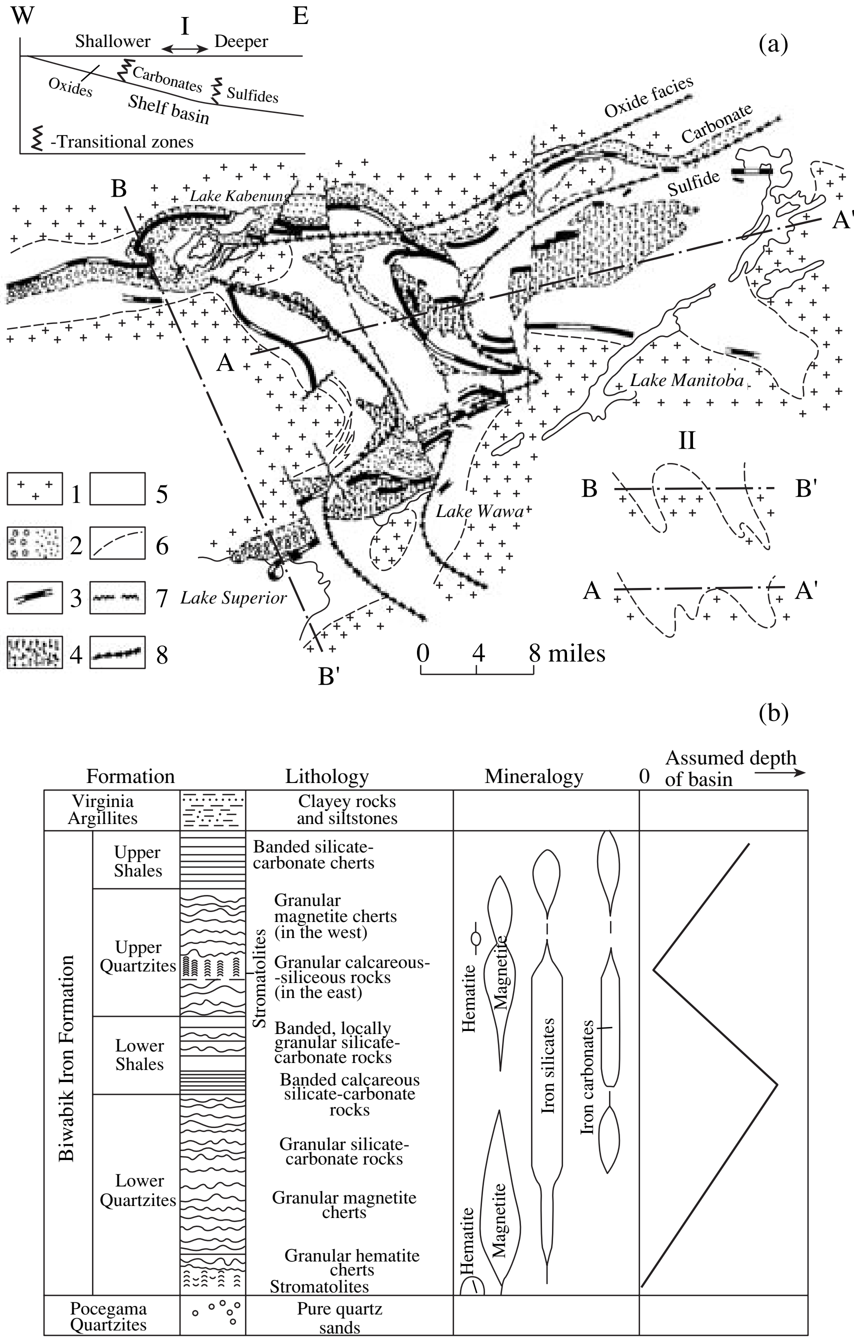



**Fig. 1.** Normal mineralogical–geochemical zoning in Precambrian deposits. (a) Distribution of iron formations in the Michipicoten Basin (Goodwin, 1973). (1) Granites; (2) deepwater sediments (left part): conglomerates, graywackes, and shales; (3) iron formation; (4) felsite volcanics; (5) mafic volcanics; (6) geological boundaries; (7) faults; (8) gradual or approximate boundaries of iron formations. (I) idealized section across the Michipicoten Basin demonstrating relationships between facies with the depth increase; (II) the structural cross section. (b) Stratigraphic column of the Biwabik iron formation in Minnesota, the United States. Compiled by Menard (1981) using data of W.A. White, V.M. French, R.W. Mersden, and G.W. Morey.

It should be emphasized that, despite the close spatial relation between the paleogeographic setting in the paleobasin and the composition of ore minerals in various facies of iron formations, the formation of ore mineral associations is presumably an intricate and multistage phenomenon including sedimentation, diagenesis, superimposed processes of catagenesis and regional metamorphism, and hypergene weathering.

Using the iron formations of the Chara–Tokkin deposit in the Aldan region and some other deposits of Siberia and Khingan as example, Timofeeva (1987)

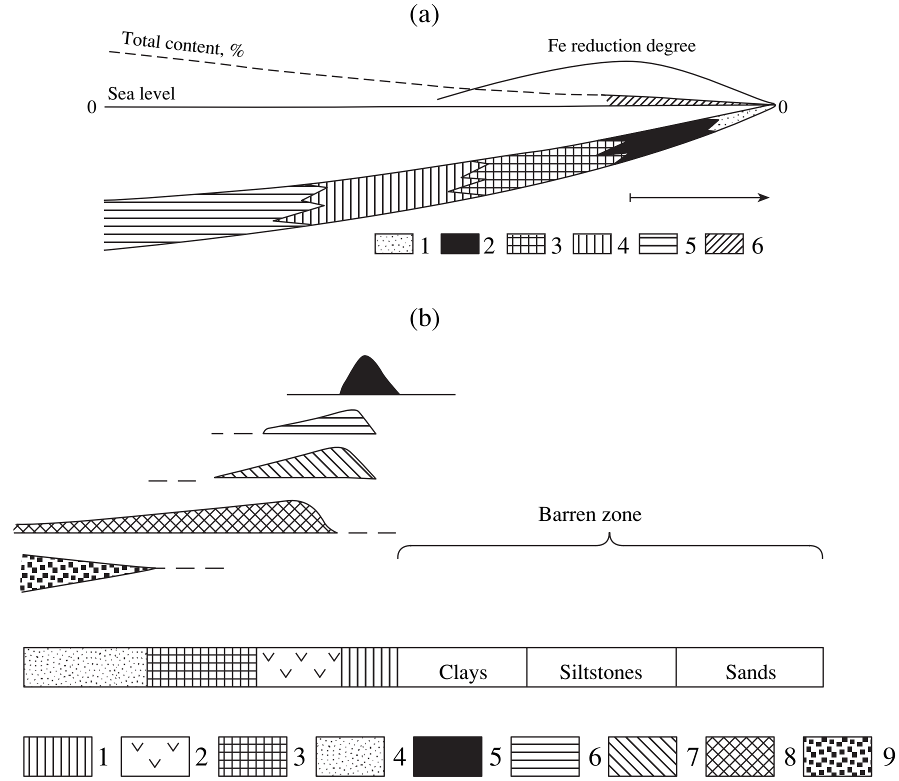



**Fig. 2.** Reverse mineralogical–geochemical zoning in Precambrian deposits. (a) Schematic mineralogical–geochemical zoning in the iron formation (Strakhov, 1960). (1, 2) Barren facies: (1) sandstones and siltstones, (2) shales; (3–6) ore facies: (3) silicate and siderite hornfels with pyrite, (4) magnetite hornfels, (5) hematite hornfels, (6) clarke Fe contents. (b) Authigenic mineralogical zoning along the facies profile of the ferruginous–siliceous–shaly formation (Plaksenko *et al.*, 1972). Rock types of the KMA iron formation: (1) low-ore and barren quartzites, (2–4) quartzites: cummingtonite–magnetite (2), magnetite (3), and hematite–magnetite (4); (5–9) indicator-minerals: (5) pyrite, (6) siderite–pistomesite, (7) iron silicate (cummingtonite), (8) magnetite, (9) hematite.

demonstrated that metamorphic alterations completely inherit sedimentation and diagenesis settings.

The succession of mineral formation in the Precambrian iron formations was studied by many works of Yu.A. Aleksandrov, Ya.N. Belevtsev, G.L. La Berge, I.I. Chauvel, E. Dimroth, V.S. Fedorchenko, B.M. French, Yu.G. Gershoig, F.F. Grond, G.W. Gruner, C.R. van Hise, A.A. Illarionov, H.L. James, P.P. Kanibolotskii, C. Klein, F. Lepp, R.V. Mersden, G. Persival, B.I. Pirogov, V.V. Pirogova, E. Spenser, N.I. Svital'skii, V.P. Troshchenko, D. F. White, and others.

Best studied are the Lower Proterozoic iron formations of the Lake Superior area (Mesabi, Gunflint, Guyuna, and Biwabik formations (Minnesota, the United States) and approximately coeval iron formations of the KMA and Krivoi Rog areas (Russia and Ukraine).

Most of the researchers believe that iron formations of the Lake Superior area are typical chemogenic and biochemogenic sediments. Textural relationships between different ore components suggest that siderite, "primary silicate," and amorphous silica with iron hydroxides were the primary minerals formed in sediments of the paleobasin (Gruner, 1946; James, 1954; White, 1954). Many researchers assume that magnetite and, probably, greenalite are also primary minerals. However, La Berge (1964) and French (1968) concluded that magnetite is a secondary mineral in the Biwabik iron formation.

The comparison of more and less metamorphosed areas in the Biwabik iron formation (the Gunflint and Kuyuna zones) reveals that Fe-silicates (greenalite, minnesotaite, and stilpnomelane) are more abundant in the more metamorphosed variety (Morey, 1972). Previously, White (1954) had showed that they are confined to certain stratigraphic intervals. On the whole, most of the Canadian and American researchers consider minnesotaite and stilpnomelane as typical metamorphic minerals.

In addition to minnesotaite and stilpnomelane, riebeckite (crocidolite) is widespread in the Kuruman iron formation of the Witwatersrand Group in South Africa (Fockema, 1967; Bukes, 1973) and in the approximately coeval iron formations of the Mount Bruce Supergroup in Western Australia (Trendall and Block-ley, 1970; Trendall, 1975). This amphibole

($Na_2Fe_3^{+2}Fe_2^{+3}[(Si_8O_{22})(OH,F)_2]$) associated with magnetite and siliceous material forms extended beds and probably is of metamorphic origin.

Similar data were obtained by the Russian and Ukrainian scientists during the study of the mineral composition in iron formations of the Krivoi Rog and KMA areas.

Semenenko (1955) and Gershoig (1937, 1940, 1956) emphasized the primary character of iron carbonates in the Krivoi Rog iron formations. Gershoig substantiated the following stages of mineralization in iron formations of the Ingulets and Saksagan areas:

(1) Sedimentation and diagenesis: iron carbonate (siderite), iron hydroxides, opal matter, clayey material, Fe-chlorites;

(2) Metamorphism: magnetite, hematite, siderite, dolomite, riebeckite, sericite, muscovite, sulfides; and

(3) Weathering: magnetite, hematite, limonite, hydrogoethite, opal matter.

This author emphasized that the primary mineral composition was probably completely changed by the subsequent metamorphism. Only relicts of primary siderite indicate a substantial role of iron carbonates in sedimentation and diagenesis. In addition, Gershoig (1956) affirmed that metamorphogenic magnetite formed after the primary siderite.

Fedorchenko (1956) also studied the Krivoi Rog iron formations and concluded that siderite is the main and most widespread mineral in ore-bearing rocks. He believed that magnetite autonomously formed at the diagenesis stage and did not replace siderite. On the whole, Fedorchenko showed that the Krivoi Rog iron formations can be divided into numerous siderite facies.

Tochilin (1952, 1956) and Tugarinov *et al.* (1972) contended that the wide distribution of siderite, stadial relationships of this mineral with magnetite, and relative depletion of iron formations of the KMA and Krivoi Rog areas in accessory elements unambiguously indicate the primary carbonate nature of iron formations.

We do not share such extreme conclusions. However, we should emphasize that the role of siderite facies in the Precambrian ore formations was undoubtedly significant. Moreover, it was evidently substantial in deposits of both Lake Superior and Algoma types.

In all likelihood, the primary role of siderite facies in the composition of iron formations reflects two specific features of the Precambrian Earth: 1) the steady existence of $CO_2$-rich atmosphere until 2.2 Ga ago and subsequent transition to the oxygen atmosphere; (2) the paramount influence of the volcanogenic-hydrothermal Fe influx, which was comparable with the quantity of terrigenous material.

The issue of the atmosphere evolution in the Earth's history was considered in works by A. B. Burkner, M.I. Budyko, P. Cloud, E.M. Galimov, H.D. Holland, L. Marshall, A.B. Ronov, A.V. Sochava, N.M. Strakhov, V.I. Vernadsky, A.P. Vinogradov, V.I. Vinogradov, A.L. Yanshin, and many other scientists. At present, one can outline three groups of factors that served as the basis for concepts of oxygen atmosphere development.

(1) The wide distribution of reductive facies in Precambrian (Archean) sequences and the appearance of typical redbeds in the younger (Proterozoic) sections (Anatol'eva, 1978; Holland, 1989; Sinitsyn, 1990).

(2) The finds of rounded uraninite (and pyrite) grains in gold-bearing conglomerates underlying iron formations of the Lake Superior type. According to recent data, they are older than the conglomerates (Shidlowski, 1968; Rundle and Shelling, 1977; Meddaugh, 1983).

(3) The sulfur isotopic composition. Study of the sulfur isotopic composition in sections spanning the time interval of 3.7–1.0 Ga (Shidlowski, 1981; Vinogradov *et al.*, 1976; Hattori *et al.*, 1985) revealed that the oxygen atmosphere, which was compositionally close to the present-day one, formed during the period corresponding to deposition of iron formations of the Lake Superior type. As is evident from Fig. 3, the $\delta^{34}S$ data scattering increases in the post-Archean time, particularly in the Michipicoten and Woman River iron formations and the Sudbury Province. At the same time, precisely the transition from stable $\delta^{34}S$ values to their variations indicates the involvement of processes of the oxidation of sulfide sulfur to sulfate sulfur, the subsequent selective extraction of light sulfur isotopes by microorganisms in semiclosed systems, and the formation of new sulfides.

In one of our previous works, we considered the issue of matter source in the formation of Precambrian iron ores (Kholodov and Butuzova, 2001) and made the following conclusions:

(1) Ores of the Algoma type (undoubtedly related to volcanogenic processes) and ores of the Lake Superior type (related to unclear genesis) are similar in the geochemical composition (Gole and Klein, 1981).

(2) All Precambrian ores older than 2.3 Ga are characterized by the positive Eu anomaly (Danielson *et al.*, 1992; Bau and Moller, 1993). The Eu anomaly is typical of modern oceanic iron formations linked to the hydrothermal process (Michard, 1989; and others);

(3) The mass balance of Nd isotopes suggests that the influx of material from the hydrothermal source in the Hamersley iron formation (2.35–2.65 Ga) was as high as 50% (Albert and McCulloch, 1993).

It should also be noted that huge quantities of Fe accumulated in iron formations can be explained only by the combined contribution of the sedimentary and hydrothermal sources. Indeed, according to calculations by Holland (1989), iron formations of the world formed during the period of 2.5–2.0 Ga enclose approximately $2 \times 10^{14}$ t of iron.

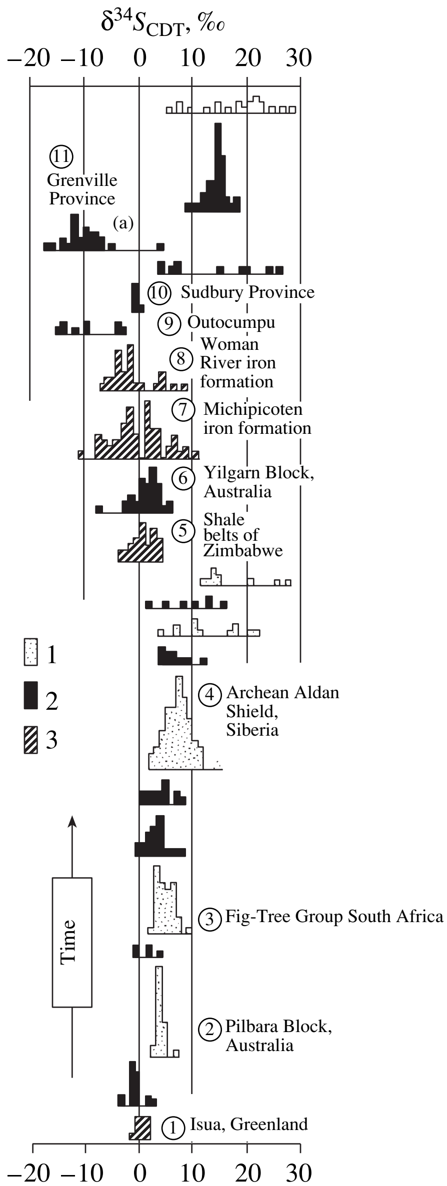



**Fig. 3.** $\delta^{34}S$ variations in sedimentary sulfides in the 3.7–1.0 Ga interval (Schidlowski, 1979). (1) Sedimentary sulfates; (2) sedimentary sulfides; (3) sedimentary sulfides associated with iron formations.

The *present-day* annual Fe influx to the World Ocean is considered insignificant ($9.47 \times 10^8$ t), including $9.45 \times 10^8$ t contributed in the silicate and organomineral form and only $0.02 \times 10^8$ t in the form of solutions (Gordeev, 1983). Thus, it becomes clear that the modern conditions are not suitable for explaining the Precambrian ore-forming processes.

When reconstructing pre-Proterozoic continental settings, one should take into consideration that drainage basins of that time enclosed a huge quantity of Fe. Its main sources were komatiites, iron formations, and basic volcanics of Archean greenstone belts, spacious Fe-rich basic and ultrabasic plutons formed during the post-Archean tectonomagmatic cycle (Stillwater and Laramie, the United States; Glavnyi Ridge pluton of the Kola Peninsula, Kolar, and Dhugdzhur, Russia; Fiskanisset, Greenland; the Great Dike, Zimbabwe; and many others), as well as paragneisses and crystalline schists, which are widespread throughout Archean continents, with the average Fe content ranging from 4.4 to 7.91% (Ronov, 1980). Even Precambrian granitoids contain approximately 13 674 g/t of magnetite, which is an order of magnitude higher than its average content in Phanerozoic granitoids (Lyakhovich and Sidorenko, 1986).

The oxygen deficiency in the atmosphere and carbonic acid weathering provided the almost complete release of bivalent Fe from the parental substrate and its active transfer to terminal drainage basins. However, it should be emphasized that, like the present-day basins, Early Proterozoic basins undoubtedly received Fe in both dissolved and suspended forms (silicate and carbonate phases).

The submarine hydrothermal activity in the Early Proterozoic probably differed from the modern one. Because of the relatively thin crust, the hydrothermal Fe flux was governed by the mantle rather than the water circulation in basalts. According to calculations reported in (Ringwood, 1969), the average Fe content in the mantle is 6.5%, almost 95% of which are represented by the hydrothermal mobile form. The influx of hydrothermal Fe to sedimentation basins was also stimulated by the sharp intensification of magmatic differentiation in the upper mantle during the period of 3.5–2.5 Ga and the probable prevalence of the vertical differentiation over the horizontal one (Ringwood, 1969).

Favorable conditions for the Early Proterozoic iron ore epoch were mainly created by *planetary* factors. Therefore, the formation mechanism of separate iron ore deposits or basins should also be controlled by global processes, although it can vary depending on particular settings.

Unfortunately, the insufficient knowledge of iron formations hampers the elaboration of adequate models of their formation. For instance, one can hardly agree with the ore genesis model proposed by Borchert (1952, 1960), Holland (1973, 1978), and Drever (1974). According to this model, the World Ocean is the main source of Fe and upwellings delivering Fe from the reducing and deep zones of the ocean to the shallow-water oxidation zone is the major ore-forming mechanism. This model is undoubtedly inconsistent with the reverse geochemical zoning revealed by Strakhov and Plaksenko, abundance of carbonate facies in iron formations of the Lake Superior type, shallow depths of platformal seas with occasional deposition of ferruginous–siliceous sediments (Hamersley, Australia), and Fe and $SiO_2$ contents in the present-day coastal upwelling zones.

In our opinion, the elaboration of adequate models for explaining iron ore formation should lean upon a wider range of empirical data that fully characterize separate deposits. They should take into consideration specific features of iron formations in riftogenic and epicontinental paleobasins, initial distribution of organic matter, intensity of the microbiological activity in bottom sediments, probable microbiological precipitation of various Fe forms, and many other factors responsible for the concentration of ore components.

## PHANEROZOIC SIDERITE FORMATION

### *Siderite Deposits of the Bakal Type*

The Bakal group of deposits (more than 100 km$^2$ in area) is located in the western part of the southern Urals. It has been described in works of L.V. Anfimov, G.A. Braun, V.A. Filippov, A.M. Kalinskaya, M.T. Krupenin, O.P. Sergeev, M.L. Skobnikov, G.A. Sokolov, Z.M. Starostina, V.A. Timeskov, A.A. Yanitskii, A.N. Zavaritskii, and others.

In the Bakal deposit area, folded and eroded Archean rocks of the Tartash metamorphic complex are overlain by the Riphean (Burzyanian) sequence composed of the Ai, Satka, and Bakal formations.

The **Ai Formation** (1500–2000 m) consists of the lower conglomerate–sandstone–volcanogenic (Navysh) and upper sandy–shaly subformations.

The **Satka Formation** (2300–2500 m) is largely composed of dolomites and limestones alternating with marls and carbonaceous phyllite schists. The formation is subdivided into several subformations and characterized by significant lateral facies changes. Its lower part encloses ore-bearing carbonate rocks of the Akhten siderite deposit, while the upper part incorporates magnesite-bearing carbonates of the Satka deposit group.

The **Bakal Formation** (1200 to 1400 m) is the main ore-bearing sequence of the region. It is composed of alternating stromatolite limestones and dolomites with phyllite-type sericite–quartz–clay schists. In the Bakal deposits area, the formation is divided into two subformations and seven lithologically different (Makarov, Berezov, Irkuskan, lower Bakal, middle Bakal, upper Bakal, and Bulandikha) horizons. The lower and upper Bakal carbonate units enclose the Novyi Bakal, OGPU, Bulandikha, Shikhany, Ob'edinennoe, Vostochnoe, Rudnichnoe, Irkuskan, and other siderite deposits. The carbonate rocks also enclose magnesite (Shikhany, Ivanov, Bakal, Zolotaya Yama, and others), barite (Petlya), and polymetal (Pb, Zn, and Cu sulfides) deposits. The Lower Riphean rocks, the absolute age of which is estimated at 1650–1400 Ma (*Unifitsirovannye…*, 1980), are overlain with hiatus and angular unconformity by the Yurmatinian Zigal'ga (or Mashak) Formation composed of terrigenous rocks and basic volcanics.

In terms of tectonics, the area is referred to the Bashkir Anticlinorium, a large zone of nappes thrust over each other from the east to west (Kamaletdinov, 1986).

The deposits are confined to the Verkhnii Bakal Synclinorium in the central part of the first-order structure. The synclinorium, in turn, is complicated by faults and numerous third-order folds, axes of which coincide with the Shuida, Bulandikha, and Irkuskan ridges (Fig. 4a) and extend to northeast.

The siderite ore bodies occur among carbonate rocks and make up stratiform lodes, nests, lenses, and stocks from several tens to 2500 m long and from 2–4 to 80–100 m thick. Above the groundwater level, siderite ores grade into brown iron ores and turjaites that form gossans.

The siderite ores are composed of siderite, sideroplesite (Mg 5–30%), and pistomesite (Mg 30–50%). The Fe content varies from 27 to 45%. Reserves of pure (S- and P-free) siderite ores in the Bakal deposits are estimated at more than 1 Gt (Anfimov, 1997).

According to (Anfimov, 1978, 1982, 1997), siderite mineralization in the Bakal area is characterized by the following features: (1) ore bodies have intricate forms that are often inconsistent with the bedding in host rocks; (2) ore bodies cross facies and layer boundaries; (3) siderite lodes contain relicts of stromatolites and magnesites; (4) ores show signs of the metasomatic replacement of ore-hosting rocks (dolomites, limestones, and magnesites) by siderite; and (5) genetic relationships between the siderite content in formations and the abundance of intrusions are absent.

All these specific features allow siderite mineralization to be considered a typical epigenetic process superimposed on the sedimentary process during the Riphean, but they cast doubts on the concept of direct relations between ore formation and magmatism.

Using the geochronological method, Krupenin (1999, 2001, 2003) obtained results that are consistent with data reported in (Anfimov, 1997) and demonstrated that magnesites formed only a few tens of million years after the deposition of carbonate (host) sediments. The siderites accumulated 1100 Ma ago (Rb and Th–Pb isotope methods), i.e., 300–550 Ma after the deposition of carbonate sediments, whereas the barite and polymetal mineralizations are later phenomena related to the mantle sources. It should be emphasized, however, that the issue of Fe source for the Bakal deposits is less clear.

Anfimov convincingly demonstrated that phyllite schists of ore-bearing sequences are slightly depleted in Fe relative to their counterparts in ore-barren sequences. Reverse relationships are observed only in dolomites, which are relatively enriched in Fe and Mg in ore-bearing deposits. Siderite deposits are usually associated with zones of strong catagenetic rock transformation. Therefore, Anfimov concluded that Fe is mainly derived from clayey sequences altered in elision systems. A similar formation model was previously proposed for Jurassic iron ore deposits in the Greater Caucasus (Kholodov and Kiknadze, 1989).

In contrast to Anfimov (1997), Krupenin (2001, 2003) considers siderite mineralization a constituent of the Riphean metallogeny and emphasizes the signifi-

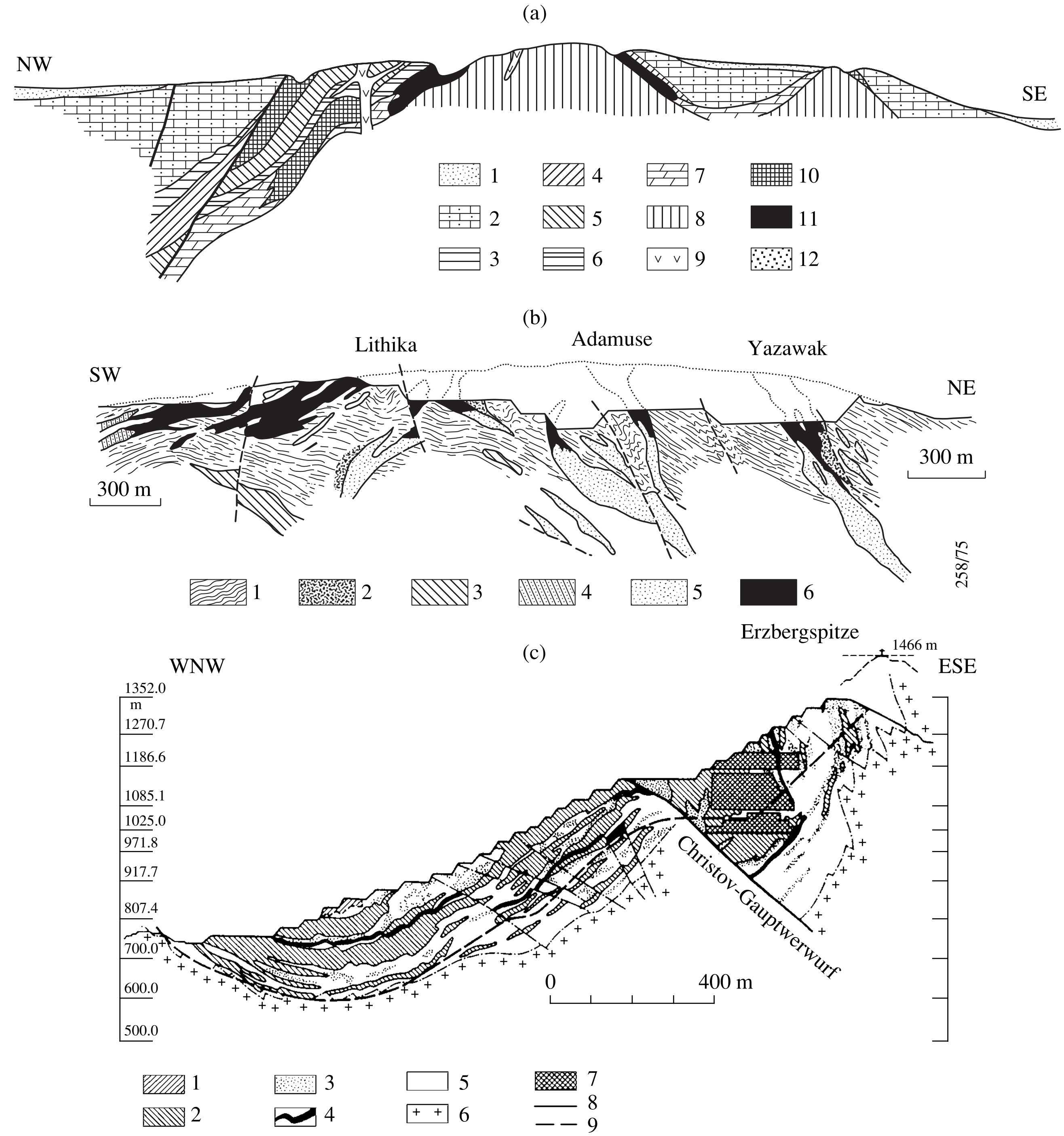



**Fig. 4.** Typical geological sections of the Bakal-type siderite deposits. (a) Schematic geological section of the Bakal ore field. (1) Quaternary sediments (talus, clayey–quartzose); (2–12) Proterozoic rocks: (2) Zigal'ga Formation (quartzites and quartz sandstones), (3–12) Bakal Formation: (3) shales and phyllites of the Bulandikha Horizon, (4) carbonate–clayey rocks and phyllites of the lower subhorizon, (5) Middle Bakal Horizon (undivided), (6) shales and dolomites of the lower subhorizon, (7) dolomites of the Lower Bakal Horizon, (8) shales and phyllites of the Irkuskan Horizon, (9) diabases and their destruction products, (10) siderite ores, (11) oxidized and semioxidized ores, (12) siderite–shaly and siliceous–shaly breccias. (b) Geological section of the Lubich deposit (Noth, 1952). (1) Paleozoic shales and sandstones; (2) metamorphosed shales; (3) Paleozoic limestones; (4) metamorphosed limestones; (5) siderites; (6) limestones. (c) Geological section of the Erzberg deposit (Zitzman and Neumann-Redling, 1977). (1) Exposed shales; (2) siderites; (3) ankerites; (4) deformed shales; (5) ore-bearing limestones; (6) porphyroids (quartzose keratophyres); (7) mines; (8) mines in 1959; (9) mines after 1959.

cance of mantle-derived components in the formation of the latest barite–polymetallic ore manifestations. Krupenin also affirms the major role of elision and exfiltration (hydrothermal) mechanisms in the formation of iron ores. According to this researcher, hydrothermal solutions could not only redeposit Fe within the ore-bearing formation (siderite–ankerite veins), but also deliver ore components from the crust and underlying rocks during the intensification of tectonic activity.

The concept of the Fe flux from the underlying metamorphosed Archean sequences is consistent with the abundance of ferruginous quartzites (jaspilites) in old rocks of the Tartash Complex in the Bashkir Anticlinorium. The Proterozoic complex of this region encloses two different-age ore-bearing sequences (Chebotarev and Naumova, 1971). According to Aleksandrov (1975), the lower ore-bearing unit characterizes the iron ore epoch of the Russian Platform and represents, in fact, the eastern continuation of the KMA and Krivoi Rog deposits.

Keeping in mind the significant role of siderite facies in the formation of Proterozoic iron formations and extreme instability of siderite during catagenetic metamorphic transformations, we can assume that ancient iron-ore sequences could actively affect the composition of Bakal hydrothermal solutions.

One cannot also rule out the Fe and $CO_2$ flux from deeper levels of the mantle. In modern hydrothermal systems of rift zones in the World Ocean, the Fe content ranges from 42 to 1046 mg/kg, which is several orders of magnitude higher than its concentration in seawater (Von Damm and Bischoff, 1987), and the $CO_2$ concentration amounts to 252–484 mg/kg (Mottle, 1983; Merlivat *et al.*, 1987). According to isotope data, the main share of $CO_2$ in hydrothermal solutions is of juvenile origin (Galimov, 1968).

Siderite deposits of the Bakal type are sufficiently widespread in Paleozoic–Mesozoic sequences of the world. All of them are localized in carbonate facies and bear signs of siderite or ankerite metasomatism.

The Bakal group includes the Abail deposit (Kazakhstan) confined to Cambrian–Ordovician sequences; the Erzberg, Polster, Tulljak, and Konnerslam (Austria), and Ziegerland (Germany) deposits connected with Devonian limestones; the Erzberg (Germany) and Lubich (former Yugoslavia) deposits localized in Carboniferous–Permian carbonate sequences; the Rudobanja deposit (Hungary) within Triassic carbonate rocks; and the Uenza (Algeria) and Bilbao (Spain) deposits occurring among Cretaceous carbonate rocks (Zavaritskii, 1939; Yanitskii and Sergeev, 1962).

Figures 4b, 4c demonstrates schematic geological sections of the Bakal, Lubich, and Erzberg deposits. They display striking similarity in occurrence conditions and forms of ore bodies. In addition, relationship between the siderite–ankerite mineralization and tectonic fractures is better manifested in the Lubich and Erzberg deposits than in the Bakal area. Moreover, siderite–ankerite bodies in the Lubich deposit are controlled by faults.

### *Continental–boggy Siderites Associated with Coaliferous Sequences*

Nodular stratiform ore bodies associated with coaliferous sequences sharply differ from all previous types of siderite deposits. They are described in works by P. Kukuk, R. Matsumoto, A.V. Makedonov, Chr. Neumann-Redling, T.H. Phillips, L.V. Pustovalov, I.W. Schopf, P.I. Stepanov, N.M. Strakhov, Z.V. Timofeeva, V. I. Yavorskii, M. D. Zalesskii, P.V. Zaritskii, Yu.A. Zhemchuzhnikov, A. Zitzman, and many others researchers. The siderite accumulations closely associate with coal seams and are usually localized in both paralic and limnetic sequences.

Significant siderite concentrations are established in the Upper Carboniferous paralic coaliferous sequences of Appalachians (the United States), central England, the Ruhr coal basin (Germany) and Donbas (Russia). Huge dimensions of these basins imply the significant role of siderite lodes in iron ore formation.

The Great Appalachian Basin (Fig. 5a), located in the territory of Pennsylvania, Virginia, Ohio, Kentucky, Tennessee, Alabama, and Georgia, occupies an area of 180000 km$^2$ and contains more than 400 Gt of anthracite coals. The Lower–Upper Carboniferous (Pennsylvanian–Mississippian) coaliferous sequences ranging from 700–800 to 1500 m in thickness are deformed into gentle synclinal folds. They contain 28–30 coal seams 1 to 3 m thick. The section is composed of alternating coal seams, sandstones, shales, and limestones. Siderite concretions, lenses, and beds are widespread in rocks underlying and overlying the coal seams.

In the 1980s, total coal reserves of England were estimated at 45 Gt. The coaliferous sequences of this country are confined to the Westphalian (Middle Carboniferous) Stage and localized in basins of the northern, central, and southern groups.

The northern group includes the Durham–Northumberland, Cumberland, and Scotland coal basins. They comprise 8–10% of coal reserves of the Great Britain. In addition, potential reserves of siderite ores with the Fe content of 28–44% are estimated at 590 Mt in the Northumberland and Cumberland basins.

The central group consists of the Yorkshire (Yorkshire–Derbyshire–Nottingham), Leicestershire, Warwickshire, Lancashire, Northern and Southern Staffordshire, and Northern Wales coal basins. The Yorkshire Basin hosts approximately 30% of the total coal reserves in the Great Britain. The potential reserve of siderite ores with the Fe content of 29–39% in the Yorkshire and Staffordshire basins, where they were intensely mined at the beginning of the last century, amounts to 2 Gt. Moreover, the deposits in the Staffordshire Basin were considered ore-bearing rather than coaliferous structures (Zitzman and Neumann-Redling, 1977).

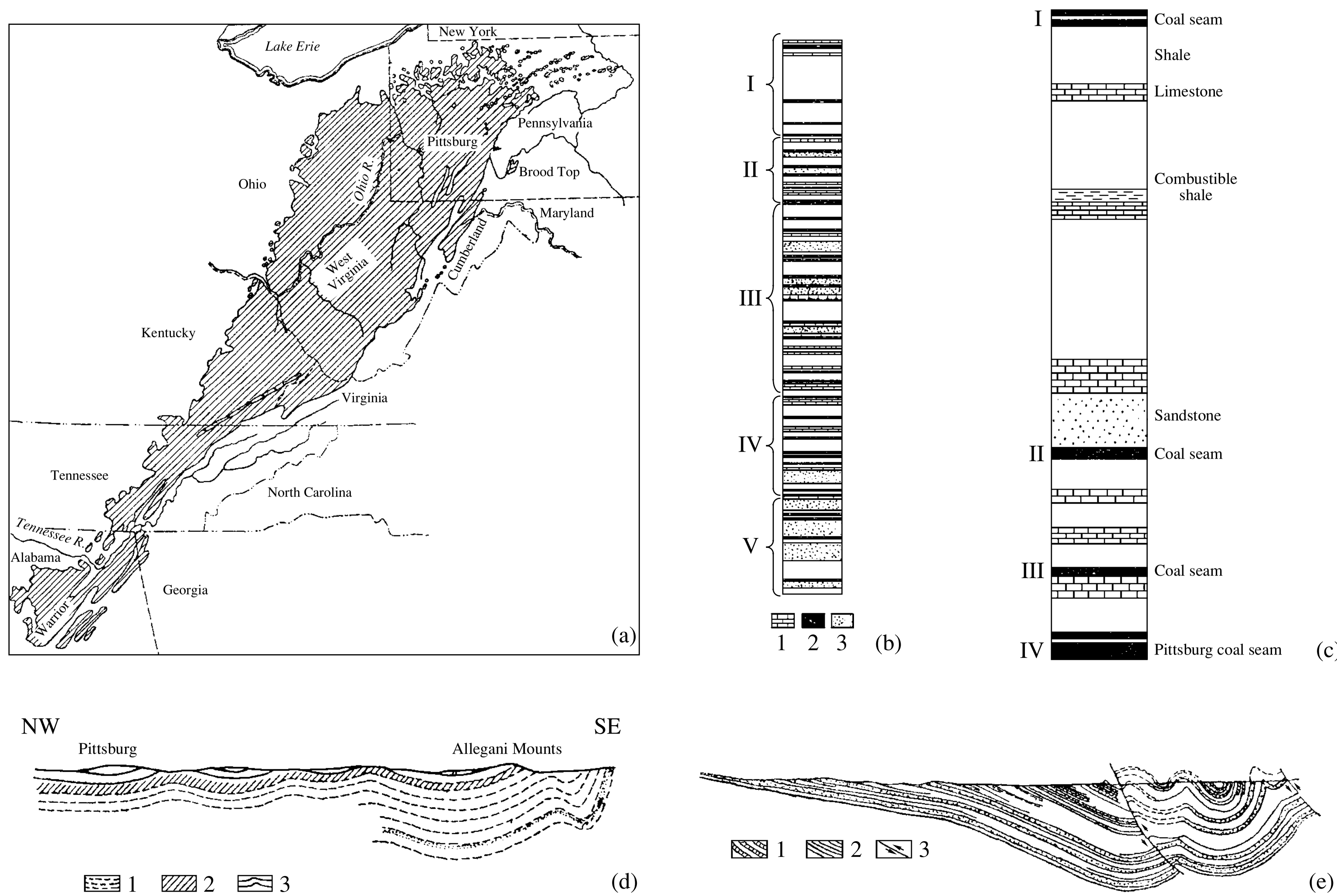



**Fig. 5.** Geological structure and coaliferous levels of the Great Appalachians Basin (Stepanov and Mironov, 1937). (a) Great Appalachians Basin (the coaliferous area is hatched). (b) Section of the coaliferous sequence in Maryland. (I–V) Bed groups: (I) Dunkard, (II) Monongahela, (III) Konymauch, (IV) Allegani, (V) Pottsville; (1) limestones; (2) coals; (3) sandstones. (c) Section of the Monongahela Bed group in western Virginia; (d) geological section of the Appalachians Basin in Pennsylvania: (1) Lower Paleozoic, (2) Mississippian (Pocono); (3) Pennsylvanian with coal seams; (e) geological section across the southern part of the Appalachians Basin (Cahaba Basin): (1) sandstones, (2) coal seams; (3) upthrow faults.

The southern group comprises the South Wales, Forrest-of-Dean, and Bristol–Somerset basins. The South Wales Basin has the highest significance. It is located north of the Bristol Bay and occupies an area of 2600 km$^2$, 400 km$^2$ of which is below the sea level. The Middle Carboniferous (Staffordian and Westphalian) coaliferous sequence (700–2800 m) is composed of coals, sandstones, and shales (Fig. 6a). The sequence forms a large sublatitudinal syncline complicated by numerous faults and second-order structures (Figs. 6b, 6c).

The coaliferous sequence encloses 80 coal seams. Generally, they include 12–25 productive seams with a thickness of 0.3–3.3 m. The coal density is 22.3 Mt/km$^2$ down to a depth of 1200 m. The South Wales Basin provides high-quality coals and ranks first in terms of anthracite production in England.

The Fe content in siderites at the base and top of coal seams ranges from 34 to 38% and their reserves is estimated at 2 Gt.

The Ruhr coal basin is the most important source of energy in Germany. Reserves in the basin account for approximately 25% of the total coal reserves of the country. The coal seams are confined the Middle Carboniferous sequences. The total area occupied by the basin is as large as 6200 km$^2$. The Ruhr Basin is located on the northern limb of a large sublatitudinal tectonic structure strongly complicated by second-order folding and faults. The basin is unconformably overlain by Permian, Cretaceous, and Cenozoic flat rock sequences.

The coaliferous part of the section includes 80 coal seams with an average thickness of 1 m. The reserves of medium- and high-volatile coals (down to a depth of 1200 m) are estimated at 38.4 Gt (Zitzman and Neumann-Redling, 1977). The reserves of lenticular siderite interlayers within the coals are approximately 20 Mt.

The old (prospected) part of Donbas (Russia) occupies an area of 23000 km$^2$. Boundaries of the Greater Donbas have not been outlined, but this coaliferous structure is undoubtedly comparable with the Great Appalachian Basin in terms of dimensions.

In Donbas, the Lower Carboniferous limestones are overlain by a tremendously thick (>20 km) Carboniferous–Permian sequence composed of alternating sandstones, shales, and limestones with more than 200 coal seams. The main part of coals (125 seams ranging from 3 to 6–7 m in thickness) is confined to the Middle Carboniferous sediments. According to Stepanov and Mironov (1937), the total coal reserves of the Donbas area are 71 Gt.

Specific features of the structure and occurrence of siderite ores in coaliferous sequences of Donbas are discussed in works by Kukuk (1938, 1939), Strakhov (1947), Makedonov (1965), and Zaritskii (1970, 1971). They have established that siderite concretions usually occur at the top and base of coal seams forming the so-called "coaly kidneys" (siderite concretions) with well-preserved fragments of stigmaria, wood, coalified fragments of stems, leaves, and other plant remains. Siderites also occur beyond coal seams as chains of bun-shaped concretions within host rocks that locally merge into a single plate. The abundance of dispersed plant remains imparts black color to this plate. Therefore, such plate is called black band in coal basins of England. Figures 7a and 7b demonstrate spatial relationships of siderite concretions and lenses with coal seams. Kukuk noted the frequent coexistence of siderites and freshwater mollusks remains in the Ruhr coals and coaliferous sequences.

As is known, freshwater lowmoor peat bogs, where paralic coals form, are characterized by intense decomposition of Fe-bearing silicate minerals (Strakhov, 1947; Kovalev, 1985). In addition, the concentration of plant biomass in peat results in the development of redox potential sufficient for the transfer of trivalent Fe into highly mobile bivalent phase. The hydrogen content is high (pH = 3–6.5) in the acid gleyey medium (Perel'man, 1979).Therefore, waters of peat bogs usually contain 100–250 mg/l of dissolved Fe and, in fact, represent ferruginous ore-bearing solutions (Kaurichev, 1957; Kovalev and Generalova, 1969; Korotkov and Khodina, 1981; Kovalev, 1985).

Plant biomass in peat bogs undergoes digenetic transformations (decay, humification, and bituminization) under the influence of thermophile bacteria. The main trend of the decay is expressed by the formula

$$\underset{\text{diss. mass}}{\underline{C_6H_{12}O_6}} + O_2 = \underset{\text{gas}}{\underline{6CO_2}} + \underset{\text{l}}{\underline{6H_2O}} + \text{heat (kcal)}.$$

The released carbon dioxide actively influences carbonate equilibrium in freshwater sulfate-free waters of peats and eventually promotes the formation of siderite concretions.

The study of Permian sequences in the Pechora coal basin (Makedonov, 1957) and Carboniferous sequences in the Donbas (Zaritskii, 1985) showed that the specific coal and concretion indexes, which reflect the accumulation and transformation rates of organic matter, show positive correlation with the rate of siderite concretion formation (Fig. 8c). This indicates that coal accumulation and siderite formation are genetically interrelated.

It is noteworthy that coal accumulation in paralic basins is characterized by the cyclic pattern. In freshwater bogs, peat accumulation is usually interrupted by transgressions and one can see the following facies succession: coal-free lagoonal facies, coastal-marine facies of bay barriers and bars, and typical marine brackish-water facies marked by the development of shallow-water limestones.

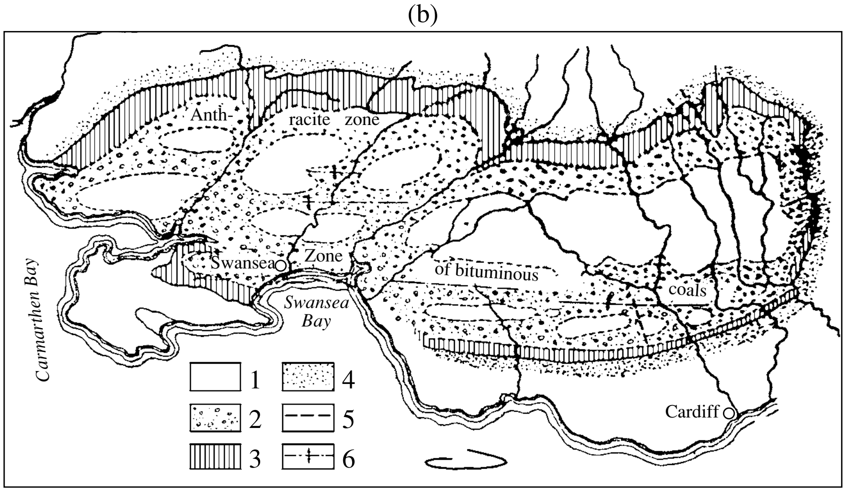
The subsequent regressive phase results in the formation of the reverse facies succession up to the point of peat accumulation in freshwater bogs.

Makedonov (1957) examined the distribution of siderite lodes through the entire cycle of coaliferous sediments in the Vorkuta Formation of the Pechora Basin (Fig. 8a). His results were confirmed by the statistical studies of coaliferous sequences in the Donets,

(a)

| Subdivisions | | | Thickness | |
|---|---|---|---|---|
| | | | NE | SW |
| Middle Carbonife-rous | Upper Coal Measures, Radstockian Stage | Upper coaliferous sequence | 122 | 300 |
| | Middle Coal Measures, Staffordian and Westphalian stages | Penant Sandstone; coals in the west | 213 | 914 |
| | | Steam Coal Series; shales and main coal measures | 300 | 1210 |
| | Millstone Grit | Sandstones, shales, and conglomerates at the base | 90 | 456 |
| Lower Carbonife-rous | Carboniferous Limestone | Limestones, iron ores | | |
| Devonian | Red sandstones | | | |

(b)




(c)

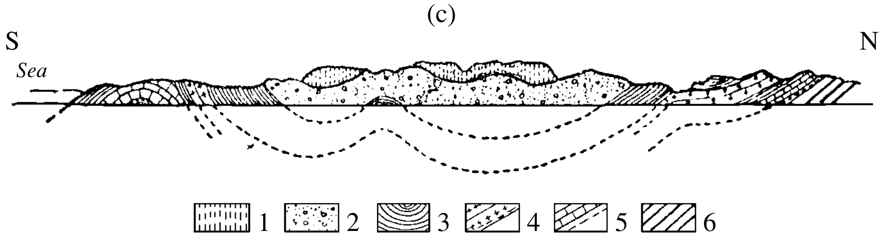



**Fig. 6.** Geological structure and coaliferous levels of the Wales Basin (Stepanov and Mironov, 1937). (a) Section of the coaliferous formation. (b) Schematic geological map of the eastern South Wales Basin: (1–3) Carboniferous productive formations: (1) upper series, (2) middle series, (3) lower series; (4) Millstone Grit; (5) faults; (6) anticline axis; (c) geological section of the South Wales Basin: (1) Upper Coal measures, (2) Pennant Sandstone, (3) Steam Coal series, (4) Millstone Grit, (5) Carboniferous Limestone, (6) Red Old Sandstone (Devonian).

Karaganda, Tungus, Moscow region, Kizelov, and other coal basins of the former USSR (Zaritskii *et al.*, 1971) (Fig. 8b).

Figure 9 demonstrates that siderite beds among coaliferous facies are distinctly confined to freshwater–boggy and semimarine facies, while sediments of the

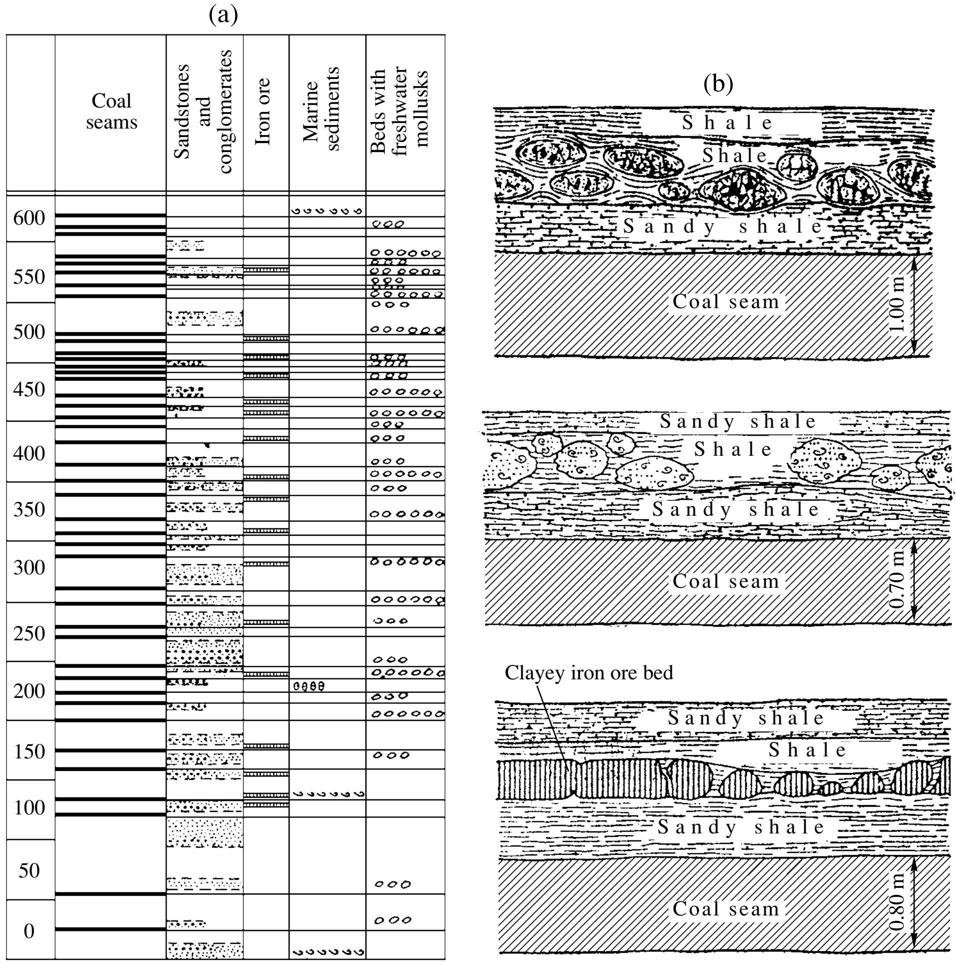
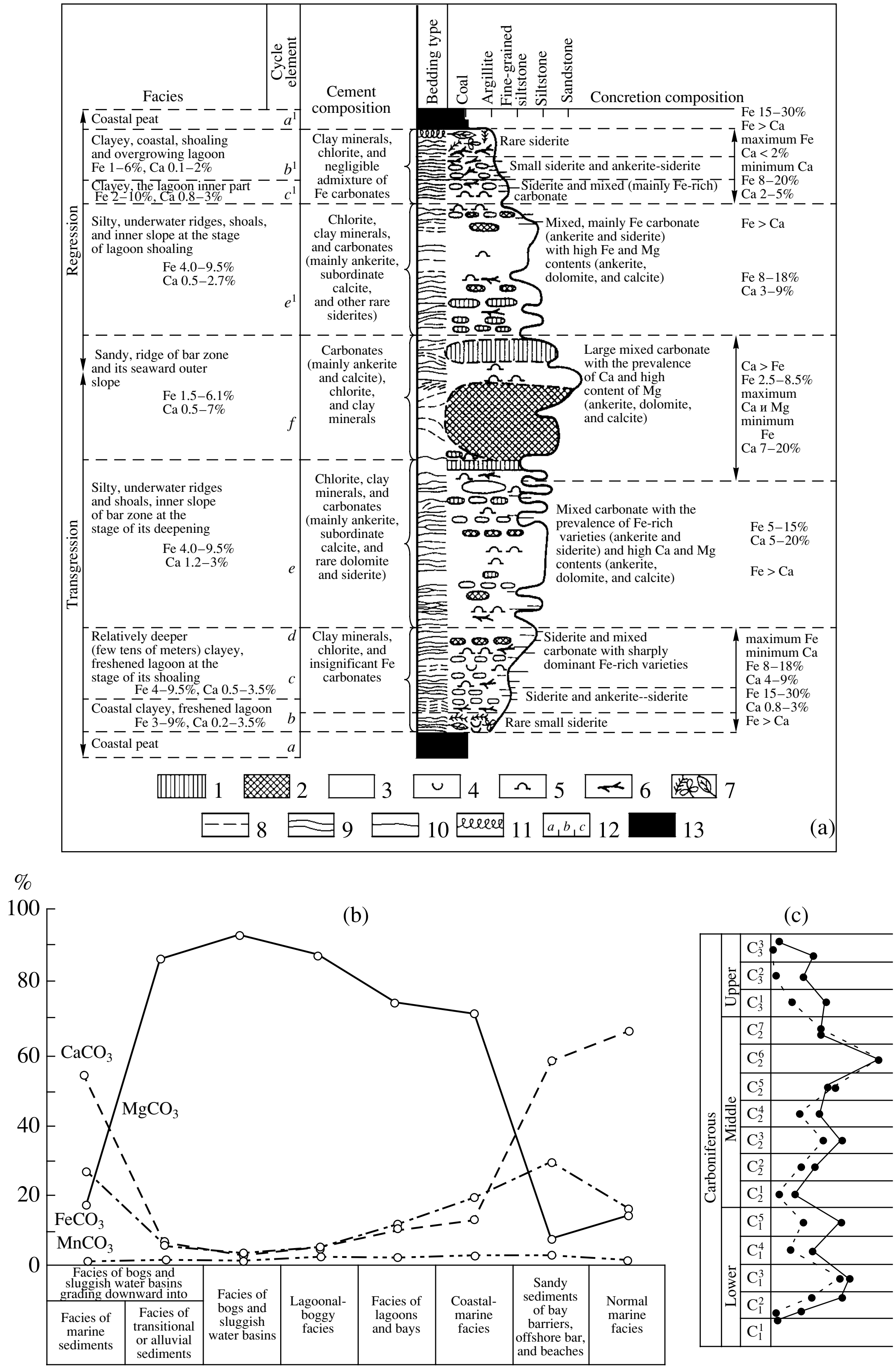



**Fig. 7.** Proportions of coal and siderite beds in the Ruhr Basin (Kukuk, 1938, 1939). (a) Distribution of coal seams, siderite beds, lenses, and concretions through the section of the coaliferous basin. (b) Detailed structure of beds, lenses, and concretions and their relationships with coal seams.

normal marine facies are characterized by insignificant contents of iron carbonates. Works by Newhouse (1927), Baas-Becking and Moore (1961), Zavaritskii (1970), Kizel'shtein (1974), and Kovalev (1985) suggest that precisely this part of the section may enclose diagenetic sulfide concretions, the formation of which is considerably governed by the sulfate content in seawater and the presence of organic matter that is responsible for the intense sulfate reduction in bottom sediments.

Carboniferous siderite deposits and occurrences associated with coal are widespread in the world. In North America, they are recorded in the Pennsylvanian anthracite basin (Foster and Feicht, 1946) and Inner coaliferous province (Mamay and Vochelson, 1962) of the United States and in coal basins of Canada (Baxter, 1960). In Eurasia, they occur in ore occurrences of the Donbas (Butova, 1954), the Karaganda coal basin (Koperina, 1956) and the Ekibastuz coal deposit. The Kuznetsk coal basin is of significant interest in terms of the spherosiderite distribution. The Carboniferous, Permian, and Jurassic coaliferous sequences in this basin include siderite concretions and lenses (Yavorskii and Butov, 1927; Kolotukhina, 1949). The Carboniferous–Permian coaliferous sequences and siderite lodes are also present also in the Minusa coal basin (Labunskii *et al.*, 1977). There are grounds to believe that coal-bearing sequences with siderite accumulations mined in India (Ranigani Group) (Fermor, 1935) and northern China (Shansi, Shensi, and Ordos provinces) (Vil'ner, 1959) are also Carboniferous–Permian deposits. They are also known in South Africa (Orlova, 1950).

The second epoch coal–siderite deposit formation corresponds to the Jurassic–Cretaceous. The Jurassic coal and iron carbonate deposits are well known in England and Germany. In Russia, they are developed in the Urals (Bogoslov deposit) (Timoshenko, 1953), Caucasus (Tkvarcheli deposit) (Kuprov, 1953), Siberia (Timofeev, 1970; Volkova, 1977; Semerikov, 1977), and Central Asia (Ishina and Sal'nikova, 1977). The Jurassic–Cretaceous deposits are mined in southern provinces of China and the Zyryansk Basin of the Verkhoyansk Ridge (Stepanov and Mironov, 1937; Strakhov, 1947).



Facies
Cycle element
Cement composition
Bedding type
Coal
Argillite
Fine-grained siltstone
Siltstone
Sandstone
Concretion composition
Regression
Transgression
Coastal peat
$a^1$
Clayey, coastal, shoaling and overgrowing lagoon Fe 1–6%, Ca 0.1–2%
$b^1$
Clayey, the lagoon inner part Fe 2–10%, Ca 0.8–3%
$c^1$
Silty, underwater ridges, shoals, and inner slope at the stage of lagoon shoaling Fe 4.0–9.5% Ca 0.5–2.7%
$e^1$
Sandy, ridge of bar zone and its seaward outer slope Fe 1.5–6.1% Ca 0.5–7%
f
Silty, underwater ridges and shoals, inner slope of bar zone at the stage of its deepening Fe 4.0–9.5% Ca 1.2–3%
e
Relatively deeper (few tens of meters) clayey, freshened lagoon at the stage of its shoaling Fe 4–9.5%, Ca 0.5–3.5%
d
c
Coastal clayey, freshened lagoon Fe 3–9%, Ca 0.2–3.5%
b
Coastal peat
a
Clay minerals, chlorite, and negligible admixture of Fe carbonates
Chlorite, clay minerals, and carbonates (mainly ankerite, subordinate calcite, and other rare siderites)
Carbonates (mainly ankerite and calcite), chlorite, and clay minerals
Chlorite, clay minerals, and carbonates (mainly ankerite, subordinate calcite, and rare dolomite and siderite)
Clay minerals, chlorite, and insignificant Fe carbonates
Rare siderite
Small siderite and ankerite-siderite
Siderite and mixed (mainly Fe-rich) carbonate
Mixed, mainly Fe carbonate (ankerite and siderite) with high Fe and Mg contents (ankerite, dolomite, and calcite)
Large mixed carbonate with the prevalence of Ca and high content of Mg (ankerite, dolomite, and calcite)
Mixed carbonate with the prevalence of Fe-rich varieties (ankerite and siderite) and high Ca and Mg contents (ankerite, dolomite, and calcite)
Siderite and mixed carbonate with sharply dominant Fe-rich varieties
Siderite and ankerite--siderite
Rare small siderite
Fe 15–30%
Fe > Ca
maximum Fe
Ca < 2%
minimum Ca
Fe 8–20%
Ca 2–5%
Fe > Ca
Fe 8–18%
Ca 3–9%
Ca > Fe
Fe 2.5–8.5%
maximum
Ca и Mg
minimum
Fe
Ca 7–20%
Fe 5–15%
Ca 5–20%
Fe > Ca
maximum Fe
minimum Ca
Fe 8–18%
Ca 4–9%
Fe 15–30%
Ca 0.8–3%
Fe > Ca
1 2 3 4 5 6 7
8 9 10 11 12 13
a b c
(a)
%
100
80
60
40
20
0
(b)
$CaCO_3$
$MgCO_3$
$FeCO_3$
$MnCO_3$
Facies of bogs and sluggish water basins grading downward into
Facies of marine sediments
Facies of transitional or alluvial sediments
Facies of bogs and sluggish water basins
Lagoonal-boggy facies
Facies of lagoons and bays
Coastal-marine facies
Sandy sediments of bay barriers, offshore bar, and beaches
Normal marine facies
(c)
Carboniferous
Upper
Middle
Lower
$C_3^3$
$C_3^2$
$C_3^1$
$C_2^7$
$C_2^6$
$C_2^5$
$C_2^4$
$C_2^3$
$C_2^2$
$C_2^1$
$C_1^5$
$C_1^4$
$C_1^3$
$C_1^2$
$C_1^1$

*Continental–Marine Oolitic Goethite–Chlorite–Siderite Ores*

The entire Phanerozoic was marked by the abundance of oolite–goethite–chlorite–siderite deposits described in works by L. Berg, K.I. Bogdanovich, R.C. Dunham, V. Emmons, R.L. Folk, L.N. Formozova, A.V. Glebov. A. Hallem, A.F. Hallimond, E. Harder. B.P. Krotov, V. Lindgren, G. Menard, V.A. Obruchev, D. P. Serdyuchenko, R. P. Sheldon, E.F. Shnyukov, N.M. Strakhov, J.N. Taylor, and others.

This type of iron ore deposits is well exemplified by the Kerch iron ore basin (Ukraine, Russia) associated with Pliocene (Cimmerian) beds. The Kerch Basin is described in many works (Arkhangel'skii *et al.*, 1930; Konstantov *et al.*, 1933; Malakhovskii, 1956; Shnyukov and Naumenko, 1961; Kholodov, 1968, 1973; Golubovskaya, 1993, 1999, 2001; and others).

The Cimmerian ore-bearing marine sediments are spread over the vast territory extending from the Arabat and Feodosiya bays of the Kerch Peninsula to the middle part of the West Kuban Depression in the Ciscaucasus, but ore beds are usually localized in synsedimentary synclinal basins (Fig. 9a).

The largest iron ore deposits in this region were mined in the El'tigen–Ortel and Kamysh–Burun depressions, where the iron ore bed varies from 6 to 12 m in thickness. Mineralization is represented by three lithogeochemical types identified in the Russian geological literature as the tobacco (pelitic), brown (transitional), and roe (reddish granular) ores. Figure 9b demonstrates variations in their proportions over the Kamysh–Burun Syncline.

Goethite–chamosite–siderite oolites with multiple alternations of goethite and chlorite laminae are the main textural element of the iron ores. Siderite usually replaces external spheres and rock cement; i.e., this mineral shows obvious signs of late formation (Fig. 9c). Oolite cores include detrital material, fragments of the same (but deformed) oolites, and less common mineralized shell fragments.

The tobacco ores occasionally contain large siderite concretions. Their relationships with ores unambiguously indicate that siderite is the latest mineral, which terminates the diagenetic ore transformation, in the goethite–chlorite–siderite association.

In addition to abundant remains of brackish-water mollusks (mainly, Dreissenidae and Cardidae), accumulations of zoo- and phytomorphs are common in ore-bearing beds of the Kerch Basin. These structures have been scrutinized by Chukhrov (1937, 1940) and Litvinenko (1956). They showed that bones of animals (seals, whales, rhinoceros, hypparions) and wood remains, up to 0.20 m across and 1.7 m long, are replaced by barite, Fe-phosphates, siderite, chlorite, and hydrogoethite. Figures 9d and 9e demonstrate microtextures related to the replacement of wood by siderite.

Similar oolitic goethite–chamosite–siderite deposits are widespread in Russia (eastern slope of the Urals, Turgai Depression, and southern part of the West Siberia Lowland) and Kazakhstan (northern Aral region). Jurassic and Paleogene iron ore deposits of this region include two facies types of oolitic iron ore. The first type is localized in ancient river valleys (Lisakov, Ayatsk, Shiely, Kirov, Kutan-Bulak, and other deposits), while the second type associates with typical marine facies (Kok-Bulak, Kolpashev, Bakchar, and other deposits of the West Siberian Basin). They have been scrutinized in several works (Formozova, 1959, 1962; Yanitskii, 1960; Kazarinov, 1958; Nagorskii, 1958; Serdyuchenko and Glebov, 1964).

As shown in (Formozova, 1959), Paleogene ores of the northern Aral region contain abundant phytomorphs developed after wood fragments 1.0–1.5 m long and 10–15 cm across. Wood is generally replaced by phosphates and less commonly by siderites and siliceous minerals. Most of wood fragments are allochthonous materials. They are widespread in alluvial ores and relatively rare in marine facies.

The Cretaceous and, less commonly, Paleogene iron ore occurrences of the northern Aral region contain autochthonous phytomorphs (tubular relicts of wood stems and stumps (remains of bog cypresses) replaced by iron and silicon minerals (Shul'ts, 1967, 1972; Kholodov and Reimov, 1996; Reimov, 1996). The automorphs were altered by erosion in the arch zones of anticlinal folds and transformed to large tubular bodies.

These data are consistent with materials of Lavrov (1955, 1961) who identified the Middle Oligocene carbonaceous–leptochlorite formation in the Aral–Siberian plains. The formation includes abundant interbeds and lenses of brown coals that locally make up carbonaceous–sulfide lodes. Lavrov described a great variety of plant remains and fruit remains and revealed their synchronism with goethite–chlorite–siderite oolitic

←

**Fig. 8.** Facies–paleogeographic relationships between siderite bodies and coal seams. (a) distribution and compositional changes of concretions in a typical cyclothem of the Rudnitskaya Subformation in the Pechora Basin (Makedonov, 1957). (1–3) Concretions: (1) limestone–ankerite and limestone–dolomite–ankerite, (2) ankerite, ankerite–dolomite, and limestone–siderite–ankerite, (3) ankerite–siderite and siderite; (4) anthracosid and other freshwater fauna; (5) plant sludge; (6) plant remains; (7) Equisetales, pteridophytes, and cordaites; (8) obscure bedding; (8) distinct bedding; (10) cryptic bedding; (11) lumpy structure; (12) indices of cycle elements; (13) coal seam. (b) Compositional variations of carbonate components in concretions depending on the facies affinity of host sediments (Zaritskii, 1985). (c) Specific coal (dash line) and concretion (sold line) indices in the Carboniferous section of Donbas (Zaritskii, 1985).

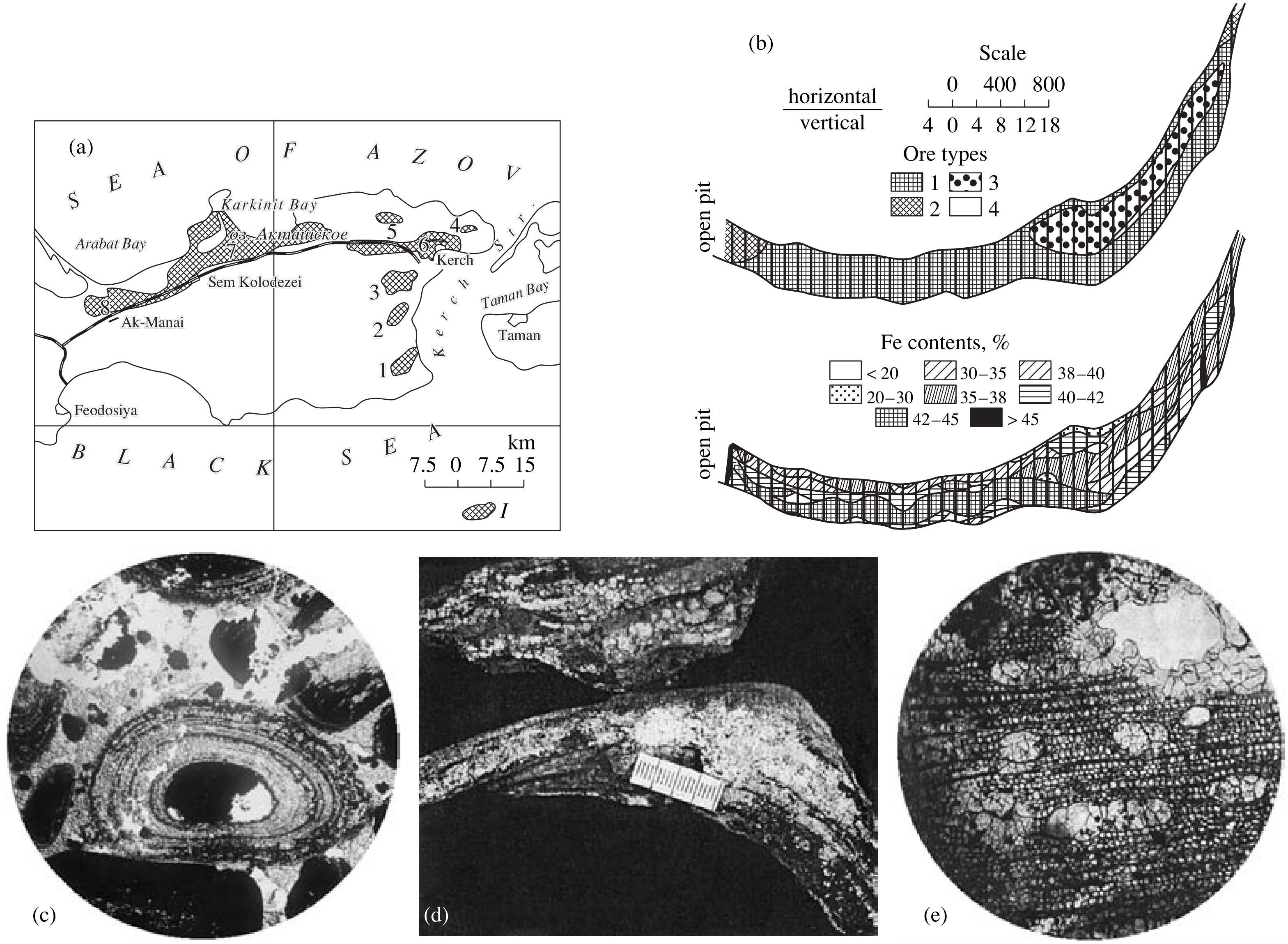



**Fig. 9.** Occurrence conditions and textures of marine oolitic goethite–chlorite–siderite ores in the Kerch iron ore basin. (a) Schematic map of iron ore deposits in the Kerch Peninsula. (1–8) Iron ore deposits: (1) Kyz-Aul, (2) El'tigen-Ortel, (3) Kamysh-Burun, (4) Baksin, (5) Kezen. (6) Katerlez, (7) Severnaya Mul'da, (8) Akmanai Mul'da. (b) Geological section of the Kamysh-Burun deposit (Shnyukov and Naumenko, 1961). (1–3) Ore types: (1) tobacco, (2) brown, (3) roe, (4) clay. (c) Photomicrograph of the goethite–chlorite–siderite oolite with siderite replacing other minerals in outer spheres, light areas correspond to chlorite–siderite cement, magn. 17, parallel nicols. (d) Photograph of the phytomorph (Litvinenko, 1956), wood partly replaced by barite and with barite inclusions. (e) Photomicrograph of the oak wood section partly replaced by siderite (Litvinenko, 1956).

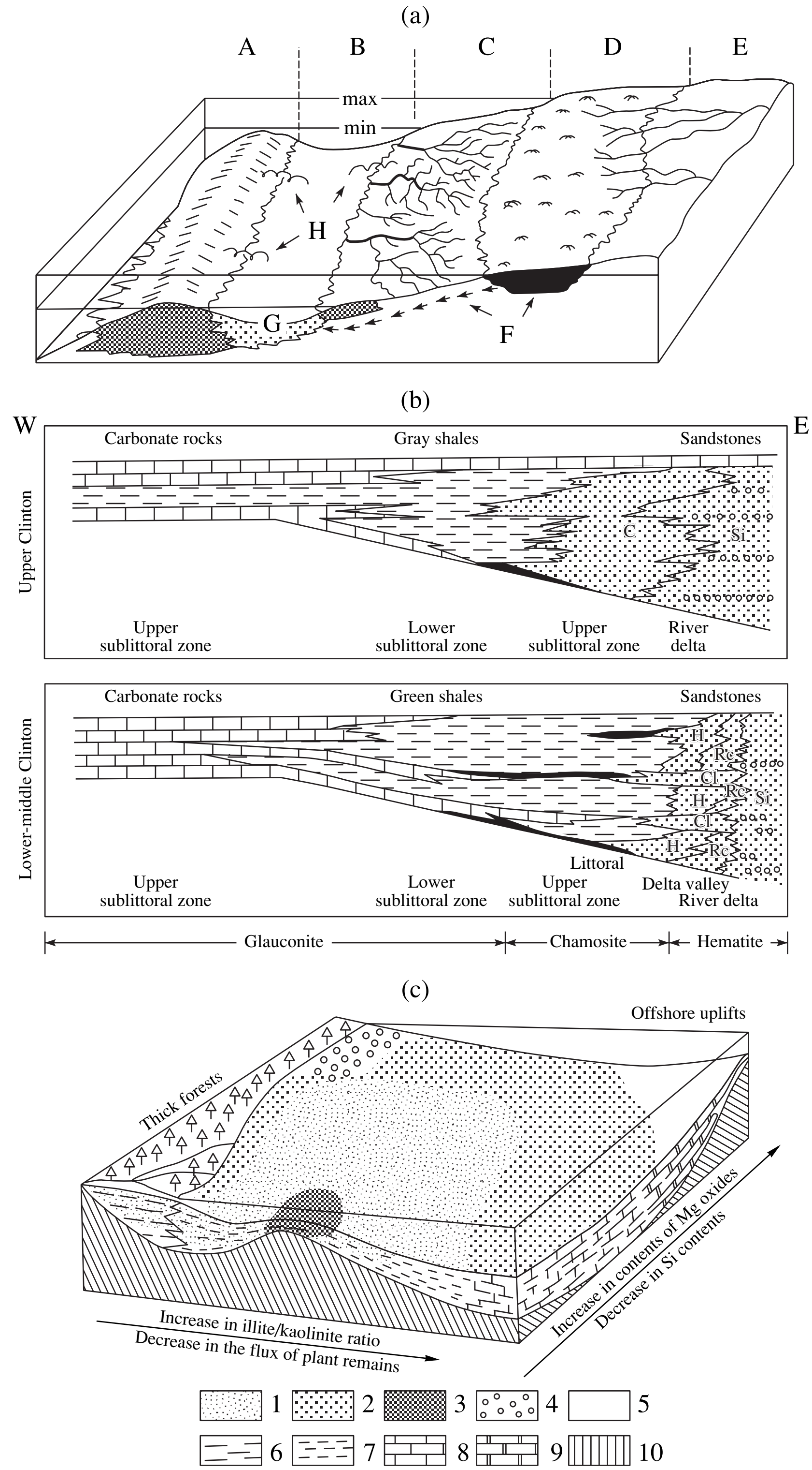



**Fig. 10.** Facies–paleogeographic settings of marine oolitic goethite–chlorite–siderite ores. (a) Formation conditions of the Ordovician Wabana iron ores (Ranger, 1979): (A) coastal bar, (B) lagoon (sedimentation at low Eh values), (C) tidal zone, (D) supralittoral algal bogs (high Eh values and high $CO_2$ pressure), (E) former river channels, (F) Fe is leached out of sediments in boggy environments, (G) Fe is removed by groundwater into lagoon and precipitates in the form of chamosite oolites, which are subsequently redeposited in coastal bars and sediments of the tidal zone (H). (b) Facies of Silurian ore-hosting rocks in the Appalachia Basin (Hunter, 1979) (black color shows iron ore beds). Sandstones with different cement types: (C) calcite, (Si) siliceous, (H) hematite, (Cl) chlorite, (Rc) red clayey. (c) Facies of ferruginous sediments in Jurassic iron ores of England (Hallem, 1967): (1) sand, (2) siltstone and clay, (3) chamosite oolites, (4) carbonate oolites and shelly sand, (5) calcareous clay, (6) sandstone, (7) shale, (8) marble, (9) gray limestone, (10) red limestone.

ores of the Lisakov (Turgai), Loshchinov (Irtysh region), and Kutan-Bulak (Aral region) deposits.

Paleogeographic studies carried out by E.F. Bubnoff, L. Cayeux, H.F. Hallimond, E.C. Harder, A.O. Hayes, and others to reconstruct facies conditions of Jurassic oolitic iron ores in England, France, Germany and their Ordovician and Silurian counterparts in the United States and Canada yielded interesting results. Strakhov (1947, p. 135) summarized these data and concluded that all of them "…formed in extremely shallow-water and coastal parts of sea and represent sediments of bays, bights, lagoons, and the uppermost part of the shelf; of course, they are associated with different coastal landscapes in various environments."

In fact, this inference was convincingly confirmed by Meynard (1983) who analyzed the goethite–chlorite–siderite ore formation models proposed by Hallem (1967, 1975), Hunter (1970) and Ranger (1979) (Fig. 10). It is remarkable that oolitic goethite–chlorite–siderite deposits in all these models usually associate with coal formation on land, where significant quantities of organic matter accumulate in lowmoor peat bogs. In the Ordovician (Fig. 10a), when terrestrial vegetation in Newfoundland was still insufficiently developed, boggy settings probably resulted from the concentration of cyanobacterial communities and primitive algae that formed underwater meadows (Kanygin, 2001). It can be suggested that first lycopsids, the existence of which in the pre-Silurian time is debatable (Meyen, 2001), appeared precisely in such paralic environments.

In the Silurian (Fig. 10b), the formation of Clinton marine oolitic goethite–chlorite–siderite ores in Appalachia (the United States) could form in the boggy delta of a large paleoriver. According to Folk (1962), the formation of iron ores in this region was always accompanied by the notable shoaling of the basin.

In the Jurassic (Fig. 10c), iron ores of England formed in areas of the terrigenous facies formation in the immediate vicinity swampy forests (Hallem, 1975).

As is evident from Fig. 10c, coal-producing peat bogs located in forests were frequently coeval with the marine oolitic goethite–chlorite–siderite ores.

In summary, it should be emphasized that the succession of mineralization in the Kerch iron ore deposits is probably also typical of all oolitic iron ore accumulations. As shown in (Lindgren, 1933; Novokhatskii, 1949, 1958; Litvinenko and Kucherenko, 1957; Formozova, 1959), goethite and chlorite are confined to the central parts of goethite–chlorite–siderite oolites and accumulated at the initial stage of ore formation, while siderite appears slightly later. Thus, these two mineral phases display sedimentary-diagenetic and diagenetic relationships.

## CONCLUSIONS

(1) Siderite facies were widespread during the deposition of Precambrian iron formations. Siderite formed at the initial stage of ore formation. This was stimulated by oxygen deficiency and excess of carbon dioxide in the Precambrian atmosphere, mass influx of Fe to the terminal drainage basins from provenances composed of basic and ultrabasic igneous rocks, and intense volcanic and hydrothermal activities that regulated the additional flux of Fe and Si to Archean and Proterozoic basins.

(1) The Riphean and Early Paleozoic were marked by the intense formation of elision-hydrothermal and hydrothermal siderite deposits, where this mineral replaced carbonate sequences to form stratiform bodies, lenses, and stocks. The appearance of hydrothermal siderite-forming solutions of the Bakal type was related to elision-catagenetic and metamorphic transformations of Precambrian iron formations and other underlying rocks.

(3) Siderite and ankerite concretions, lenses, and beds spatially and genetically associated with coals are widespread in Upper Paleozoic, Mesozoic, and Cenozoic coaliferous sequences. They formed during the diagenetic and catagenetic transformations of plant organic matter and contained huge reserves of iron.

(4) The Phanerozoic marine and continental sequences often contain oolitic goethite–chlorite–siderite ores. They usually associate with boggy facies and contain abundant plant remains and phytomorphs. Siderite in these ores is the latest mineral that replaces goethite–chlorite spheres in oolites. It serves as cement and forms nodules.

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## REFERENCES

Albert, Ch. and McCulloch, H., Rare Earth Elements and Neodymium Isotopic Compositions of the Banded Iron-Formations and Associated Shales from Hamersley, Western Australia, *Geochim. Cosmochim. Acta*, 1993, vol. 57, pp. 187–204.

Aleksandrov, Yu.A., Precambrian Iron Ore Formations of the USSR, in *Dokembriiskie zhelezorudnye formatsii mira* (Precambrian Iron Ore Formations of the World), Moscow: Mir, 1975, pp. 172–205.

Anatol'eva, A.I., *Glavnye rubezhi evolyutsii krasnotsvetnykh formatsii* (Main Events in the Evolution of Red Beds), Novosibirsk: Nauka, 1978.

Anfimov, L.V., Postdiagenetic Transformations and Rational Classification of Riphean Quartz Psammites in the Central Ural Uplift in the Southern Urals, in *Dokembriiskie osadoch-*

*nye tolshchi Bashkirskogo megantiklinoriya na Urale i ikh metallogeniya (Precambrian Sedimentary Sequences in the Bashkir Meganticlinorium of the Urals and Their Metallogeny)*, Inst. Geol. Geokhim. Ural. Nauchn. Tsentr Akad. Nauk SSSR, 1978, no. 133, pp. 25–32.

Anfimov, L.V., Lower Riphean Formations and Mineralization in the Bakal–Satkin Region of the Southern Urals, *Dokl. Akad. Nauk SSSR*, 1982, vol. 265, no. 5, pp. 1227–1230.

Anfimov, L.V., *Litogenez v rifeiskikh osadochnykh tolshchakh Bashkirskogo megantiklinoriya* (Lithogenesis in the Riphean Sedimentary Sequences of the Bashkir Meganticlinorium), Yekaterinburg: Ural. Nauchn. Tsentr Ross. Akad. Nauk, 1997.

Arkhangel'skii, A.D., Blokhin, A.A., Menner, V.V., *et al.*, *Kratkii ocherk geologicheskogo stroeniya i neftyanykh mestorozhdenii Kerchenskogo poluostrova*, (Overview of the Geological Structure and Oil Fields in the Kerch Peninsula), Tr. GGU VSNKh, 1930, issue 13.

Baas-Becking, L.G. and Moore, D., Biogenic Sulfides, *Econ. Geol.*, 1961, vol. 56, no. 2, pp. 259–272.

Bau, M. and Moller, P., Rare Element Systematics of the Chemically Precipitated in Early Precambrian Iron Formations and Evolution of the Terrestrial Atmosphere-Hydrosphere-Lithosphere System, *Geochim. Cosmochim. Acta*, 1993, vol. 57, pp. 2239–2249.

Baxter, R.W., A First Report of Coal Balls from the Pennsylvanian of New Brunswick, Canada, *Can. J. Bot.*, 1960, vol. 38, no. 4, pp. 44–68.

Borchert, H., Die Bildungsbedingungen Mariner Eisenerlagerstatten, *Chemie Erde*, 1952, vol. 16, pp. 49–74.

Borchert, H., Genesis of Marine Sedimentary Iron Ore, *Trans. Inst. Min. Metal.*, 1960, vol. 69, pp. 261–279; Discussion, pp. 530–535.

Butova, E.P., Litological Characteristics and Formation of Coal-Bearing Series in the Ekibastuz Coal Deposit, *Tr. Laborat. Geol. Uglya Akad. Nauk SSSR*, 1954, no. 11, pp. 72–103.

Bukes, N.J., Precambrian Iron Ore Formations in South Africa, *Precambrian Iron-Formations of the World*, Skinner, B., Ed., Lancaster: Econ. Geol. Publ. Co., 1973. Translated under the title *Dokembriiskie zhelezorudnye formatsii mira*, Moscow: Mir, 1975, pp. 70–129.

Chebotareva, N.A. and Naumova, E.N., Specific Features of Iron Formations of the Tartash Formation in the Southern Urals, *Byull. Mosk. O-va. Ispyt. Prirody, Ser. Geol.*, 1971, issue 3, pp. 154–155.

Chukhrov, F.V., Mineralogy and Geochemistry of Barium in Sedimentary Rocks: Implication for Kerch Barites, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1937, no. 3, pp. 24–38.

Chukhrov, F.V., Mineralogy of Phytomorphs and Fossil Bones, *Tr. Inst. Geol. Nauk Akad. Nauk SSSR, Miner.-Geol. Ser.*, 1940, issue 10, no. 2, pp. 82–104.

Danielson, A., Moller, P., and Dulski, P., The Europium Anomalies in Banded Iron Formations and the Thermal History of Oceanic Crust, *Chem. Geol.*, 1992, vol. 97.

Drever, J.J., Geochemical Model for Origin of Precambrian Banded Iron Formations, *Bull. Geol. Soc. Am.*, 1974, vol. 85, pp. 1099–1106.

Fedorchenko, V.S., "Sedimentary" Siderites in the Middle Krivoi Rog Formation: Their Role in the Formation of Ferruginous Rocks and Some High-Grade Ore Types, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1956, no. 12, pp. 69–82.

Fermor, L.L., India's Coal Resources, *Records Geol. Survey India*, 1935, vol. 69, no. 3, pp. 38–67.

Formozova, L.N., *Zheleznye rudy Severnogo Priaral'ya* (Iron Ores in the Northern Aral Region), Moscow: Akad. Nauk SSSR, 1959, issue 20.

Formozova, L.N., *Usloviya obrazovaniya oolitovykh zheleznykh rud v nizhnem paleozoe i dokembrii* (Formation Conditions of Lower Paleozoic and Precambrian Oolitic Iron Ores), Moscow: Akad. Nauk SSSR, 1962, issue 70.

Fockema, P.D., Crocidolite and Associated Rocks of the Kuruman Area in the Northern Cape, in *Ph. D. Thesis, Univ. Witwatersrand*, 1967, pp. 67–82.

Folk, R.L., Petrography and Origin of the Silurian Rochester and McKenzie Shales, Morgan County, West Virginia, *J. Sed. Petrology*, 1962, vol. 32, pp. 539–578.

Forster, W.D. and Feicht, F.L., Mineralogy of Concretions from Pittsburg Coal Seams with Special Reference to Analcite, *Am. Min*, 1946, vol. 31, nos. 7–8, pp. 32–68.

French, V.M., Progressive Contact Metamorphism of the Biwabik Iron Formation, Mesab Range, Minnesota, *Minnesota Geol. Survey Bull.*, 1968, vol. 45, pp. 3–103.

Galimov, E.M., *Geokhimiya stabil'nykh izotopov ugleroda* (Geochemistry of Stable Carbon Isotopes), Moscow: Nedra, 1968.

Gershoig, Yu.G., Refined Stratigraphic Scheme of the Krivoi Rog Region, *Problemy Sov. Geol.*, 1937, vol. VII, no. 4, pp. 35–42.

Gershoig, Yu.G., Petrogenesis Phases in Crystalline Schists from the Krivoi Rog Region, *Sov. Geol.*, 1940, no. 37, pp. 24–38.

Gershoig, Yu.G., Processes of Mineralization in the Metasedimentary Rocks of the Krivoi Rog Region, in *Voprosy mineralogii osadochnykh obrazovanii* (Problems of the Mineralogy of Sedimentary Rocks), L'vov: L'vov Gos. Univ., 1956, books 3/4, pp. 160–173.

Gibson, W., *Coal in Great Britain*, London, 1927.

Gole, M.I. and Klein, C., Banded Iron-Formation through Much of Precambrian Time, *J. Geol.*, 1981, vol. 89, pp. 169–183.

Golubovskaya, E.V., Problem of Glauconite in the Kerch Iron Ores, *Litol. Polezn. Iskop.*, 1993, vol. 28, no. 1, pp. 140–143.

Golubovskaya, E.V., Origin of the "Brown" Ore in Iron Ore Deposits of the Kerch Peninsula, *Litol. Polezn. Iskop.*, 1999, vol. 34, no. 3, pp. 244–251 [*Lithol. Miner. Resour.* (Engl. Transl.), 1999, vol. 34, no. 3, pp. 210–216].

Golubovskaya, E.V., Facies and Geochemical Features of the Iron Ore Complex of the Kerch Peninsula, *Litol. Polezn. Iskop.*, 2001, vol. 36, no. 3, pp. 259–273 [*Lithol. Miner. Resour.* (Engl. Transl.), 2001, vol. 36, no. 3, pp. 224–235].

Goodwin, A.M., Archean Iron-Formation and Tectonic Basins of the Canadian Shield, *Econ. Geol.*, 1973, vol. 68, no. 7, pp. 915–933.

Gordeev, V.V., *Rechnoi stok v okean i cherty ego geokhimii* (River Discharge into the Ocean and Its Geochemistry), Moscow: Nauka, 1983.

Gross, G.A., Geology of Iron Ore Deposits in Canada, *Geol. Surv. Can.*, 1965, vol. 1.

Gross, G.A., A Classification of Iron Formation Based on the Depositional Environments, *Can. Mineral*, 1980, vol. 18, no. 2, pp. 215–232.

Hallem, A., Siderite and Calcite-Bearing Concretionary Nodules in the Lias of Yorkshire, *Geol. Mag.*, 1967, vol. 104, pp. 222–227.

Hallem, A., *Jurassic Environments*, Cambridge: Cambridge Univ. Press, 1975.

Hattori, K., Campbell, F.A., and Krouz, H.R., The Distribution of Sulfur Isotopes in Sedimentary Rocks and Evolution of Precambrian Atmosphere, *Geokhimiya*, 1985, no. 6, pp. 834–849.

Holland, H.D., The Oceans: A Possible Source of Iron Formations, *Econ. Geol.*, 1973, vol. 68, pp. 1169–1172.

Holland, H.L., *The Chemistry of the Atmosphere and Oceans*, New York: Wiley and Sons Publ., 1978.

Holland, H. D., *The Chemical Evolution of the Atmosphere and Oceans* (Princeton Univ. Press, Princeton, 1984). Translated under the title *Khimicheskaya evolyutsiya okeanov i atmosfery*, Moscow: Mir, 1989.

Hunter, R.E., Facies of Iron Sedimentation in the Clinton Group, *Studies of Appalachian Geology, Central and Southern*, New York: Wiley and Sons, 1970. P. 101–121.

Ishina, T.A. and Sal'nikova, L.L., Nodulal Complexes in the Essential Jurassic Coal–Bearing Sequences in Central Asia, in *Konkretsii i konkretsionnyi analiz* (Nodules and Nodular Analysis), Moscow: Nauka, 1977, pp. 116–121.

James, H.L., Sedimentary Facies of Iron Formation, *Econ. Geol.*, 1954, vol. 49, pp. 235–393.

James, H.L., Distribution of Banded Iron Formation in Space and Time, *Iron Formation: Facts and Problems*, Amsterdam: Elsevier, 1983, pp. 470–491.

Kamaletdinov, M.A., Upper Precambrian Tectonics in the Riphean Stratotype Locality, *Korrelyatsiya dokembriya* (Correlation of the Precambrian), Moscow: Nauka, 1986, vol. 2, pp. 224–235.

Kanygin, A.V., The Ordovician Phenomenon of Explosive Divergence of Organic Life on the Earth: Causes and Evolutionary Consequences for the Biosphere, *Geol. Geofiz.*, 2001, vol. 42, no. 4, pp. 631–668.

Kaurichev, I.S., Forms of Iron in the Perched Water Table of the Turf-Podzolic Soil Zone, *Dokl. TSKhA*, 1957, no. 31, pp. 219–223.

Kazarinov, V.P., *Mezozoiskie i kainozoiskie otlozheniya Zapadnoi Sibiri* (Mesozoic and Cenozoic Rocks in West Siberia), Moscow: Gostoptekhizdat, 1958.

Kholodov, V.N., *Vanadii (geokhimiya, mineralogiya i geneticheskie tipy mestorozhdenii v osadochnykh porodakh)* (Vanadium: Geochemistry, Mineralogy, and Genetic Types of Mineral Deposits in Sedimentary Rocks)), Moscow: Nauka, 1968.

Kholodov, V.N., *Osadochnyi rudogenez i metallogeniya vanadiya* (Sedimentary Mineralization and Metallogeny of Vanadium), Moscow: Nauka, 1973.

Kholodov, V.N. and Butuzova, G.Yu., Phosphorus in the Hydrothermal Process, *Litol. Polezn. Iskop.*, 1999, vol. 34, no. 3, pp. 227–244 [*Lithol. Miner. Resour.* (Engl. Transl.), 1999, vol. 34, no. 3, pp. 195–209].

Kholodov, V.N. and Butuzova, G.Yu., Problems of Iron and Phosphorus Geochemistry in the Precambrian, *Litol. Polezn. Iskop.*, 2001, vol. 36, no. 4, pp. 339–353 [*Lithol. Miner. Resour.* (Engl. Transl.), 2001, vol. 36, no. 4, pp. 291–302].

Kholodov, V.N. and Kiknadze, Z.R., *Kolchedannye mestorozhdeniya Bol'shogo Kavkaza* (Massive Sulfide Ore Deposits in the Greater Caucasus), Moscow: Nauka, 1989.

Kholodov, V.N. and Reimov, M.R., Problem of the Origin of Ferruginous–Siliceous Pipe-Shaped Bodies in the Aral Sea Region, *Litol. Polezn. Iskop.*, 1996, vol. 31, no. 5, pp. 476–493 [*Lithol. Miner. Resour.* (Engl. Transl.), 1996, vol. 31, no. 5, pp. 425–439].

Kissin, I.G. and Pakhomov, S.I., The Possibility of Carbon Dioxide Generation in the Earth's Interior at Moderately High Temperatures, *Dokl. Akad. Nauk SSSR*, 1967, vol. 174, no. 2, pp. 1210–1218.

Kissin, I.G. and Pakhomov, S.I., Geochemistry of Carbon Dioxide in Deep Zones of the Subsurface Hydrosphere, *Geokhimiya*, 1969, no. 4, pp. 44–86.

Kizil'shtein, L.Ya., Formation of Iron Sulfide Nodules in Coal Beds, *Litol. Polezn. Iskop.*, 1974, no. 2, pp. 58–65.

Klein, K., Changes in Mineral Assemblages as a Result of Metamorphism in Some Precambrian Banded Iron Ore Formations, *Dokembriiskie zhelezorudnye formatsii mira* (Precambrian Iron Ore Formations of the World), Moscow: Mir, 1975, pp. 221–237.

Kolotukhina, S.E., Carbonate Rocks of the Kolchugin Formation in the Kuznetsk Basin, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1949, no. 4, pp. 97–118.

Konstantov, S.V., Kechek, G.A., Belorusov, V.V., and Krasil'nikov, L.V., *Kerchenskie zhelezorudnye mestorozhdeniya*, (The Kerch Iron Ore Deposits), Tr. VGRO, 1933, issue 325.

Koperina, V.V., Composition and Depositional Environments of the Nadkaraganda, Naddolin and Shakhan Formations in the Karaganda Basin, *Tr. Laborat. Geol. Uglya Akad. Nauk SSSR*, 1956, issue 4, pp. 147–158.

Korotkov, A.I. and Khodina, V.A., Evolution of the Chemical Composition of Ferruginous Waters, *Zonal'nost' podzemnykh vod platformy i gorno-skladchatykh oblastei* (Groundwater Zoning in Platforms and Orogenic Foldbelts), Leningrad: Nauka, 1981, pp. 166–169.

Kovalev, V.A., *Bolotnye mineralogo-geokhimicheskie sistemy* (Boggy Mineralogical–Geochemical Systems), Minsk: Nauka Tekhnika, 1985.

Kovalev, V.A. and Generalova, V.A., Geochemistry of Iron Migration in Recent Peat Bogs of Byelorussia, *Geokhimiya*, 1969, vol. 7, no. 2, pp. 210–220.

Krupenin, M.T., *Usloviya formirovaniya sideritonosnoi Bakal'skoi svity nizhnego rifeya* (Evolution Conditions of the Lower Riphean Siderite-Bearing Bakal Formation), Yekaterinburg: Inst. Geol. Geokhim., 1999.

Krupenin, M.T., Minerageny of Riphean Sedimentary Sequences, *Rifei zapadnogo sklona Yuzhnogo Urala* (The Riphean of the Western Slope of the Southern Urals), Yekaterinburg: Inst. Geol. Geokhim., 2001, vol. 1, pp. 134–244.

Krupenin, M.T., Models of Ore Formation Associated with Lithogenesis in Sedimentary Basins of the Riphean Stratotype (Southern Urals), *Geneticheskii formatsionnyi analiz osadochnykh kompleksov fanerozoya i dokembriya* (Genetic Formation Analysis of Phanerozoic and Precambrian Sedimentary Complexes), Moscow: Mosk. Gos. Univ., 2003, pp. 365–371.

Kukuk, P., *Geologie des Niederrheinischen-Westfalischen Steinkohlengebietes*, Texband, 1938.

Kukuk, P., Die Westfalischen Steinkohlbecken, *Gluckauf*, 1939, vol. 35, pp. 28–41.

Kukuk, P., Breddin, H., Gothan, W., and Hirmer, M., *Geologie des Niederrheinischenwestfalischen Steinkohlengebietes*, Berlin, 1938.

Kuprov, I.G., Nodules in the Coal-Bearing Sequence of the Tkvarcheli Deposit, *Zap. Leningr. Gorn. Inst.*, 1953, vol. 29, issue 2, pp. 15–42.

La Berge, G.L., Development of Magnetite in Iron Formation of Lake Superior Region, *Econ. Geol.*, 1964, vol. 59, pp. 1313–1342.

Labunskii, L.V., Fedchishin, E.B., and Aseev, N.M., Nodules in the Overburden of Coal Deposits in the Minusa Basin, *Konkretsii i konkretsionnyi analiz* (Nodules and Nodular Analysis), Moscow: Nauka, 1977, pp. 111–116.

Lavrov, V.V., Stages of Tertiary Coal Accumulation in Kazakhstan, *Dokl. Akad. Nauk SSSR*, 1955, vol. 100, no. 2, pp. 82–89.

Lavrov, V.V., Paleogene Coaliferous and Ore Rock Associations in Kazakhstan and Western Siberia, *Uglenosnye formatsii nekotorykh regionov SSSR* (Coaliferous Rock Associations in Some Regions of the USSR), Moscow, Leningrad: Akad. Nauk SSSR, 1961, pp. 339–362.

Lindgren, W., *The Oolitic Hematite Ores. Mineral Deposits*, New York: McGraw-Hill, 1933, pp. 250–256.

Litvinenko, A.U., Mineralogy of Biomorphs in Terms of the Origin of Hypergene Iron Ores in the Kerch Region, *Voprosy mineralogii osadochnykh obrazovanii* (Problems of the Mineralogy of Sedimentary Rocks), L'vov: L'vov. Gos. Univ., 1956, pp. 174–189.

Litvinenko, A.U. and Kucherenko, M.T., Oolitic Siderite–Chamosite Ores in Marine Sediments of the Dnieper–Donets Basin, *Dokl. Akad. Nauk SSSR*, 1957, vol. 116, no. 5, pp. 847–850.

Lyakhovich, V.V. and Sidorenko, A.V., Role of Accessory Minerals in the Study of the Precambrian Evolution, in *Aktsessornye mineraly dokembriya* (Precambrian Accessory Minerals), Moscow: Nauka, 1986, pp. 6–21.

Makedonov, A.V., Paragenesis of Coals and Nodules in the Vorkuta Group in the Pechora Basin, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1957, no. 8, pp. 77–95.

Makedonov, A.V., Coal-Bearing Sequence in the Pechora Coal Basin, *DSc (Geol.-Miner.) Dissertation*, Leningrad: Leningr. Gos. Univ., 1965.

Malakhovskii, V.F., *Geologiya i geokhimiya kerchenskikh zheleznykh rud i ikh vazhneishikh komponentov* (Geology and Geochemistry of the Kerch Iron Ores and Their Main Components), Kiev: Akad. Nauk SSSR, 1956.

Mamay, S.H. and Vochelson, E.L., Occurrence and Significance of Marine Animal Remains in Coal Balls, *Am. Geol. Survey Prof. Paper*, 1962, vol. 31.

Meddaugh, W.S., Age and Origin of Uraninite in the Elliot Lake Ontario Uranium Ore, *Ph. D. Dissertation, Harvard Univ.*, 1983, pp. 29–45.

Maynard, J.B. Geochemistry of Sedimentary Ore Deposits, Heidelberg: Springer-Verlag, 1983. Translated under the title *Geokhimiya osadochnykh rudnykh mestorozhdenii*, Moscow: Mir, 1985.

Merlivat, J., Pineau, F., and Javely, M., Hydrothermal Vent Waters at 13° N on the East Pacific Rise: Isotopic Composition and Gas Concentration, *Earth Planet. Sci. Lett.*, 1987, vol. 84, no. 1, pp. 100–108.

Meyen, C. V., *List'ya na kamne* (Leaves on Stone), Moscow: GEOS, 2001.

Michard, A., Rare Earth Elements Systematics in Hydrothermal Fluids, *Geochim. Cosmochim. Acta*, 1989, vol. 53, no. 3, pp. 754–751.

Mori, G.B., Mesabi, Gunflint and Guyuna Iron Ore Regions in Minnesota, *Geologiya i genezis dokembriiskikh zhelezisto-kremnistykh i margantsevykh formatsii mira* (Geology and Genesis of the Precambrian Ferruginous–Cherty and Manganese Formations of the World), Kiev: Nauk. Dumka, 1972, pp. 204–221.

Mottle, M.J., Metabasalts, Axial Hot Springs and the Structure of Hydrothermal Systems at Mid-Ocean Ridges, *Bull. Geol. Soc. Am.*, 1983, vol. 94.

Nagorskii, M.P., The West Siberian Iron Ore Basin, *Sov. Geol.*, 1958, no. 9, pp. 68–85.

Newhouse, W.H., Some of Iron Sulphide Occurring in Coal and Other Sedimentary Rocks, *J. Geol.*, 1927, vol., 35, no. 1, pp. 40–92.

Noth, L., Die Eisenerzlagerstatten Gugoslawiens XIX Congr., *Geol. Int. Alger*, 1952, pp. 529–563.

Novokhatskii, I.P., Some Specific Features of Oolitic Iron Ores, *Izv. Akad. Nauk Kazakh SSR. Ser. Geol*, 1949, no. 11, pp. 118–124.

Novokhvatskii, I.P., Mineralogy and Geochemistry of Oolitic Iron Ore Deposits in Kazakhstan, *Tr. Ob'ed. Kustanaiskoi nauchnoi sessii, posvyashchennoi problemam Turgaiskogo regional'no-ekonomicheskogo kompleksa. Geol. Sektsiya* (Proc. Joint Kustanai Scentific Session on Problems of the Turgai Regional Economic Complex), Alma-Ata: Izd. Akad. Nauk Kazakh SSR, 1958, vol. 11, pp. 82–92.

Orlova, E.V., The South African Union, *Mineral'nye resursy zarubezhnykh stran* (Mineral Resources of Foreign Countries), Moscow: GIGL, 1950, issue 18, pp. 17–28.

Perel'man, A.I., *Geokhimiya* (Geochemistry), Moscow: Vyssh. Shkola, 1979.

Plaksenko, N.A., Some Structural Features of Precambrian Metamorphic Rocks in the KMA, Their Origin, and Stratigraphic Significance, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1959, no. 3, pp. 60–81.

Plaksenko, N.A., *Main Trends of the Precambrian Iron Ore Deposition*, Voronezh: Voronezh. Izd., 1966.

Plaksenko, N.A., Koval, I.K., and Shchegolev, I.N. Precambrian Ferruginous–Cherty Formations in the Kursk Magnetic Anomaly, *Geologiya i genezis dokembriiskikh zhelezisto-kremnistykh i margantsevykh formatsii mira* (Geology and Genesis of Precambrian Ferruginous–Cherty and Manganese Formations of the World), Kiev: Nauk. Dumka, 1972, pp. 76–85.

Ranger, M.R., The Sedimentology of a Lower Paleozoic Peritidal Sequence and Associated Iron Formations, Bell Island, Conception Bay, Newfoundland, *Unpubl. M. Sc Thesis*, Newfoundland: Memorial Univ., 1979.

Reimov, M.R., Consequent Bodies in Sedimentary Rocks of the Central Turan Platform and Their Origin, *PhD (Geol.–Miner.) Dissertation*, Moscow: Geol. Inst. Akad. Nauk SSSR, 1996.

Ringwood, A.E., Composition and Evolution of the Upper Mantle, *The Earth's Crust and Upper Mantle*, Hart, P., Ed., Washington: Am. Geophys. Union, 1969. Translated under the title *Zemnaya kora i verkhnyaya mantiya*, Moscow: Mir, 1972, pp. 7–28.

Ronov, A.B., *Osadochnaya obolochka Zemli (kolichestvennye zakonomernosti stroeniya, sostava i evolyutsii)* (Sedimentary Cover of the Earth: Quantitative Parameters of the Structure, Composition, and Evolution), Moscow: Nauka, 1980.

Rundle, C.C. and Snelling, N.J., The Geochronology Uraniferous Minerals in the Witwatersrand Triad: An Interpretation of New and Existing Uranium-Bad Date on Rocks and Mineral from the Dominion Reef, Witwatersrand and Ventersdorp Supergroups, *Phil. Trans. R. Soc*, London, 1977, vol. 286, pp. 567–583.

Schidlowski, M., Beitrage zur Kenntnis der Radioaktiven Bestand Teile der Witwatersrand-Konglomerate: 1. Uranpecherz in den Konglomeraten den Orange-Freistaat-Goldfeldes, *N. Jh. Mineral. Abh.*, 1968, vol. 105, pp. 183–202.

Schidlowski, M., Uraniferous Constitutions of the Witwatersrand Conglomerates: Ore-Microscopic Observations and Implications for the Witwatersrand Metallogeny, *U.S. Geol. Survey Prof. Paper*, 1981, no. 1161.

Schmidt, R.G., Geology and Ore Deposits of Guyuna Range, Minnesota, *U.S. Geol. Survey Prof. Paper*, 1963, vol. 407, pp. 5–67.

Semenenko, N.N., Ferruginous–Cherty–Shaly Volcanogenic Formations, Their Types, and Genesis, *Petrografiya zhelezisto-kremnistykh formatsii SSSR* (Petrography of the Ferruginous-Cherty Formations of the USSR), Kiev: Akad. Nauk Ukrain. SSR, 1955, pp. 24–68.

Semerikov, A.A., The Comparative Characteristics of Nodular Complexes in Jurassic Coal–Bearing Formations, *Konkretsii i konkretsionnyi analiz* (Nodules and Nodular Analysis), Moscow: Nauka, 1977, pp. 96–104.

Serdyuchenko, D.P. and Glebov, A.V., Iron, *Metally v osadochnykh porodakh* (Metals in Sedimentary Rocks), Moscow: Nauka, 1964, pp. 18–100.

Shnyukov, E.F. and Naumenko, P.I., *Margantsevo-zheleznye rudy Kerchenskogo basseina* (Manganese–Ferruginous Ores in the Kerch Basin), Simferopol: Krymizdat, 1961.

Shul'ts, S.S., Geological Structure of the Sultanuizdag Range and Its Geological Position at the Ural–Tien Shan Junction, *PhD (Geol.-Miner.) Dissertation*, Leningrad: Vses. Geol. Inst., 1967.

Shul'ts, S.S., *Geologicheskoe stroenie zony sochleneniya Urala i Tyan-Shanya* (Geologic Structure of the Ural–Tien Shan Junction), Moscow: Nedra, 1972.

Sinitsyn, A.V., *Regional'naya tektonika i metallogeniya rannego dokembriya* (Regional Tectonics and Metallogeny of the Early Precambrian), Leningrad: Nedra, 1990.

Stepanov, P.I. and Mironov, S.I., *Geologiya mestorozhdenii kaustobiolitov* (Geology of Caustobiolith Deposits), Leningrad: Otd. Nauchn. Tekhn. Inform. NKTP, 1937.

Strakhov, N.M., *Zhelezorudnye fatsii i ikh analogi v istorii Zemli* (Iron Ore Facies and Their Analogues in the Earth's History), Tr. IGN Akad. Nauk SSSR, Ser. Geol., 1947, issue 73, no. 22.

Strakhov, N.M., *Osnovy teorii litogeneza* (Fundamentals of the Theory of Lithogenesis), Moscow: Akad. Nauk SSSR, vol. 2, 1960.

Strakhov, N.M., *Tipy litogeneza i ikh evolyutsiya v istorii Zemli* (Types of Lithogenesis and Their Evolution in the Earth's History), Moscow: Gos. Izd. Nauchn. Tekh. Lit., 1963.

Timofeev, P.P., *Yurskaya uglenosnaya formatsiya Yuzhnoi Sibiri i usloviya ee obrazovaniya* (The Jurassic Coal-Bearing Sequence in Southern Siberia and Its Depositional Environment), Tr. Geol. Inst. Akad. Nauk SSSR, 1970, issue 18.

Timofeeva, M.V., Factors Guiding the Formation of Ferromanganese Carbonates and Silicates in Banded Iron Formations, *Dokl. Akad. Nauk SSSR, Ser. Geol.*, 1987 vol. 295, no. 4, pp. 940–943.

Timoshenko, N.A., Spherosiderites of the Bogoslovskoe Coal Deposit, *Priroda*, 1953, no. 8, pp. 29–46.

Tochilin, M.S., Relict Indications in Magnetite Quartzites of the KMA and Their Genetic Interpretation, *Miner. Sb. L'vov. O-va L'vov. Gos. Univ.*, 1952, no. 6, pp. 33–64.

Tochilin, M.S., Geochemistry of Authigenic Siderites, *Voprosy mineralogii osadochnykh obrazovanii* (Mineralogy of Sedimentary Rocks), L'vov, 1956, books 3/4, pp. 203–217.

Trendell, A.F. and Blockley, J., The Iron Formations of the Precambrian Hamersley Group, Western Australia, with Special Reference to the Associated Crocidolite, *West. Austral. Geol. Survey Bull.*, 1970, vol. 119, pp. 336–369.

Trendell, A.F., Precambrian Iron Ore Provinces of Australia, *Dokembriiskie zhelezorudnye formatsii mira* (Precambrian Iron Ore Formations of the World), Moscow: Mir, 1975, pp. 155–172.

Tugarinov, A.I., Bergman, I.A., and Gavrilova, L.K., Facies Composition of the Iron Ore Formation in the Krivoi Rog Region, *Geologiya i genezis dokembriiskikh zhelezisto-kremnistykh i margantsevykh formatsii mira* (Geology and Genesis of the Precambrian Ferruginous–Cherty and Manganese Formations of the World), Kiev: Nauk. Dumka, 1972, pp. 27–33.

*Unifitsirovannye i korrelyatsionnye stratigraficheskie skhemy Urala (UKSS)* (Unified and Correlated Stratigraphic Schemes (UCSS) of the Urals), Sverdlovsk, 1980.

Vil'ner, A.I., Coal, *Mineral'nye resursy kapitalisticheskikh stran* (Mineral Resources of the Capitalist Countries), Moscow: Gos. Izd. Nauchn. Tekh. Lit., 1959, pp. 5–64.

Vinogradov, V.I., Reimer, T.O., Leites, A.M., and Smelov, S.B., Ancient Sulfates in Archean Rocks from the South African and Aldan Shields and the Evolution of the Oxygen Atmosphere of the World, *Litol. Polezn. Iskop.*, 1976, no. 4, pp. 12–28.

Volkova, A.N., Carbonate Nodules in the Balakhon Group of the Kuznetsk and Gorlovka Basins, *Konkretsii i konkretsionnyi analiz* (Nodules and Nodular Analysis), Moscow: Nauka, 1977, pp. 74–80.

Von Damm, K.L. and Bischoff, J.J., Chemistry of Hydrothermal Solution from the Southern Juan de Fuca Range, *J. Geophys. Res.*, 1987, vol. 92, no. 11, pp. 344–346.

Yanitskii, A.A., *Oligotsenovye oolitovye zheleznye rudy Severnogo Turgaya i ikh genezis* (Oligocene Oolitic Iron Ores in Northern Turgai and Their Genesis), Tr. Inst. Geol. Rudn. Mestor. Petrogr. Miner. Geokhim. Akad. Nauk SSSR, 1960, no. 37.

Yanitskii, A.A. and Sergeev, O.P., *Bakal'skie zhelezorudnye mestorozhdeniya i ikh genezis* (The Bakal Iron Ore Deposits and Their Genesis), Moscow: Akad. Nauk SSSR, 1962.

Yavorskii, V.I. and Butov, P.I., *Kuznetskii kamennougol'nyi bassein* (The Kuznetsk Coal Basin), Tr. Geolkoma, 1927, Nov. Ser., issue 177.

White, D.A., The Stratigraphy and Structure of the Mesabi Range, Minnesota, *Minnesota Geol. Survey Bull*, 1954, vol. 92, pp. 44–92.

Zaritskii, P.V., *Mineralogiya i geokhimiya diageneza uglenosnykh otlozhenii* (Mineralogy and Geochemistry of the Diagenesis of Coal-Bearing Rocks), Kharkov: Khar. Gos. Univ., 1970.

Zaritskii, P.V., *Mineralogiya i geokhimiya diageneza uglenosnykh otlozhenii* (Mineralogy and Geochemistry of the Diagenesis of Coal-Bearing Rocks), Kharkov: Kharkov. Gos. Univ., 1971.

Zaritskii, P.V., *Konkretsii i znachenie ikh izucheniya pri reshenii voprosov ugol'noi geologii i litologii* (Nodules and Their Inplication in Coal Geology and Lithology), Kharkov: Kharkov. Gos. Univ., 1985.

Zaritskii, P.V., Makedonov, A.V., and Sal'nikova, L.L., Nodules from Carboniferous and Permian Coal-Bearing Rocks in the USSR, *Osadkoobrazovanie i genezis uglei karbona SSSR* (Sedimentation and Genesis of Carboniferous Coals in the USSR), Moscow: Nauka, 1971, pp. 163–173.

Zavaritskii, A.N., *K voprosu o proiskhozhdenii zheleznykh rud Bakala* (Problem of the Origin of Iron Ores in Bakal), Moscow: Akad. Nauk SSSR, 1939.

Zitzman, A. and Neumann-Redling, Chr., *The Genetic Types of Iron Ore Deposits of Europe and Adjacent Areas*, Hannover, 1977, vol. 1.