

## Problems of Siderite Formation and Iron Ore Epochs: Communication 2. General Issues of the Precambrian and Phanerozoic Ore Accumulation

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Received December 22, 2003

**Abstract**—It is shown that peat bogs, which accumulate coal- and siderite-bearing sediments, serve as a generator of ferruginous solutions with the significant part of Fe migrating from them in the form of metalloorganic compounds. The stability of organic Fe-bearing complexes provides favorable conditions for the late diagenetic–catagenetic siderite formation in adjacent sea basins. It has been established that the formation of Phanerozoic coals, oil shales, and black shales was nearly coeval with the formation of goethite–chlorite–siderite ores. The paper discusses the influence of volcanic activity on the formation of Precambrian–Phanerozoic iron ore deposits and emphasizes the significance of siderite formation in the general evolution of the sedimentary iron ore formation.

### PEAT BOGS AS A SOURCE OF FERRUGINOUS SOLUTIONS

Since the middle of the 18th century, peat bogs were studied by many researchers (V.V. Dokuchaev, I.I. Zhilinskii, V.I. Vernadsky, V.N. Sukachev, N.A. Tutkovskii, D.A. Gerasimov, G.I. Panfil'ev, S.N. Tyuremnoi, N.M. Strakhov, D.S. Orlov, G.I. Bushinskii, M.N. Nikonov, P.P. Timofeev, L.I. Bogolyubova, V.A. Kovalev, A.I. Perel'man, V.G. Matukhina, and others).

Based on the recharge mode of bogs, Sukachev (1964) proposed to divide the peat bogs into the highmoors, which originate under the influence of atmospheric precipitation, and the lowmoors related to the activity of groundwater and atmospheric precipitation.

From the viewpoint of metallogeny of iron ore deposits, the lowmoors, which are frequently located along seacoasts and in river deltas, are of the greatest interest, because the large-scale paralic coal accumulation is usually associated with such peat bogs.

The peats represent specific basins, which accumulate a significant amount of vegetative biomass and polygenous mineral compounds during the persistent or temporal excess humidity. Processes of peat accumulation and coalification of the vegetative mass are accompanied by a substantial transformation of geochemical environment in bog waters. This triggers the formation of iron ore, phosphate, and aluminosilicate compounds inside bogs and along their peripheries.

During this process, the vegetative mass is gradually transformed into peat. In the course of subsidence, the peat is successively transformed into the brown and other varieties of coal, and, finally, into anthracites that

terminate the long-term process of compaction, dehydration, molecular reorganization, and coalification.

The main geochemical process typical of peat bogs is the peat formation (decay, humification, and bituminization of terrestrial organic matter under the activity of soil bacteria). This results in the excess of CO<sub>2</sub> and organic acids that determine all specific features of the *gleyey* geochemical environment in freshwater peats in the absence of sulfate waters (Perel'man, 1974; Kovalev, 1985). In this medium, many polyvalent metals (Fe and others), which readily pass into solutions, are reduced and partly bound with the dissolved organic matter to form organic iron (hereafter, metalloorganic) complexes. They are partly removed from solutions in the form of phosphates, such as vivianite Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> · 8H<sub>2</sub>O and others, and carbonates (siderite FeCO<sub>3</sub> and others). It is also conceivable that the behavior of Fe in boggy environments depends on the degradation of aluminosilicates, opal precipitation, and formation of kaolinite and chlorites (Timofeev and Bogolyubova, 1972; Kovalev, 1985; Drits and Kossovskaya, 1991).

Iron in bog waters is derived from underlying rocks, on the one hand, and the terrigenous material delivered to the bog formation area as suspended matter, on the other hand.

Iron is widespread in sediments. Its average content in the stratisphere is estimated at 3.33% (Vinogradov, 1962). The share of Fe<sub>2</sub>O<sub>3</sub> and FeO is estimated at 2.42 and 2.38%, respectively (Ronov, 1993). The average Fe content amounts to 5.8% in red clays and decreases to 2.5% in green clays (Walker, 1967). In arkosic sandstones, the FeO content ranges from 0.31 to 1.31%; the Fe<sub>2</sub>O<sub>3</sub> content, from 0.59 to 2.90%. In graywackes, the

FeO content varies from 2.03 to 7.63%; the Fe<sub>2</sub>O<sub>3</sub> content, from traces to 1.41% (Pettijohn *et al.*, 1976).

Red clays, siltstones, and sandstones are rapidly reduced under the influence of boggy gleyey waters. They acquire the greenish color and lose a significant share of initial Fe that passes into the solution.

The intense interaction between boggy waters and sediments is related to the usual distinct rhythmic alternation of terrigenous, terrigenous–calcareous, and coaly layers in the coaliferous sections. This suggests that the peat bog facies was repeatedly replaced by the marine, coastal-marine, and continental facies, which could simultaneously accumulate during a long geological time.

Bog waters are usually enriched in dissolved Fe. For instance, the Fe content is 100 mg/l in peats from the upper floodplain of the Zapadnaya Dvina River (Korotkov and Khodina, 1981), approximates this value in gleyey waters of the West Siberian Plain (Udodov *et al.*, 1983), and as high as 250 mg/l in water leachate from the humus-peat soil of the Moscow region (Kaurichev, 1957). Since the average content of dissolved Fe in river waters is estimated at 40 µg/l (Martin and Mayback, 1979), it is easy to calculate that the Clarke concentration of this metal in the gleyey medium of bogs should vary between 2500 and 6250.

In order to adequately estimate the huge influx of Fe from peat bogs into terminal discharge basins, one should remember that areas of coaliferous basins approximately corresponding to dimensions of peat bogs were spacious during some coal accumulation epochs. For example, the Carboniferous Period was marked in Eurasia by coal accumulation in the Kuznetsk (26000 km<sup>2</sup>), Moscow (120000 km<sup>2</sup>), and Donets (35000 km<sup>2</sup>) basins. In the North American continent, coals accumulated in the Great Appalachian (180000 km<sup>2</sup>) and Inner Provinces (approximately 344000 km<sup>2</sup>) basins at that time.

The Permian Period is known for giant coaliferous structures, such as the Tungus (1045000 km<sup>2</sup>), Pechora (90000 km<sup>2</sup>), and Taimyr (50000 km<sup>2</sup>) basins.

The Lena (400000 km<sup>2</sup>) and Irkutsk (43000 km<sup>2</sup>) coaliferous basins formed in the Jurassic and Cretaceous periods.

It is also worth mentioning that the enormous thickness of coaliferous formations (sometimes reaching a few kilometers) and extreme abundance of coal seams (up to 100–200) indicate the stability of boggy facies. Thus, these areas of vegetative biomass concentration served as powerful and permanent sources of ore components. This is evident from numerous iron hydroxide accumulations around areas of present-day and older bogs.

On the whole, bog systems are usually characterized by a sufficiently distinct mineralogical–geochemical zonality. Lenticular bodies of siderite, ankerite, vivianite, peat vivianite, various iron hydroxides and less common manganese hydroxides accumulate inside

peat bogs (Bushinskii, 1952; Kovalev, 1985; Matukhina and Mikhant'eva, 2001). Ocherous and nodular iron ores composed of goethite, hydrogoethite, and cryptocrystalline iron hydroxides with a P<sub>2</sub>O<sub>5</sub> admixture occur along their periphery. Marine oolitic hydroxide–chlorite–siderite ores are concentrated in the remote parts of boggy areas with the river valley or shallow-water settings.

#### IRON MOBILIZATION MODES IN PROCESSES OF PEAT AND COAL ACCUMULATION

It is well known that Fe is a constituent of many minerals in sedimentary rocks. In line with the method of the determination of Fe forms proposed in (Zalmanzon, 1957) and widely used in (Strakhov, 1957; Strakhov *et al.*, 1959), the Fe budget can be presented in the following way:

$$Fe_{\text{bulk}} = Fe_{\text{detr}} + Fe_{\text{sulf}}^{+2} + Fe_{\text{HCl}}^{+3} + Fe_{\text{HCl}}^{+2} \text{ ('detr' and 'sulf' are the detrital and sulfide forms, respectively).}$$

Among these Fe forms, the detrital Fe is extracted from terrigenous minerals by the decomposition in hydrofluoric and sulfuric acids under heating; sulfide Fe is calculated based on the sulfur content; ferrous Fe is determined by the decomposition in a weak hydrochloric acid (therefore, it includes Fe from carbonates and lepto-chlorites); and soluble ferric Fe is estimated from the sulfuric acid leachate by subtracting the soluble ferrous Fe from its total quantity.

Although the accepted chemical determinations are tentative, we attempted to trace the transformation of Fe forms in different facies settings of coaliferous basins and, correspondingly, in different peat-bog systems. We chose argillites and argillite-type clays as indicators; clays differ from the well-permeable sandstones and, partly, argillites by the capability for retaining a distinct record of primary redox settings, which are rarely distorted by the oxidizing catagenetic solutions.

Clays and argillites from the Karaganda and Donets coaliferous basins were chosen as the main investigation objects. They represent typical Carboniferous paralic basins described in detail by many researchers (Logvinenko, 1953, 1956; Ishina, 1955; Koperina, 1956; and others). Geochemical peculiarities of these basins are discussed in the monograph (Strakhov *et al.*, 1959), the data from which are presented in Tables 1 and 2. Figure 1 demonstrates the general behavior of Fe along the hypothetical continent–sea profile.

It should be emphasized that Koperina (1956) and Strakhov *et al.* (1959) recognized two contrast processes in the paleogeographic development of the Karaganda region: (1) the regression of the marine paleobasin that commenced in the Ashlyarik time and lasted until the Nadkaraganda time, when deltaic–lacustrine–boggy landscapes with intense coal formation became dominant; (2) the formation of uplifts bordering the Karaganda Synclinorium and development

**Table 1.** Iron forms and content of organic carbon in clays and argillites of the Karaganda Basin (Strakhov *et al.*, 1959)

Facies, formations	Fe <sub>tot</sub>	Iron forms				C <sub>org</sub> , %
		Fe <sub>detr</sub>	Fe <sub>sulf</sub>	Fe <sub>HCl</sub> <sup>+3</sup>	Fe <sub>HCl</sub> <sup>+2</sup>	
Facies of dry plains and fans						
Naddolin and Shikhan formations	5.17	2.10	0.07	0.60	2.40	0.24
	100	40.6	1.35	11.60	46.45	
Nadkaraganda Formation	7.37	2.29	0.05	2.10	2.93	0.36
	100	31.07	0.63	28.50	39.8	
Lacustrine facies in association with fans						
Naddolin Formation	3.33	1.26	0.12	0.20	1.95	1.06
	100	35.99	5.62	3.47	54.92	
Dolin Formation	3.07	0.83	0.14	Not detected	2.10	1.32
	100	27.03	4.56	Not detected	68.41	
Facies of marine shoals						
Karaganda Formation	5.55	0.42	2.03	0.20	2.90	5.82
	100	7.57	36.58	3.60	52.25	
Ashlyarik Formation	5.77	0.56	0.62	0.18	4.41	2.73
	100	9.70	10.76	3.12	76.42	

**Table 2.** Iron forms and content of organic carbon in clays and argillites of the Donets Basin (Strakhov *et al.*, 1959)

Facies, formations, areas	Fe <sub>tot</sub>	Iron forms				C <sub>org</sub>
		Fe <sub>detr</sub>	Fe <sub>sulf</sub>	Fe <sub>HCl</sub> <sup>+3</sup>	Fe <sub>HCl</sub> <sup>+2</sup>	
Continental facies						
Dolzhan area	5.20	1.78	0.05	1.64	1.73	0.63
	100	34.23	0.96	31.54	33.27	
Transitional facies						
Dolzhan area	5.22	1.32	0.40	0.21	3.28	1.08
	100	25.37	7.66	4.02	62.95	
Bokov area	4.92	1.61	0.17	0.63	2.51	0.70
	100	32.72	3.46	12.82	51.00	
Marine facies						
Dolzhan area	5.90	0.93	0.66	0.09	4.22	1.31
	100	15.75	11.18	1.52	71.55	

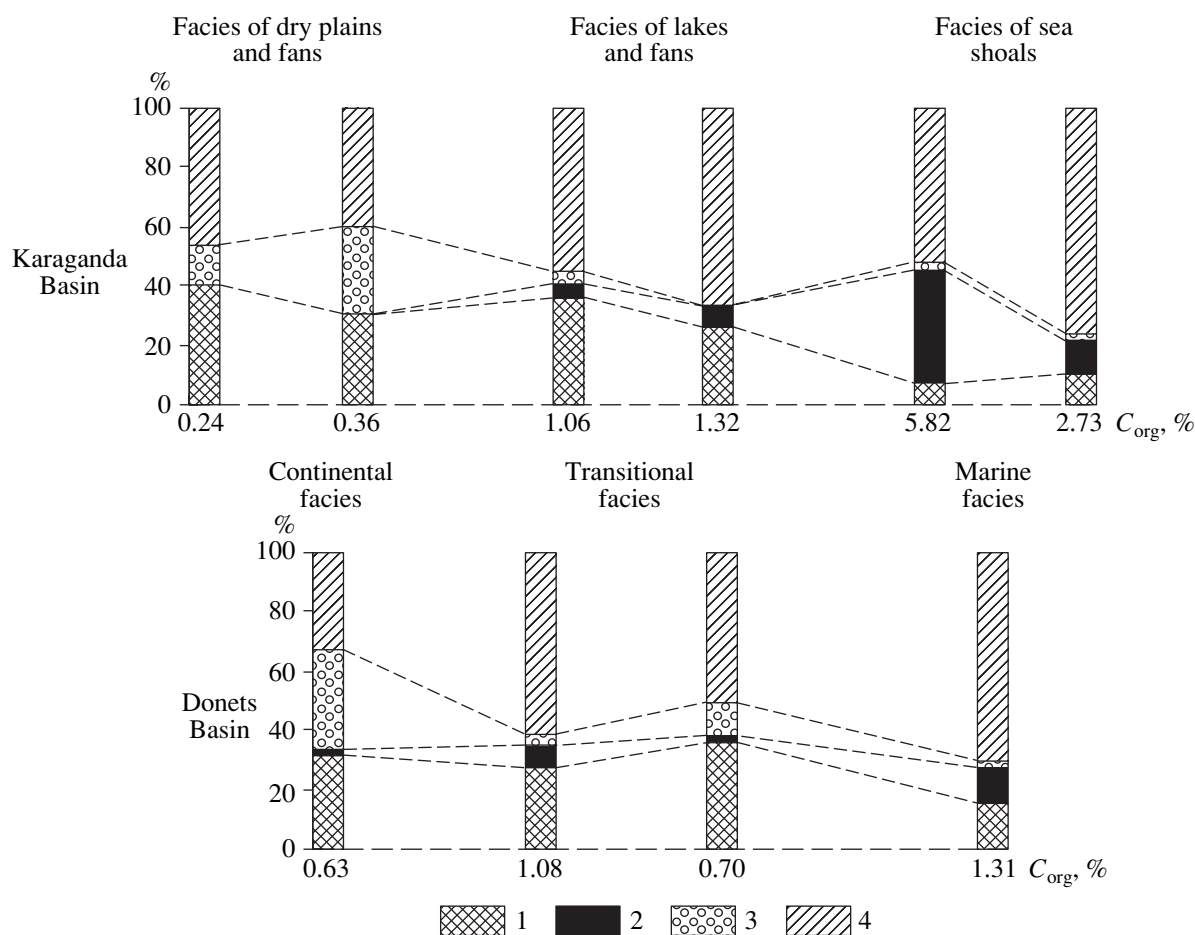
of the arid climate that suppressed coal accumulation in the Naddolin and Shikhan time.

The behavior of Fe forms in argillites distinctly demonstrates a decrease in the proportion of detrital Fe and increase in the content of HCl-soluble Fe<sup>+2</sup> when moving from dry plains and fans to sea shoals (Fig. 1). Moreover, continental facies are characterized by the presence of HCl-soluble Fe<sup>+2</sup>, while marine sediments typically contain sulfide Fe. This indicates the undoubted presence of SO<sub>4</sub><sup>-2</sup> anion in seawater and the

intense microbiological sulfate reduction in sediments because of the organic matter excess.

The behavior of Fe forms in clayey sediments of the Donets Basin is principally similar. In both cases, marine clays and argillites located near the sites of coal and peat bog formation are significantly enriched in the HCl-soluble bivalent Fe and depleted in Fe<sub>detr</sub>.

Microscopic observations revealed that the reduced Fe in clayey sediments of coaliferous formations mainly occurs as siderite or less common chlorites (Strakhov *et al.*, 1959).



**Fig. 1.** Distribution of iron forms in argillites and clays of different facies zones in coaliferous formations of the Karaganda and Donets basins. (1)  $\text{Fe}_{\text{detr}}$ ; (2)  $\text{Fe}_{\text{sulf}}$ ; (3)  $\text{Fe}_{\text{HCl}}^{+3}$ ; (4)  $\text{Fe}_{\text{HCl}}^{+2}$ .

The comparison of Fig. 1 with Fig. 2, which characterizes proportions of different Fe forms in different-aged marine clayey sequences that are unrelated to processes of peat and coal accumulation processes, clearly demonstrates the unusual behavior of Fe in marine clayey sediments spatially associated with peat bogs and coals.

Figure 2 shows the relative contents of different Fe forms in marine clayey sequences calculated for Frasnian sediments of the Urals region, Middle Miocene sediments of eastern Ciscaucasia, and Quaternary mud of the Black Sea using the data from (Strakhov *et al.*, 1959; Rozanov *et al.*, 1974; Kholodov and Nedumov, 1981).

It is clearly seen that  $\text{Fe}_{\text{detr}}$  and  $\text{Fe}_{\text{HCl}}^{+2}$  are usually present in approximately equal proportions in the marine clay and mud, while the ferric and sulfide Fe forms occur as subordinate ones in stable proportions.

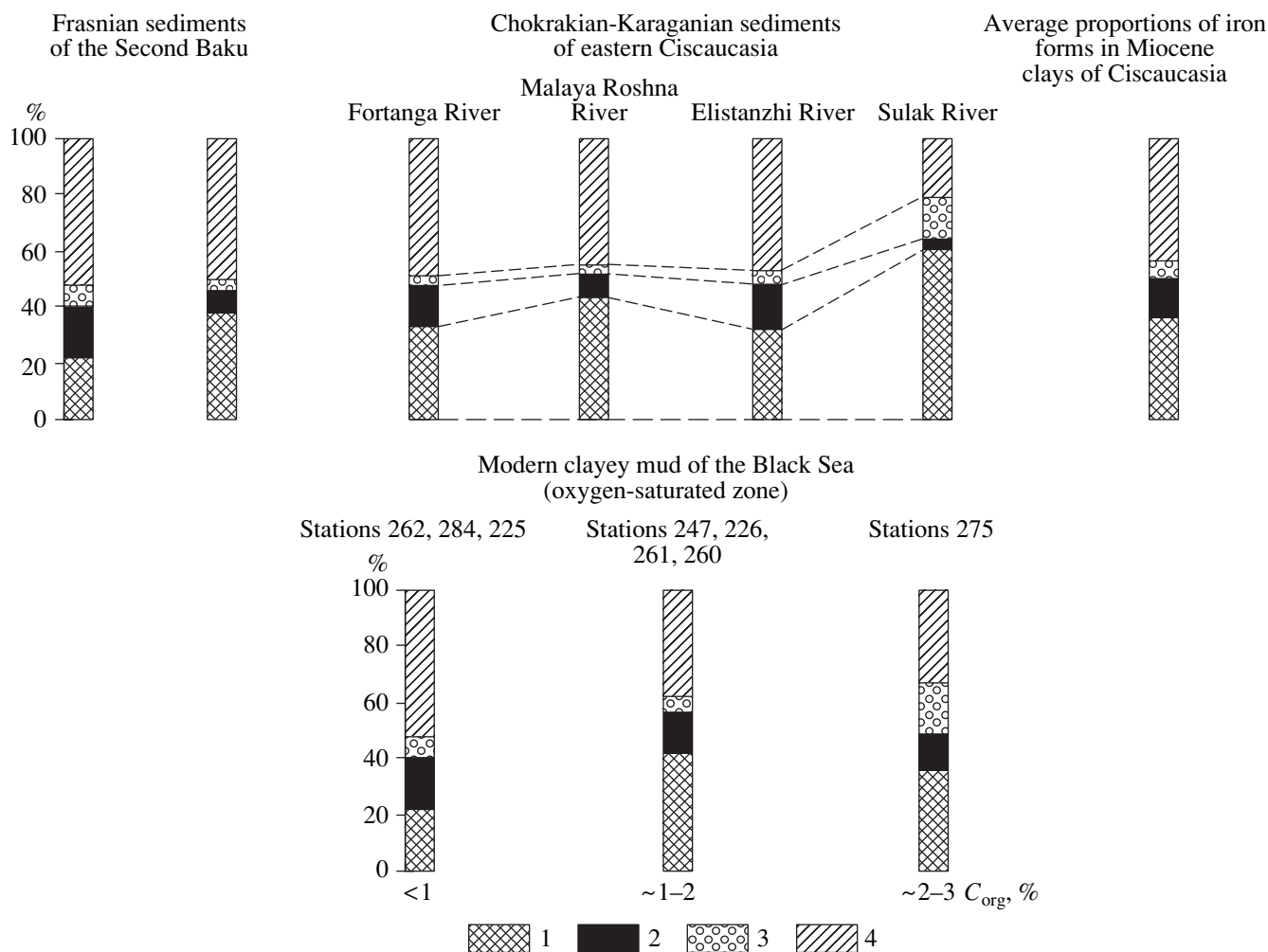
It is interesting that the total content of dispersed carbonates in the Domanic and Chokrakian-Karaganian sediments ranges from 1.0–1.5 to 4–6% (Strakhov *et al.*, 1959; Kholodov and Nedumov, 1981). This sug-

gests that the decrease of the HCl-soluble bivalent Fe reflects the decrease of dispersed  $\text{FeCO}_3$  in clays.

It is apparent that the peat bogs, which subsequently generated coal deposits, supplied the adjacent marine basins with Fe of a different occurrence mode relative to its counterparts in the river runoff.

Indeed, the above conclusion has been substantiated by Gordeev (1983) who studied the behavior of dissolved Fe in waters of 20 rivers falling into the Black, Azov, and Caspian seas. He extracted the dissolved Fe with the help of chloroform and the GMDTK-GMA system based on butyl acetate before and after the sample treatment by potassium persulfate with sulfuric acid. The results showed that 25–60% of dissolved Fe in the modern river runoff migrates as inorganic forms, such as molecules, ions, and inorganic complexes, while 40–60% of the metal migrates as complex metal-organic compounds, the organic constituent of which is represented by humic and fulvic acids and lipids.

Kojhi *et al.* (1982), who studied the distribution of Fe in waters of rivers, lakes, and coastal areas of the Sea of Japan, obtained similar results.



**Fig. 2.** Distribution of iron forms in marine clayey sequences of the Ural region, eastern Ciscaucasia, and Black Sea. (1)  $Fe_{detr}$ ; (2)  $Fe_{sulf}$ ; (3)  $Fe_{HCl}^{+3}$ ; (4)  $Fe_{HCl}^{+2}$ .

The behavior of dissolved Fe in bog waters is substantially different. According to Efimov (1961, p. 136), who studied the composition of leachates from high- and lowmoors of the Leningrad region, “the major part of Fe is bound with organic matter as organomineral compounds.” The only exclusion is the lowmoor peat with an extremely high content of Fe, which is also accumulated here as free hydroxide. In acid highmoor and transitional peats, some Fe occurs as free ion.”

Antipov-Karataev (1937), Strakhov (1960), Kovalev (1985) and many other researchers have emphasized the crucial role of metalloorganic compounds in bog waters. They have shown that humic and fulvic acids make up with Fe stable metalloorganic compounds, such as chelates that stimulate the migration of bivalent Fe over a great distance. Carbonaceous acids, tannic compounds, and some other organic structures also show similar chelate properties relative to Fe (Hem

and Cropper, 1959; Hem, 1960; Kovalev, 1985; Varshal *et al.*, 1993).

Therefore, there are grounds to assume that different Fe forms take part in ore genesis under the direct influence of  $CO_2$  during the accumulation of siderite ores, which are spatially associated with peat and coal-forming basins, although inorganic compounds prevail. Complex metalloorganic compounds played the major role during the formation of siderite lodes in sea basins located far from peat bogs and coaliferous deposits.

This fact has been demonstrated by Matsumoto and Jijima (1981) who scrutinized the behavior of carbonates in Paleogene coaliferous sediments of the Ishikari, Kado, Ioban, and Miike deposits located in the Kyushu, Honshu, and Hokkaido islands of Japan (Fig. 3).

It should be emphasized that these authors tried to reconstruct the history of carbonate accumulation in coaliferous formations from the day surface to the depth of 3000 m. They examined the diagenetic trans-

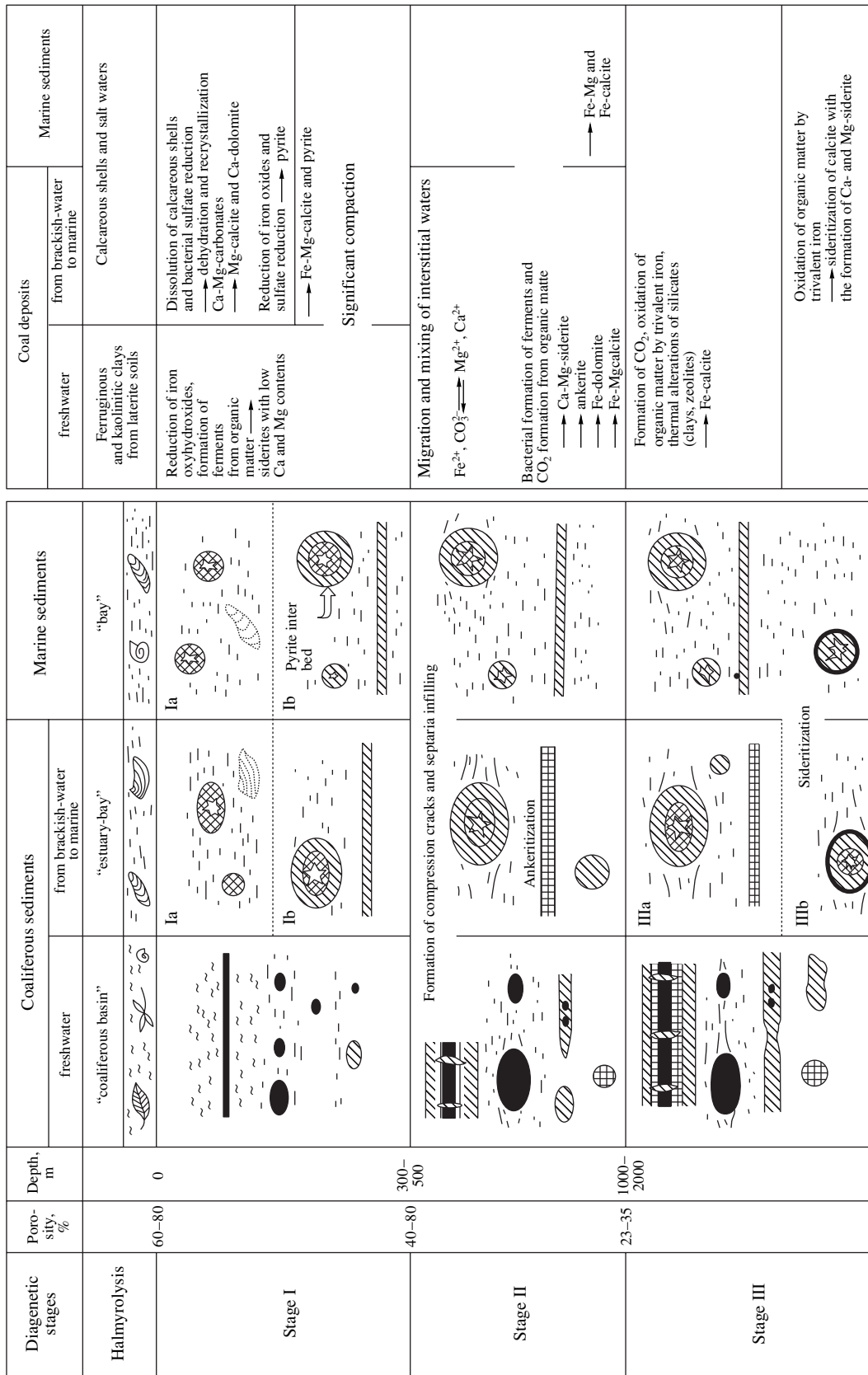


Fig. 3. Secondary alterations of authigenic carbonates in coaliferous formations of Japan (Matsumoto and Jijima, 1981). (1) Siderite; (2) ankerite; (3) calcite; (4) magnesian calcite.

formations (halmyrolysis and stage I, Fig. 3) and catagenetic alternations that correspond to stages II and III. Thus, the compaction boundary located at depths of 300–500 m corresponds to the lower limit of subaqueous diagenesis defined in (Strakhov, 1960).

The figure also clearly shows that the freshwater coal accumulation closely associated with the river run-off sharply differs from the same process in brackish-water and sea basins in terms of morphology and succession.

In the first case, the siderite concretions and lenses accumulated by the diagenetic mode owing to the influx of iron oxides and hydroxides from humid weathering zones. It is conceivable that Fe migration was related to kaolinite redeposition (Carroll, 1958). In peat bogs, Fe was reduced to the bivalent state.

The CO<sub>2</sub> formation was a more complicated process. It could result from the bacterial oxidation of plant remains (according to the reaction  $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ ), the activity of sulfate-reducing bacteria ( $2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow 2\text{CO}_2 + \text{S}^{2-} + \text{H}_2\text{O}$ ), or the fermentative decomposition of organic matter ( $2\text{CH}_2\text{O} \rightarrow \text{CH}_4 + \text{CO}_2$ ). The last reaction is most probable.

Anyway, siderite nodules formed at the earliest stages would be preserved in this case during all of the subsequent stages of coaliferous sediment transformation (Fig. 3).

It is more difficult to explain the siderite accumulation in brackish-water and marine facies of coaliferous formations. We suppose that ankerite and siderite formed in this case as a result of the subsidence of coaliferous sequences to great depths and the reduction of iron hydroxides to the bivalent state at high temperatures.

We assume that the brackish-water setting of estuaries and bays could promote the delivery of some Fe to sediments in the bivalent form as stable metalloorganic complexes. Diagenetic transformations, including even intense ones, such as microbiological sulfate reduction and pyrite formation at the expense of iron hydroxides reduced to the bivalent form, as well as the migration and mixing of interstitial and infiltration waters with the formation of Mg-calcites and ankerites, did not affect these stable chelate metalloorganic compounds.

Only under conditions of high temperatures at great depths, thermolysis and thermocatalysis of the organic component resulted in the release of carbon dioxide and bivalent Fe and the formation of siderite, the latest carbonate mineral that makes fringes around calcite cores (concretions).

Thus, Fe forms developed in the course of mobilization and redeposition of sedimentary material probably governed the formation of the sedimentary-diagenetic siderite, on the one hand, and the diagenetic-catagenetic variety, on the other hand.

**Table 3.** Distribution of coal reserves in time (Zheleznova and Matveev, 1973)

Age	Reserves, 10 <sup>12</sup> t	Reserves, %
Paleogene + Neogene	2.124	14.6
Cretaceous	2.9	21.0
Jurassic	2.3	16.0
Triassic	0.006	0.04
Permian	3.780	27
Carboniferous	2.890	21
Devonian	0.0002	0.001

### STRATIGRAPHIC RELATIONSHIPS BETWEEN FOSSIL FLORA BURIALS AND SEDIMENTARY NODULAR-OOLITIC IRON ORES IN THE PHANEROZOIC

The stratigraphic distribution of coaliferous formations in Russia and the world has been discussed in many works by P.I. Stepanov, A.I. Egorov, G.V. Korotkov, A.K. Matveev, M.M. Prigorovskii, A.V. Tyazhnov, G.F. Krashennnikov, V.P. Maksikovskii, A.V. Make-donov, P.P. Timofeev, G.A. Ivanov, A. Parker, P. Averrit, M. Smyth, A.C. Cook, and others.

Zheleznova and Matveev (1973) scrutinized the stratigraphic distribution of world coal reserves and estimated that the total coal reserves of the world range from 12000 to 23000 Gt averaging 16000 Gt or  $16 \times 10^{12}$  t (as of 1970). Table 3 presents their distribution in the Phanerozoic sedimentary succession.

The table does not include reserves of the giant Alta Amazona brown coal deposit associated with Neogene sediments of South America (approximately  $2.2 \times 10^{12}$  t of low-rank coal).

As was shown in our first communication (Kholodov and Butuzova, 2004), many coal deposits of Europe and Asia are enriched in nodular siderite ores. Coal deposits are occasionally mined to extract mainly iron ores, e.g., coaliferous deposits of Staffordshire (England). For some coal deposits of England and Germany, siderite ore reserves were estimated along with commercial coal reserves. Although such calculations are approximate, they allow the distribution of diagenetic nodular iron ores to be estimated for different-aged coal deposits.

The share of siderite ore is approximately 54 Mt ore/Gt coal in the coaliferous formations of South Wales and as much as 140–150 Mt ore/Gt coal in coaliferous basins of central and northern England.

If we accept the minimal coefficient for siderite ores as 20 Mt ore/Gt coal and carry out the semiquantitative estimation of only coaliferous basins where different researchers have noted the presence of diagenetic siderite, the general distribution of siderite ores in coaliferous formations can be presented as it is shown in Table 4.

**Table 4.** Distribution of nodular siderite ores in different-aged coaliferous basins

Age, coaliferous basin, country	Coal reserves, 10 <sup>9</sup> t	Reserves of siderite ores, 10 <sup>9</sup> t
Cretaceous		
Coaliferous basins of the Great Northern Plains (United States)	1242	24.84
Transbaikal basins (Russia)	24	0.48
Zyryanka Basin (Russia)	51.1	1.02
South Yakutsk Basin (Russia)	22.9	0.458
Total	1340	26.79
Jurassic		
Kansk–Achinsk Basin (Russia)	601	12.02
Lena Basin (Russia)	1647	32.94
Total	2248	44.96
Permian		
Tungus Basin (Russia)	2345	46.90
Pechora Basin (Russia)	214	4.28
Kuznetsk Basin (Russia)	240	4.50
Total	2799	55.68
Carboniferous		
Great Appalachian Basin (United States)	400	8.0
Donets Basin (Ukraine, Russia)	128	2.56
Karaganda (Kazakhstan)	51	1.02
Kuznetsk Basin (Russia)	284	10.00
Moscow Basin (Russia)	20	0.4
Total	883	21.98

It should be noted that geological coal reserves outside Russia are based on the data of Vil'ner (1959), whereas reserves in Russia and the CIS are based on materials from (Tyzhnov, 1970).

Along with nodular siderite ores associated with coals, Phanerozoic sedimentary formations of continents include abundant marine and continental oolitic ores composed of hydroxides, chlorite–chamosite compounds, and siderite. They are distributed in a wider stratigraphic interval as compared with siderite ores associated with coals. Moreover, some of the deposits of this type have commercial significance. In this communication, the distribution and reserves of such marine and continental goethite–chlorite–siderite ores are characterized based on the data of N.M. Strakhov, V. Lindgren, V. Emmons, G. Berg, K.I. Bogdanovich, N.K. Vysotskii, A.U. Litvinenko, E.F. Shnyukov, L.N. Formozova, V.P. Kazarinov, A.K. Belousov, V.P. Krotov, M.P. Nagorskii, D.P. Serdyuchenko, M.S. Tochilin, A.L. Yanitskii, A. Hayes, H. Harder, F. Blondel, P. Geijer, A. Zitzmann, H. Walter, and others (Table 5).

These data demonstrate that oolitic iron ore deposits occur in a wide stratigraphic interval ranging from the Proterozoic to Quaternary. Some gap occurs only in the Permian and Triassic, probably, related to unfavorable

climatic environments on continents and morphological features of sea basin at that time.

The oldest oolitic iron ores were first reported from Proterozoic jaspilites of the Pretoria Formation in the Transvaal and Bechuanaland regions of South Africa, where usual iron formations, itabirites, and oolitic iron ores replace each other in both lateral and vertical directions (Wagner, 1928; Strakhov, 1947; du Toit, 1957; Formozova, 1973; Button, 1976). Strakhov (1947) emphasized that the presence of abundant terrigenous material, reworking signs (clayey rolls), ripple marks, and desiccation cracks in alternating clays indicate that the oolitic iron ore facies was accumulated in extremely shallow-water coastal settings. In contrast, the laminated structure of jaspilites, large lateral extension of thin laminae, and absence of terrigenous admixture imply a deeper-water accumulation setting in large seas or lakes for this facies.

It is evident that the shallow-water oolitic iron ores gradually replaced the deeper jaspilite accumulations in the geological time. The oolitic ores are sufficiently widespread in Riphean sequences of Australia. Two thick beds of oolitic hematite–chlorite–siderite ores have been reported from the Roper River and Constant Range areas (Edwards, 1953, 1959). Such ores have also been found in the Lower Angara Basin (Ser-



**Table 5.** Distribution and total reserves of marine and continental oolitic goethite–chlorite–siderites ores

Age	Deposit, area, country	Total reserves, 10 <sup>9</sup> t
Pliocene	Kerch iron ore district (Ukraine, Russia)	2.7
Paleogene	Aral region (Kazakhstan), Lisakovsk deposits (Russia), Alabama–Appalachians (United States), Jebel Ank, Ani Babush (Algeria), Wadi Fatima (Saudi Arabia), Kressenberg (Germany)	5.01
Cretaceous	Glusby (England), Redji (Syria), Reimam and others (Israel), Ayat deposit (Russia), Bakchar, Kolpashevo, and other deposits of West Siberia (Russia), Lokoja, Jakura, Jebba (Nigeria), Aswan (Egypt)	35.92
Jurassic	Cleveland–Northampton–Frodingham (England), minette ores of Lorraine (France, Luxemburg), Schwab Albian (Bavaria), Tula and Lipetsk ores (Russia), siderites of Dagestan (Russia), siderites of the Berezov deposit (Russia)	22.05
Carboniferous	Bengal (India), Jenifra, Setat (Morocco), western slope of the Urals (Russia), Vedi-ed-Shati (Libya)	5.066
Devonian	Camidagi (Turkey), Gara Djebilet (Algeria), Eifel (Germany)	6.06
Silurian	Clinton (Alabama, United States)	14.3
Ordovician	Thuringia, Bavaria (Germany), Barrandow Syncline (Czechia), Angue-Bretagne (France), Ait Amar (Morocco), Moncorvo (Portugal), Wabana (Canada), New South Wales (Australia)	5.35
Cambrian	Ore occurrences of the Baltic region, Belarus, Poland, and North Wales (England)	?
Riphean	Lower Angara Basin (Russia), Roper Bar and Constant Range ore occurrences (Australia)	5.0

dyuchenko and Glebov, 1964; Yudin, 1968). Table 5 demonstrates that the distribution areas and reserves of oolitic iron ores generally increase from the Cambrian to Quaternary.

In contrast, jaspilite formations are atypical for the Phanerozoic. The Ordovician Bathurst (Buchans) deposit in Newfoundland (Bonatti and Joensuu, 1966; Swanson *et al.*, 1981) and Carboniferous Tynagh ferromanganese deposit in England paragenetically associated with sulfide ore occurrences (Russel, 1975; Boast *et al.*, 1981) can be referred to the jaspilite formation only with certain reservations.

Following Lindgren (1934) and Strakhov (1947), most of the researchers believed that the oolitic iron ores formed in extremely shallow-water and coastal settings, i.e., in bays, bights, and lagoons characterized by the close association with the surrounding land, delivery of a significant quantity of detrital terrigenous material, and important role of hydrodynamics (waves, currents, erosion, and redeposition) in sedimentation.

The intense mixing of river and seawaters, oxidation of bivalent Fe, and its precipitation were considered the main factors responsible for the formation of oolitic ores.

Formozova (1959) refined this concept and demonstrated that oolitic ores can also accumulate in freshwater or slightly brackish-water lakes and, sometimes, even in riverbeds, in addition to marine settings.

At present, it is evident that acid bog waters formed in lowmoor peats and accumulated in creeks and small flows provided a large-scale influx of bivalent Fe as

ions and metalloorganic compounds. Iron was accompanied by aluminum oxide, silica, and phosphorus.

In moving waters of large rivers, lakes, and sea shoals, the excess of dissolved oxygen and carbonates was responsible for the formation of oxidizing and alkaline barriers. Together with other components, the oxidized and precipitated Fe formed Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> gels, while electrostatic adhesion provided the formation of hydrogoethite–chlorite overgrowths on the detrital terrigenous material, Fe(OH)<sub>3</sub> aggregates, and oolitic sediments. Iron hydroxides and chlorite–chamosite were the earliest authigenic minerals. Siderite was later developed as a result of the more intense reaction of microbiological communities or their ferments with the stable metalloorganic compounds. This mineral frequently replaced the older minerals of oolites or cemented oolitic sediments.

This concept sufficiently well explains the formation of oolitic continental ores during the intense peat and coal accumulation. However, it poses some difficult questions concerning the sources of Fe in the Riphean and Early Paleozoic. According to paleobotanists (Scott, 1927; Mayer, 1946; Wulf, 1946; Krishtofovich, 1957; Meyen, 2001) and coal experts (Stepanov and Mironov, 1937; Zhemchuzhnikov, 1955, and others), plants did not yet occupy land and large-scale peat and coal deposits were absent in this period.

In the Early Paleozoic and Riphean, the bacterial–algal communities, which populated littoral areas of sea basins and rapidly occupied ecological niches in bights, lagoons, and bays, were probably responsible for the generation of metalloorganic compounds. This is indicated by Ordovician and Silurian graptolitic shales that

are particularly widespread in the Baltic region, Sweden, America, Europe, Asia, Africa, and Australia.

The least altered (in terms of catagenesis and metamorphism) communities are represented by *Dictyonema* shales and kukersites of the Baltic region scrutinized by N.F. Pogrebnoi, R.F. Gekker, K.B. Korde, V.P. Maslov, T.N. Davydova, M.N. Alt'gauzen, A.Sh. Davitashvili, D. Kal'yo, E.K. Kivimyagi; A.M. Obut, M.D. Zaleskii, A.Ya. Aarn; S.S. Baukov, A.A. Paap, and others.

The *Dictyonema* shales belong to the Pakerort Horizon, the lower part of which is composed of the inequigranular cross-bedded quartz sands with abundant *Obolus* phosphate shells and their fragments. The upper part includes the *Dictyonema* shales composed of dark gray thin-laminated clayey, silty, organomineral material. The shales contain up to 8–12% of organic carbon (kerogen plus amine and humic acids).

Zhmur (1988, 1999) demonstrated that organic matter of the *Dictyonema* shales was derived from heterogeneous sources. The dominant role belonged to bacterial–microbial mats composed of microorganisms *Microcoleus chthonoplastes*, green bacteria (*Chloroflexus* genus), and red bacteria (*Thiocapsa* and *Thiocystes* genera). Bacterial–algal accumulations associate with remains of graptolites *Dictyonema* and scarce foraminiferal tests. The benthic microbial community of graptolitic shales also includes *Euryterida* and *Philocardita* representatives inhabiting river waters (Miroshnikov, 1978).

Features indicating low salinity of the Ordovician sea are consistent with the presence of allochthonous organic matter that was probably delivered from adjacent land. The shales contain coaly detritus and cutinite (Zhmur, 1988). The humic acids constitute up to 40% of organic matter (Uspenskii (1938).

If it were not finds of the giant freshwater *Nematophyton* occupying the transitional position between the vascular and thallophyte plants (Krishtofovich, 1957; Davitashvili, 1971), the influx of higher plant remains to the Ordovician sea from land could seem improbable. According to Davitashvili (1971, p. 57), "...these plants grew under conditions of high humidity close to the sea" and "...nematophytes are known from the Upper Silurian and Devonian, although the oldest and most primitive representatives of this group also existed during the entire Silurian, Ordovician, Cambrian, and even, in the Proterozoic."

In addition, the discovery of moss-type *Aldanophyton* in Cambrian sequences of Siberia (Krishtofovich, 1953) and the finds of higher plant spores in the Cambrian and Silurian (Darrah, 1937; Naumova, 1949) imply their substantially earlier occupation of land.

Recent paleogeographic reconstructions suggest that bacterial–algal mats and allochthonous organic matter of *Dictyonema* shales accumulated in sublittoral settings of the northern part of a narrow strait (Myannil, 1966). The diagenetic transformation of sediments was partly related to sulfate reduction, because they contain

abundant sulfide inclusions. Therefore, Fe could form abundant metalloorganic compounds, which migrated beyond the littoral and participated in the iron ore formation during the alkalization of acidic waters by carbonates.

The kukersite facies probably served as a subordinate source of Fe delivered from shoals to the deeper parts of sea basins. The kukersites represent a brown clayey–carbonate platy rock with the high content of organic matter (25–65%). In the section, their beds (0.2 to 0.6 m thick) usually alternate with limestones. The total thickness of shales amounts to 6–7 m. The contents of volatile and resin components are as high as 37 and 29% of organic matter, respectively. The shales in Estonia estimated at  $6 \times 10^9$  t (as of the 1940s) were used as fuel.

According to Zaleskii (1916, 1917), the main share of kukersites is composed of Cyanophyceae algae remains (*Gloecapsomorpha prisca*). The electron microscopic study (Zhmur, 1988, 1999) confirmed the bacterial–algal origin of organic matter in kukersites. However, their accumulations turned out to be autochthonous deposits slightly altered by diagenetic processes of the methane generation rather than sulfate reduction trend. Anyway, there are no serious grounds to associate the diagenesis of kukersite accumulations with the process of iron ore formation.

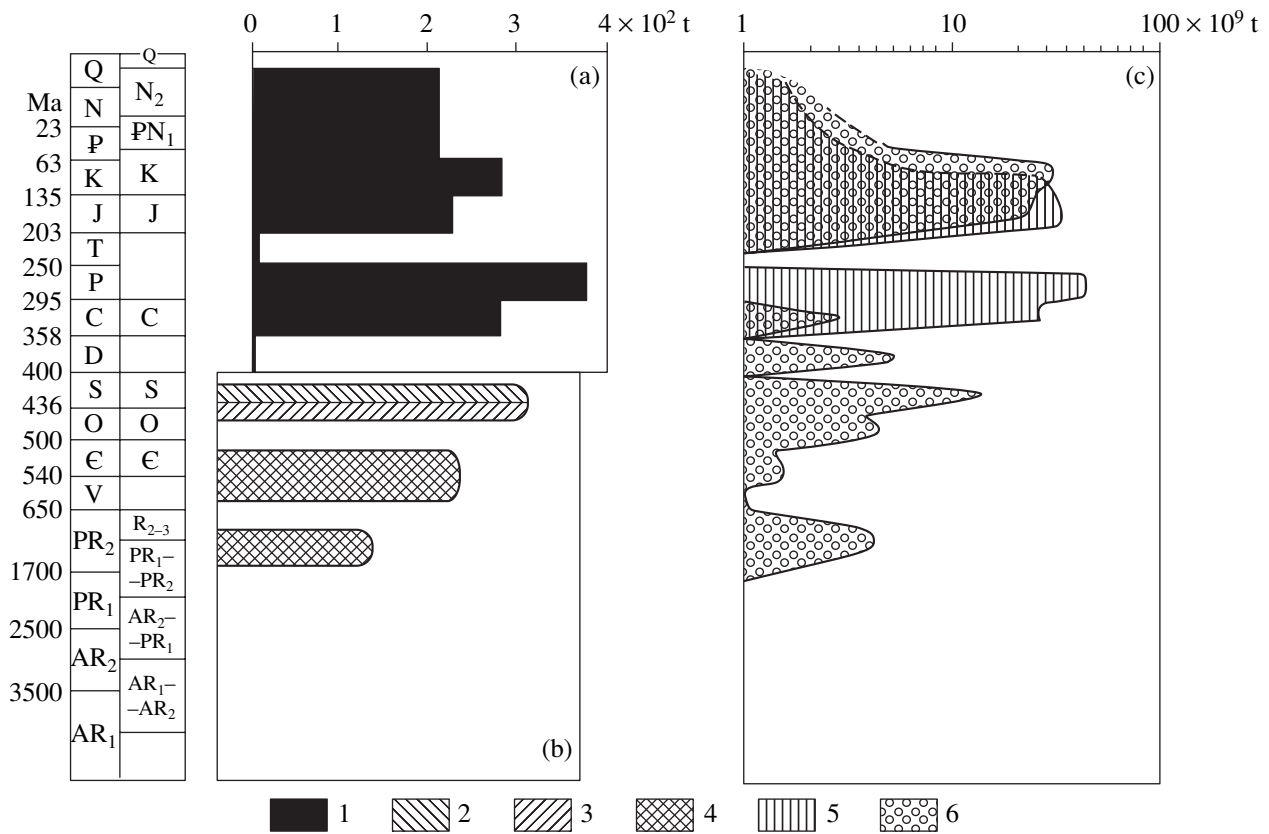
Older black shales are widespread in Vendian–Cambrian and Riphean sequences of Eurasia, America, Africa, and other continents. They are usually intensely metamorphosed and coalified, although they sometimes display undoubted paragenetic relationships with the marine oolitic iron ores (Kholodov, 1973).

Figure 4 demonstrates stratigraphic relationships of black shales, oil shales, coals, oolitic goethite–chlorite–siderite ores and nodular siderites.

Figure 4a shows world commercial coal reserves based on (Zheleznova and Matveev, 1973). Figure 4b demonstrates the stratigraphic distribution of kukersite and graptolite shales, as well as Vendian–Cambrian and Riphean (metamorphosed and coalified) shales, based on the semiquantitative calculation of shale reserves.

Figure 4c shows ore reserves and the stratigraphic distribution of iron ore deposits of two types associated with coaliferous formations of the nodular siderite and continental oolitic goethite–chlorite–siderite ores. The comparison of Figs. 4a–4c suggests that the buried vegetable biomass (coal and shales) was the factor that was responsible for the mobilization of large quantities of Fe on continents, development of its migratory forms, and their concentration in the proximal discharge basins at the same or close stratigraphic level.

Thus, it is evident that the continental and littoral biogenic activity is one of the most important factors that stimulated the accumulation of sedimentary iron ores in Phanerozoic seas.



**Fig. 4.** Stratigraphic distribution of commercial coals, kukersites, *Dictyonema* and black shales, and iron ore deposits. (a) Commercial coal reserves in the world (Zheleznova and Matveev, 1973); (b) stratigraphic position of oil and black shales; (c) commercial reserves of iron ores. (1) Coals; (2) kukersite shales; (3) *Dictyonema* shales; (4) black and metamorphosed shales; (5) nodular siderite ores; (6) oolitic hydrogoethite-chlorite-siderite ores.

**THE VOLCANIC ACTIVITY VERSUS IRON ORE DEPOSITION RELATIONSHIP IN THE PHANEROZOIC**

In addition to hydrogen and oxygen, carbon is among the most important constituents of organic matter. The carbon cycle in upper shells of the Earth has been studied by many researchers (V.I. Vernadsky, V.M. Goldschmidt, W. Noddak, P. Eskola, K. Kalle; W. Fearon, K. Sahama, H.D. Holland, A. Berner, A.B. Ronov, A.I. Perel'man, and others).

The concept of carbon phase transformations within juvenile shells of the planet, its stratified shell, and biosphere (Vernadsky, 1954) is presented in Fig. 5a. It shows that the so-called "life cycle" (Fig. 5b) is the main mechanism that controls the behavior of carbon.

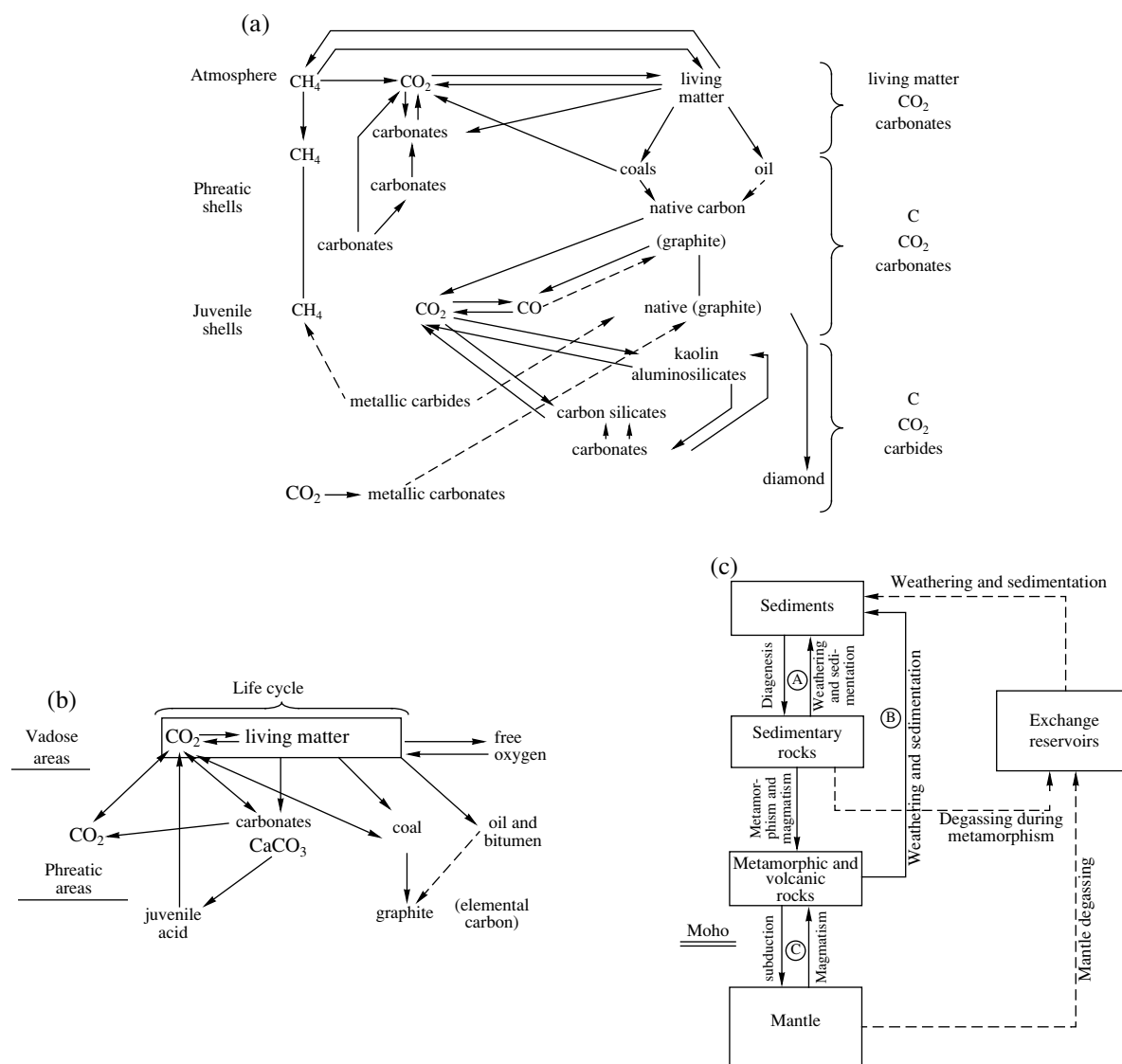
The main process of life cycle is the influx of the phreatic and juvenile forms of carbon dioxide into the atmosphere and its assimilation by living substance of the biosphere. Carbon atoms partly participate in the life cycle and partly form biogenic minerals to abandon the cycle as carbonates, coal, oil, and bitumen. In addition, a large amount of dispersed organic matter is buried in sediments of the Earth's stratosphere and leaves the life cycle.

Thus, some carbon atoms are retained by organic matter in the life cycle, while the remaining part abandons the cycle, emphasizing its partial irreversibility.

Holland (1989) presented a modern version of the global geochemical cycle of carbon (Fig. 5c). He emphasized that the system of carbon migration and concentration includes three smaller cycles. Cycle A includes the weathering of sedimentary rocks, their redeposition in the form of sediments, and the subsequent transformation of sediments into sedimentary rocks. Cycle B comprises catagenetic and metamorphic alterations of sedimentary rocks up to the point of their palingenesis. Cycle C includes the subduction of crustal matter beneath the mantle and its reanimation in the form of newly formed volcanics.

The so-called exchange reservoirs (atmosphere, biosphere, and hydrosphere) play an important role in this concept. Holland emphasizes that the share of CO<sub>2</sub> participating in the exchange reservoirs is negligible (0.1%) as compared with total carbon mass in the Earth crust. He also noted the self-regulating ability of these shells and the geologically instantaneous leveling of the CO<sub>2</sub> budget.

The behavior of carbon dioxide in the atmosphere and ocean, its relationships with the climate, solar



**Fig. 5.** Geochemical carbon cycles. (a) Geochemical carbon cycle (Vernadsky, 1934); (b) life carbon cycle (Vernadsky, 1934); (c) geological carbon cycle (Holland, 1989).

activity, and biogeochemistry of many elements have been discussed in the works of many researchers (L.A. Fakes, M.H. Hart, C. Sagan, J. Mullen, R.A. Berner, D.J. Beerling *et al.*, L.R. Kump *et al.*, M. Pagani *et al.*, D.H. Rothman, J. Veizer, and others). In this paper, we restrict ourselves to the discussion of empirical data on the behavior of carbon in rocks.

Ronov *et al.* (1981, 1982, 1993) undertook an interesting attempt to solve this problem with the help of statistical and geochemical studies based on a large body of factual material. In collaboration with V.E. Khain, K.B. Sestlavinskii, A.A. Migdisov, A.A. Yaroshevskii, A.N. Balukhovskii, and other scientists from the Vernadsky Institute of Geochemistry and Analytical Chemistry (Moscow), Ronov and his colleagues compiled a series of paleogeographic maps for the Russian Platform,

former Soviet Union, and entire world. These maps served as a basis for the calculation of distribution areas and volumes of different sedimentary and volcanosedimentary formations.

The subsequent systematic geochemical study of prospecting boreholes and exposures in the Russian, Siberian, and Scythian platforms, as well as the Caucasian, Uralian, and Carpathian geosynclines, made it possible to outline the average compositions of different rock types. A great body of published data on the North American Platform, Brazil Shield, and some other geological objects was also used. In total, 13000 analyses of clays and shales, 3000 analyses of sandy rocks, and 5000 analyses of carbonate rocks were taken into consideration. In addition, 4883 average samples compiled from the array of 103600 individual samples

taken from different sedimentary and volcanosedimentary formations were subjected to the complete chemical analysis.

Ronov and his team also paid a particular attention to the analysis of cores from DSDP and JPOD holes to substantiate the quantitative geochemistry of the oceanic sedimentary cover. In total, chemical data on 3573 samples were used to elucidate this aspect.

According to Goldschmidt (1933), Vinogradov (1944) and Rubey (1951, 1955), the total content of carbon dioxide in the present-day atmosphere, biosphere, and hydrosphere is substantially higher as compared with its quantity that could form as a result of the simple weathering of crystalline rocks in the Earth.

Such an unbalance of carbon dioxide implies that its initial involvement in the sedimentation cycle was significantly governed by endogenic origin of this gas and related to mantle degassing, catagenesis, and metamorphism.

This process probably continues today, because carbon dioxide prevails over HCl, Cl<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>, He, CH<sub>4</sub>, and CO in modern high-temperature hydrothermal solutions of the World Ocean. Its concentration in hydrothermal solutions is as much as 251 mg/kg at 21° N EPR and (Mottle, 1983) and 132–484 mg/kg at 13° N EPR (Merlivat *et al.*, 1987). Let us recall that the content of dissolved CO<sub>2</sub> in seawater ranges from 0.2 to 2.5 mg/l (Khimiya..., 1979).

The magmatogenic source of carbon dioxide in modern high-temperature hydrothermal solutions is supported by data on the carbon isotopic composition. For instance, the δ<sup>13</sup>C value in the carbon dioxide of hydrothermal solutions in the EPR varies from –4.13 to –7‰ (Welhan and Creig, 1979; Merlivat *et al.*, 1987). In the Atlantis II Deep (Red Sea) with hydrothermal solution discharges, the δ<sup>13</sup>C value is –4‰ in the bottom layer and usually +0.8‰ in the normal seawater of this basin (Deuser and Degens, 1969). If one accepts that the δ<sup>13</sup>C value is –7‰ in juvenile carbon dioxide (Galimov, 1968), the main share of CO<sub>2</sub> in oceanic hydrothermal solutions turns out to be related to a deep-seated source.

It is evident that the intensity of volcanic activity is closely related with the influx of endogenic carbon dioxide into waters of the World Ocean, groundwaters of continents, biosphere, and atmosphere. Therefore, quantitative estimates characterizing the distribution of volcanics in the Phanerozoic (Ronov *et al.*, 1990; Ronov, 1993) are of particular significance.

These authors subdivided volcanic rocks into basic rocks (basalts, spilites, diabases, picrites, basic porphyrites, and their pyroclastic analogues), intermediate rocks (andesites, dacites, trachyandesites, and their tuffs), and acid rocks (rhyolites, acid porphyrites, ignimbrites, and their tuffs). Further, based on maps and determinations of the thickness of continental and oceanic lithological sequences, they estimated the distribu-

tion of these rocks within continents, shelves, continental slopes, and the first seismic layer of oceans.

Table 6 presents the results of these studies and characterizes the distribution of total volcanics in the Phanerozoic. Probably, these data also reflect the influx of carbon hydroxide during particular periods of the geological history.

It is well known that the CO<sub>2</sub> influx was accompanied by the removal of huge amounts of carbon from the sedimentation cycle together with buried carbonates, dispersed organic matter, oil, coal, and carbonaceous shales. Since the carbon mass associated with carbonates and dispersed (clarke-level) organic matter is several orders of magnitude higher than that related to its commercial accumulations (oil, coal, and shale deposits), Ronov paid a great attention not only to the distribution of volcanics, but also to the behavior of carbonate carbon and clarke-level carbon dispersed in sedimentary formations. Their distribution in various Phanerozoic stratigraphic units is also shown in Table 6.

Figure 6 (based on data in Table 6) shows three surprisingly similar diagrams with the well-manifested Ordovician, Carboniferous, and Cretaceous maximums. Conclusions following from these diagrams are as follows.

First, the cited data are well consistent with the law formulated by Ronov (1959, 1993): *the quantity of carbonate sediments accumulated during a particular Phanerozoic epoch is directly proportional to the intensity of volcanic activity and the distribution area of intracontinental seas.*

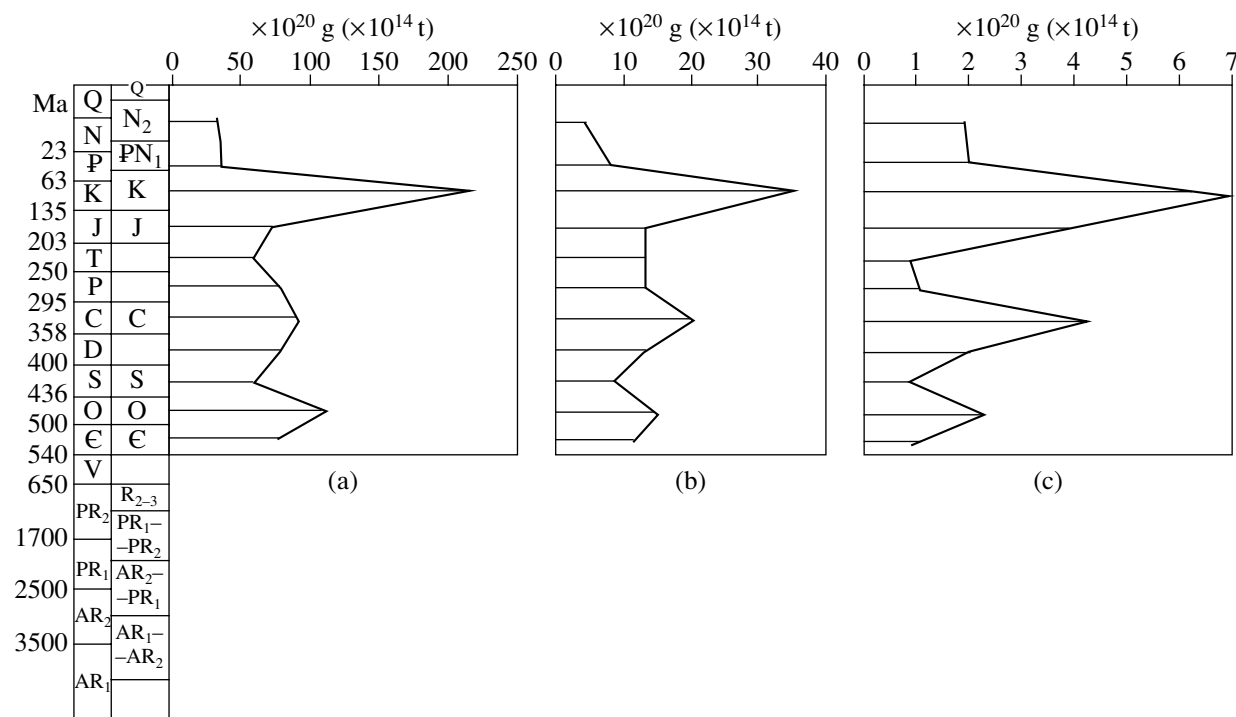
Second, if variations in the content of residual organic carbon in sedimentary sequences with an unknown (but very high) correction coefficient reflect changes in the biomass of organism populating continents and oceans, one can assume that the volcanic activity influenced the entire Earth biosphere (via carbon dioxide) and governed the epochs of its bloom and suppression.

This assumption is supported by the comparison of Figs. 5 and 6, which demonstrate that epochs of intense volcanism stratigraphically coincided with epochs of coal and shale formation. Moreover, the influence of effusive processes can be extrapolated to the stratigraphic localization of nodular siderite and oolitic hydroxide–chlorite–siderite ores.

Thus, we believe that endogenic activity of the Earth during the Phanerozoic indirectly affected the distribution of the terrestrial and marine floras and, consequently, the localization of iron ore deposits and siderite ores in them.

#### SOME EVOLUTIONARY ASPECTS OF SEDIMENTARY AND VOLCANOSEDIMENTARY IRON ORE FORMATION IN THE EARTH'S HISTORY

At present, total iron ore reserves in the world are estimated at approximately 100 Gt. Figure 7 demon-



**Fig. 6.** Distribution of (a) total volcanic rocks on continents, (b) carbon of carbonate rocks, and (c) residual organic carbon in the stratosphere (Ronov, 1993).

strates the distribution of sedimentary and volcanosedimentary iron ore deposits in the geological record of the continental block. The diagram is based on materials published by N.M. Strakhov, V.I. Smirnov, J.W. Dorr, V.E. Popov, and A. Zitzmann *et al.*, numerous reports stored in the Soyuzgeolfond Enterprise and the Ministry of Geology of the FSU, and data published in journals *Economic Geology* and *Otechestvennaya Geologiya*.

The stratigraphic distribution of commercial deposits distinctly demonstrates that maximal quantities of iron ores are concentrated in the Precambrian. This stratigraphic interval incorporates many iron ore deposits, such as the Algoma-type (probably, exhalative-volcanogenic) jaspilite deposits distinctly confined to the Archean greenstone belts and spatially associated with volcanics, Proterozoic (Lake Superior-type) jaspilites localized in iron ore basins of Australia (Hamersley), Africa (Nama-Transvaal, South African Republic), Eurasia (Kursk Magnetic Anomaly, Russia; Krivoi Rog, Ukraine), North America (Lake Superior, Canada), and South America (Iron Square, Brazil). They are characterized by huge dimensions of basins, giant ore reserves (approximately 4 Gt of iron), and mixed volcanosedimentary origin of iron and silica (Kholodov and Butuzova, 2001).

It is also clear that total commercial reserves of iron gradually decrease from the Precambrian to the Quaternary. The Paleogene, Neogene, and Quaternary iron ore reserves are negligible as compared with the Precambrian ones.

The diagram in Fig. 7 demonstrates another specific feature first noted by Strakhov (1947, 1960). The iron ore formation is a discrete process in time. During the Phanerozoic, epochs characterized by the intense formation of numerous and different iron ore deposits alternated with other epochs when the iron ore accumulation was reduced or completely absent.

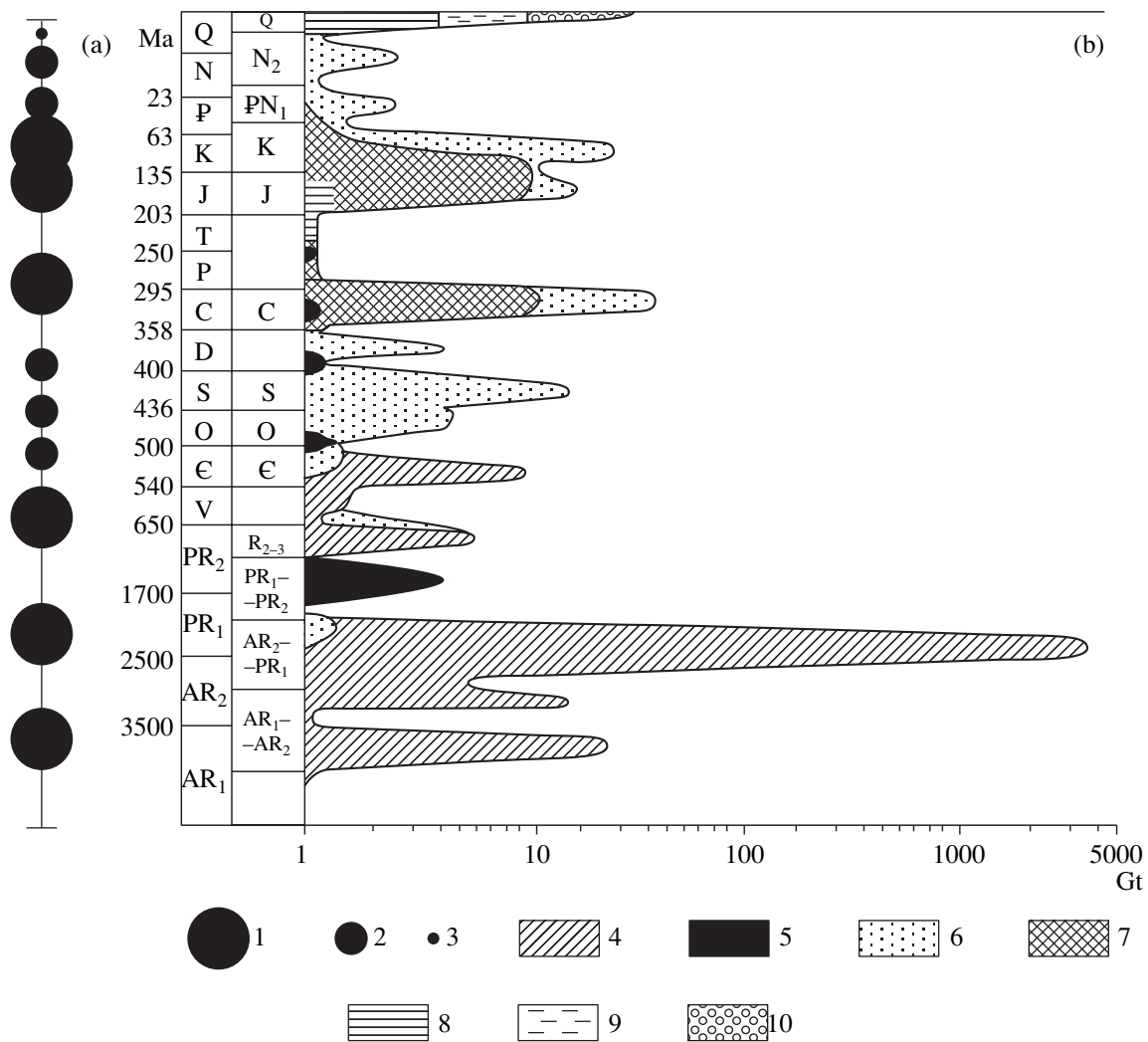
The Phanerozoic includes 10–12 such epochs of iron ore formation. According to Strakhov (1949), periods of global regressions, which intermittently occupied the continental block and subsequently gave way to global transgressions, were favorable for the intense ore accumulation. Regressions were characterized by the intensification of humid weathering and the consequent active influx of bivalent Fe from continents into seas, resulting in the intense formation of iron ore deposits.

The subsequent quantitative estimates of Phanerozoic sedimentary and volcanosedimentary formations (Ronov, 1993) compelled researchers to revise the concept of iron ore formation.

The analysis of mega-scale variations of transgressive–regressive cycles in the continental block of the Earth based on comparison with the volcanism distribution and intensity is presented in (Egyed, 1957; Ronov, 1980, 1993; Malinovskii, 1982). The results showed that these processes are closely interrelated. Moreover, the volcanism is most prominent during maximal transgressions rather than regressions. As was shown above, intense volcanic activity is the process that provides the

**Table 6.** Stratigraphic distribution of volcanogenic rocks and carbon mass on continents and in the ocean (Ronov, 1993)

Age, Ma	Stratigraphic interval	Mass of volcanics, 10 <sup>20</sup> g		Carbon mass in carbonates, 10 <sup>20</sup> g		Mass of dispersed C <sub>org</sub> in sedimentary rocks, 10 <sup>20</sup> g	
		in rocks of the interval	average	in rocks of the interval	average	in rocks of the interval	average
5.3–1.8	Pliocene	22.1	38.8	1.4	4.75	1.0	2.05
23.0–5.3	Miocene	55.4		8.1		3.1	
34–23	Oligocene	20.4	40.9	2.6	8.57	2.0	2.33
55–34	Eocene	77.8		18.5		4.0	
65–55	Paleocene	24.6		4.6		1.0	
97–65	Upper Cretaceous	220.6	217.7	40.6	36.15	6.2	6.4
145–97	Lower Cretaceous	214.8		39.7		7.4	
157–145	Upper Jurassic	75.3	70.6	20.4	14.0	4.9	3.97
178–157	Middle Jurassic	82.0		12.0		4.4	
200–178	Lower Jurassic	54.6		9.6		2.6	
241–200	Upper Triassic	82.6	63.4	18.9	13.1	1.8	1.0
246–241	Middle Triassic	45.4		11.2		0.5	
251–246	Lower Triassic	62.2		9.2		0.7	
264–251	Upper Permian	63.8	78.9	12.2	13.0	0.7	1.3
295–264	Lower Permian	94.1		13.8		1.9	
342–295	Upper + Middle Carboniferous	80.9	97.0	27.2	22.2	3.5	4.4
360–342	Lower Carboniferous	113.1		17.2		5.3	
382–360	Upper Devonian	56.6	78.5	18.6	11.36	3.7	2.23
392–382	Middle Devonian	85.4		14.4		2.3	
418–392	Lower Devonian	93.5		1.09		0.7	
424–418	Upper Silurian	50.7	63.7	7.4	9.65	0.8	0.9
443–424	Lower Silurian	76.7		11.9		1.0	
449–443	Upper Ordovician	77.8	116.0	11.5	15.43	1.7	2.43
473–449	Middle Ordovician	183.4		18.1		3.5	
490–473	Lower Ordovician	86.8		16.7		2.1	
500–490	Upper Cambrian	50.4	83.3	13.4	12.86	0.6	1.17
509–500	Middle Cambrian	102.5		14.4		1.2	
535–509	Lower Cambrian	97.2		10.8		1.7	



**Fig. 7.** Stratigraphic distribution of (a) siderites and (b) commercial reserves and types of iron ore deposits. (1–3) Siderite resources: (1) large, (2) medium, (3) small; (4) jaspilites; (5) hydrothermal–elisional metasomatic siderites; (6) oolitic hydrogoethite–chlorite–siderites ores; (7) nodular siderites in coaliferous formations; (8) iron ore of weathering crusts; (9) lacustrine–boggy iron ores; (10) titanomagnetite placers.

large-scale influx of carbon dioxide to exchange reservoirs. This is reflected in the precipitation of carbonates, intensification of the activity of the biosphere, and mobilization of the labile bivalent Fe in the acidic gleyey medium of lowmoors. Ultimately, the whole chain of events provides the large-scale formation of iron ore deposits in the adjacent discharge basins.

That is why the greatest epochs of iron ore accumulation correspond to three global transgressive cycles of the Phanerozoic (Ordovician–Silurian, Carboniferous, and Jurassic–Cretaceous).

Thus, it is evident that the volcanic activity was the source of ore components for the terminal discharge basins in the Precambrian. In the Phanerozoic, its influence on ore genesis was complicated and indirect as a result of the involvement of several mechanisms governing the processes of ore formation.

Figure 7 clearly shows that processes of the formation of sedimentary and volcanosedimentary iron ores bear distinct signs of the irreversible process—one dominant type of iron ore deposits is replaced by another type during the evolution from the Precambrian to the Quaternary.

Precambrian jaspilites are replaced by iron ore formations of different types in the Late Proterozoic, Riphean, and Phanerozoic.

Riphean jaspilites are replaced at higher stratigraphic levels by large metasomatic hydrothermal–elisional siderite deposits of the Sadkino type paragenetically associated with magnesite, barite, and sulfide ore occurrences. Their genetic analogues are known in the Ordovician, Devonian, and Carboniferous sequences of Europe and Asia.



As was shown by B. Wagner, N.M. Strakhov, A. du Toit, and others, the Early Proterozoic was marked by the appearance of the oolitic hydroxide–chlorite–siderite ores among jaspilite deposits of the coastal facies. In the stratigraphically higher (Riphean) sequences of Australia, oolitic iron ores are found as autonomous and widespread deposits that are not associated with jaspilites. Moreover, the iron ores gradually replace the jaspilites in Paleozoic basins. In Paleogene sequences, hydroxide–chlorite–siderite ores occur in both marine and continental settings. They gradually occupy not only the river valleys, but also the freshwater and brackish-water lakes.

In addition to oolitic ores, nodular siderite deposits spatially and genetically associated with coaliferous formations became widespread in the Carboniferous, Jurassic–Cretaceous, and Cenozoic. These deposits are most frequently confined to coaliferous formations. However, they are occasionally separated in space and time, e.g., in Jurassic rocks of Dagestan or Jurassic–Cretaceous sequences of the eastern Transbaikal region (Sokolova and Ryabinina, 1958; Khalif-Zade, 1959; Khalif-Zade and Abbasova, 1963; Timofeeva, 1968; Pistsov, 1969).

The iron ore deposits associated with weathering crusts are known in the Lower Paleozoic sequences (Cambrian–Silurian ores of the Appalachians, the United States; Devonian Linderen Mark deposits, Germany). However, they are more widespread in the pre-Jurassic and pre-Cretaceous periods (Orsk–Khalilovsk and Alapaevsk deposits, the Urals, Russia; Sumadija, Rjanovo, and Mokra Gora deposits, former Yugoslavia; Rajah, Syria; Jebel Anina, Algeria; and others).

The formation of iron ores related to laterite weathering was maximal in the Pliocene–Quaternary. Deposits of this age are known in Cuba, Philippines, Borneo, Sebuku, Australia, Africa (Lake Bangweulu), and other tropical regions.

In the Quaternary, lacustrine–boggy ores and titanomagnetite placers localized on coasts of seas and oceans became widespread in the humid regions.

Thus, the Tertiary and Quaternary periods are marked by extremely diverse types of iron ore deposits that were partly shifted from paleobasins to continents.

The overwhelming majority of sedimentary and volcanosedimentary iron ore deposits are polymineral formations with siderite playing an important role. The temporal distribution of siderite in iron ore deposits is shown in the left part of Fig. 7.

The wide distribution of siderite in Precambrian iron ores is noteworthy. As was shown in our first communication (Kholodov and Butuzova, 2004), siderite in these ores is a primary mineral. Together with iron hydroxides, opal, and, probably, iron silicates, siderite makes up the mineralogical basis of ore deposits. The excess of carbon dioxide and oxygen deficiency in the Precambrian atmosphere was probably responsible for

the leading role of siderite in the Precambrian iron ore formation.

Significant quantities of siderite are also enclosed in Paleozoic–Mesozoic iron ore deposits. However, in contrast to the Precambrian deposits, the younger deposits are mostly composed of secondary (diagenetic–catagenetic) iron carbonates.

Indeed, siderite ores associated with peat bogs and coaliferous formations usually form lenticular-nodular bodies undoubtedly related to diagenesis and catagenesis. Siderite, an essential constituent of the oolitic hydroxide–chlorite–siderite ores, is the latest mineral in this mineral association.

It is conceivable that the lag of siderite formation in the Phanerozoic iron ore process reflects the trend of CO<sub>2</sub> pressure decrease in the Earth's atmosphere, on the one hand, and the increasing (sometimes, primary) role of oxygen in geochemical reactions during ore genesis, on the other hand.

It is also probably important that the metalloorganic compounds, which are typical products of terrestrial vegetation, played a crucial role in Fe migration.

#### ACKNOWLEDGMENTS

This work was supported by the Foundation of the President of the Russian Federation for the Support of Leading Scientific Schools, project no. NSh-1440 2003.5).

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