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Periodicity of Copper Accumulation in the Earth's Sedimentary Shell

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Abstract—Physicochemical conditions of the migration and concentration of Cu in sedimentary rock, specific features of the formation of large and unique deposits of cupriferous sandstones and shales, distribution of copper deposits in the stratigraphic scale, and causes responsible for the reduction of Cu accumulation from Proterozoic to Cenozoic are considered. Genetic link of cupriferous sandstones and shales with arid red molassic rocks is shown. Conditions and periodicity of formation of the ore-generating red rocks are considered. An explanation for periodicity of maximum Cu accumulation in the Earth's history is proposed.

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Exogenic copper deposits (cupriferous sandstones and shales) are known in Early Proterozoic–Tertiary sedimentary rocks. Such deposits are found at different stratigraphic levels in rocks subjected to postsedimentary alterations various grades (from diagenesis to amphibolite grade and hypergenesis). They account for 32.6% of world Cu reserves mainly confined to large and giant deposits. The Cu reserve in these deposits is as much as 10 Mt or more.

Regularities in the distribution and structure of cupriferous sandstone and shale deposits are scrutinized in (Bogdanov et al., 1973; Gablina, 1983; Gustafson and Williams, 1981; Kirkham, 1989; Lur'e, 1988; Lur'e and Gablina, 1972, 1978; Narkelyun et al., 1983; and others). All giant deposits and occurrences of cupriferous sandstones are characterized by their association with terrigenous red rocks. Mineralization is localized in the organic-rich and pyrite-containing gray rocks that replace the red rocks along the vertical and lateral directions. The genetic model, which most completely explains regularities of the localization and structure of cupriferous sandstone and shale deposits, is based on ideas proposed in (Germanov, 1962; Perel'man, 1959; Rose, 1976). According to this model, Cu and other metals are transported by groundwaters from the red rocks and concentrated as sulfides on hydrosulfuric geochemical barriers (Ensign et al., 1968; Gablina, 1983; Gustafson and Williams, 1981; Hoyningen-Huene, 1963; Lur'e, 1988; Lur'e and Gablina, 1972, 1978; Wodzicki and Piestrzynski, 1986; and others).

In general, ore deposits and occurrences of this type do not show explicit periodicity across the section. The oldest objects are represented by the Flake Lake, Stag Lake, Desbarats, and other ore occurrences associated with the Early Proterozoic Lorain red rock formation (Ontario, Canada), as well as small Mangula and Alaska deposits associated with the Early Proterozoic Lomagundi Group confined to red molassic rocks of the Deweras Group in Zimbabwe, South Africa (Narkelyun et al., 1983). In Russia, the Early Proterozoic mineralization level is represented by the Udokan deposit confined to the Udokan metasedimentary rock group. Small ore occurrences are located in the Kondo–Kareng, East Aldan, and Olekma–Tokka zones of Siberia. Cupriferous rocks of these ore occurrences are usually compared with the Udokan Group. However, some researchers consider that affiliation of ore-enclosing rocks of the Udokan Group to the Early Proterozoic based on isotopic datings of rocks is invalid, because they contain Typical Riphean stromatolitic species (Amantov, 1978). Medusoid imprints detected in different suites of the Udokan Group (Vil'mova, 1987) support the Riphean age of these rocks. Thus, if we omit the Udokan deposit, Early Proterozoic sedimentary and metasedimentary complexes contain only small ore deposits and occurrences.

Small deposits and occurrences of cupriferous sandstones and shales are known in Cambrian–Ordovician sections in the Siberian Platform and Australia. Devonian representatives are known at the southern margin of the Russian Platform, the Altai–Sayan cupriferous province, and Kazakhstan. Permian and Mesozoic–Cenozoic objects are found in Central Europe, the Russian Platform, Africa, and America (Narkelyun et al., 1983).

Based on the maximal Cu concentration in the Earth's history, we can recognize the Late Precambrian, Late Paleozoic, and Mesozoic–Cenozoic stages (table). With respect to the scale of Cu accumulation, each subsequent stage is significantly inferior to the preceding stage. For example, the distribution of Cu reserve is as

Major epochs of exogenic copper accumulation in the Earth's history

Epoch	Ore-generating red rock associations		Ore-enclosing gray rocks		Deposits			Source
	age, group	distribution pattern	formation, horizon, age	facies composition, position relative to red rocks	no.	name	size	
Proterozoic	Early (?) Proterozoic, Udokan Group	In a large intermontane depression up to 10000 deep	Horizon in the upper Sakukan Subformation, Udokan Group (PR_1?)	Lagoonon shallow-water marine pyrite-bearing sediments within red rocks	1	Udokan	Large	(Bogdanov et al., 1966, 1973; Narkelyun et al., 1977, 1983; Gablina and Mikhailova, 1994; Volodin et al., 1994)
			Lower Sakukan Subformation, Aleksandrov Formation, Udokan Group (PR_1?)	Deltaic and shallow-water marine sediments at the base of red rocks	2	Unkur	Small	
					3	Aleksandrov	Small	
	Late Proterozoic, ore group	In intermontane depressions and valleys up to 1500 m deep	Lower Roan ore horizon	basal layers of marine sediments at the top of red rocks	4	Deposits of the Copper Belt in Africa	Large	(*Geology*…, 1961; Cailteux, 1973; Lur'e, 1988)
	Late Proterozoic, Copper Harbor Formation	In a large foredeep up to 1000 m deep	Nonesuch Shale (PR_2)	Organic-rich basal layers of marine sediments at the top of red rocks	5	White Pine (Lake Superior, United States)	Large	(White, 1971; Ensign et al., 1972; Lur'e, 1988)
	Vendian–Cambrian, Loikhvar Formation	In a large intermontane depression	Loikhvar Formation	Basal layers of marine sediments	6	Ainak (Afghanistan)	Large	(Yurgenson et al., 1981; Yashchinin and Giruval, 1981)
	Vendian, Izluchin Formation	In a large foredeep up to 300 m deep	Vendian Izluchin and Vendian–Cambrian Sukharikha formations	Reefogenic carbonate rocks, bar sandstones, and carbonaceous schists at the base of marine sediments within and at the top of red rocks	7	Graviika (Igarka area)	Small	(Rzhevskii et al., 1988; Lur'e, 1988)

(Contd.)

Epoch	Ore-generating red rock associations		Ore-enclosing gray rocks		Deposits			Source
	age, group	distribution pattern	formation, horizon, age	facies composition, position relative to red rocks	no.	name	size	
Late Paleozoic	Middle–Late Carboniferous, Dzhezkazgan Sequence	In a large foredeep up to 1500 m deep	Dzhezkazgan Sequence ($C_{2–3}$)	Rebleached permeable horizons within the red sequence	8	Dzhezkazgan (Kazakhstan)	Large	(Narkelyun, 1962; Gablina, 1983; Lur'e, 1988)
	Early Permian, Kartamysh Formation	Depressions up to 1200 m deep	Kartamysh Formation (P_1)	Shallow-water marine, channel, and sabkha within the red sequence	9	Berestyan deposit, Kartamysh ore occurrence, and others (Donbas)	Small	(Lur'e, 1988)
	Early Permian, Dead Red Beds	In large intermontane troughs, depth up 600 to 1000 m or more	Zechstein (P_2)	Bar(?) sandstones and carbonaceous schists at the base of marine sediments	10	Mansfeld, Sangerhausen, Reichelsdorf, and others (Germany)	Ordinary	(Eisenhut and Kautzsch, 1954; Hoyningen-Huene, 1963; Autorenkollektiv…, 1968; Lur'e, 1974; Wodzicki and Piestrzynski, 1986; Lur'e, 1988; Gablina, 1997; and others)
					11	Lubin-Sieroszowice	Unique	
					12	Deposits of the North Sudet trough (Poland)	ordinary And Small	
	Late Permian; Ufimian, Kazanian, and Tatarian stages	In the Ural Foredeep	Ufimian and Kazanian stages (P_2)	Alluvial–lacustrine sediments and sabkha within red sediments; organic-rich basal layers of shallow-water marine sediments	13	Ore occurrences of the western Ural region (Kargalin Group and others)	Small	(Lur'e and Gablina, 1972; Lur'e, 1974, 1988)

(Contd.)

Epoch	Ore-generating red rock associations		Ore-enclosing gray rocks		Deposits			Source
	age, group	distribution pattern	formation, horizon, age	facies composition, position relative to red rocks	no.	name	size	
Mesozoic–Cenozoic	Middle Jurassic–Early Cretaceous	In deep depressions (up to 10000 m)	Middle Jurassic–Early Cretaceous	Gray horizons within the red sequence	14	Deposits of the Yunnan province (China)	Large	(Narkelyun et al., 1983)
	Early Cretaceous	In marginal troughs up to 1100 m deep	Early Cretaceous	Organic-rich lagoonal–deltaic, channel, and lacustrine–oxbow sediments within red sediments	15	Ore occurrences of the Tajik depression	Small	(Bogdanov et al., 1973; Narkelyun et al., 1983)
	Paleogene–Neogene, Corocoro Group	In an intracratonic trough with a total depth of 10000–15000 m	Lower and upper parts of the Corocoro Group	River sediments within red sediments	16	Corocoro (Bolivia)	Small	(Gustafson and Williams, 1981; Narkelyun et al., 1983)
	Neogene	In an intermontane depression up to 2500 m	Pliocene Baktrin Sequence	Channel and lacustrine gray interlayers within the red sequence	17	Naukat (Fergana Valley)	Small	(Narkelyun et al., 1983)
		In a rift zone	Early Pliocene	Marine horizons within the continental red sediments	18	Boleo (Mexico)	Ordinary	(Gustafson and Williams, 1981; Cony et al., 2001)

follows: 21% in Precambrian rocks, approximately 10% in Paleozoic rocks, and 1.6% in Mesozoic–Cenozoic rocks (Yanshin, 1972). The maximum Cu concentration is related to Late Proterozoic (Late Riphean–Vendian) rocks. Deposits of this level are known at virtually all continents. Large deposits occur in the Copper Belt of Africa (Roan Antelope, Musoshi, Mufulira, and others), United States (White Pine), Afghanistan (Ainak), India, and China (Inming and Lusue). The second (smaller) Cu peak is observed in the Carboniferous–Permian. Deposits of this period are known in Kazakhstan (Dzhezkazgan, C_{2-3}), Poland (Lubin-Sieroszowice), Germany (Mansfeld, P_2), and other regions. Mesozoic–Cenozoic deposits are represented by Corocoro in Bolivia (Paleogene–Neogene) and Boleo in Mexico (Neogene). Small ore deposits and occurrences are found in Jurassic, Cretaceous, and Paleogene red rocks in the Yunnan and Hunan provinces of China (Narkelyun et al., 1983). Cupriferous rocks are also developed in the Lower Cretaceous section of the Tajik depression and the Neogene section of the Fergana Valley (Naukat).

CONDITIONS OF COPPER MIGRATION

Red Rocks and the Nature of Their Coloration

Irrespective of the age and metamorphism grade of host rocks, mineralization of cupriferous sandstones and shales is confined either to red sequences or to basal horizons of the overlying marine sequences (Fig. 1). Mineralization is less common in the underlying marine sediments at their contact with the red rocks (Northern group of deposits in the Dzhezkazgan district and Horizon A in the Igarka district). Beginning from the Proterozoic, arid red rocks are found in almost all systems, but they are most developed in the Late Proterozoic, Devonian, Permian, Triassic, Cretaceous, and Neogene (Fig. 2).

The spatial association of cupriferous sandstones and shales with the red rocks is related to specific features of the geochemical behavior of Cu in the exogenic environment. According to (Perel'man, 1959, 1968; Lur'e, 1988; and others), arid red rocks serve as source and migration medium of Cu.

In addition to color, the red rocks have the sandy–clayey composition. In some places, their matrix contains carbonates as independent lenses and interlayers sometimes associated with evaporites. In general, these rocks represent orogenic molasses accumulated in foothills and intermontane depressions (table). The red color is related to the dissemination of iron oxides and hydroxides, which can be preserved under conditions of long-term domination of oxidizing environment. Therefore, continental conditions, as well as with dry and hot climate, are most favorable for the accumulation of red rocks. The FeO/Fe_2O_3 ratio (correspondingly, the mineral form of Fe in sediments) is the major indicator of redox potential of sedimentation medium. In the red rocks, the ratio is <1; i.e., oxide forms of iron compounds prevail. In the gray rocks, the ratio is >1; i.e., bivalent iron minerals (sulfides, silicates, and carbonates) dominate (Gablina, 1990).

Chukhrov et al. demonstrated in (*Gipergennye* …, 1975) that nature of the pigmenting material of red rocks can be dualistic: either introduction as goethite (FeOOH) suspension or precipitation as ferrihydrite ($2.5Fe_2O_3 \cdot 4.5H_2O$) from solution. The first migration form is typical of tropical zones with a high oxidation rate. The second form is commonly developed in temperate zones, where the oxidation rate is less intense and Fe transferred as bicarbonate into the solution is removed by groundwaters. When such waters flow out to the surface, Fe is oxidized and ferrihydrite is formed. Rocks acquire the yellowish brown color in the course of its transport to sedimentation sites as flakes and coatings on clayey particles. At ordinary temperatures, the ferrihydrite is instantly transformed into hematite due to the release of water (*Gipergennye*…, 1975). The transitional phase can be present as hydrohematite (fine-crystalline hematite) that contains as much as 8% of the weakly bonded water, which is released at 100–150°C. Investigation of red rocks of the Middle–Upper Carboniferous Dzhezkazgan Sequence in Kazakhstan (Gablina, 1983) showed that the ferruginous pigment in these rocks is primarily represented by the fine-dispersed hematite. The less altered Ufimian (Upper Permian) red rocks of the western Ural region mainly contain hydrogoethite (Kossovskaya and Sokolova, 1972). In Late Precambrian rocks of the Diaoyutai Formation (China), hematite is supplemented with goethite in the cement of clastic rocks (*Gipergennye*…, 1975). The cement also contains goethite and hematite in Lower Roan red rocks of the Shaba province (Zaire) characterized by minimal metamorphism (Cailteux, 1973).

Domination of the oxidizing environment during sedimentation and subsequent stages of lithogenesis is essential for the appearance and preservation of red color of rocks. This condition is provided by a low or very low content of buried organic matter. According to Strakhov (1964), red rocks are formed at the C_{org} content of <0.3%. Greenish gray and gray rocks are formed at higher C_{org} contents. According to Tazhibaeva et al. (1964), the C_{org} content is 0–0.07% in red rocks of the Dzhezkazgan Sequence. Gray rocks of the underlying Lower Carboniferous Taskuduk Formation of the transitional type (relative to marine sediments) are enriched in C_{org} up to 0.74% (Arustamov et al., 1963). In the Igarka district, the average content of residual C_{org} is <0.1% in red rocks of the Late Proterozoic Izluchin Formation and varies from 0.12 to 0.38% in the gray variety from the overlying Vendian–Cambrian Sukharikha Formation (Gablina, 1990). The total Fe content in the red rocks is often higher than that in sedimentary rocks with other colors. At the same time, the Fe content is inversely correlated with the grain size of rocks. Favorable conditions for the formation and preservation of red rocks are typical of continental rocks

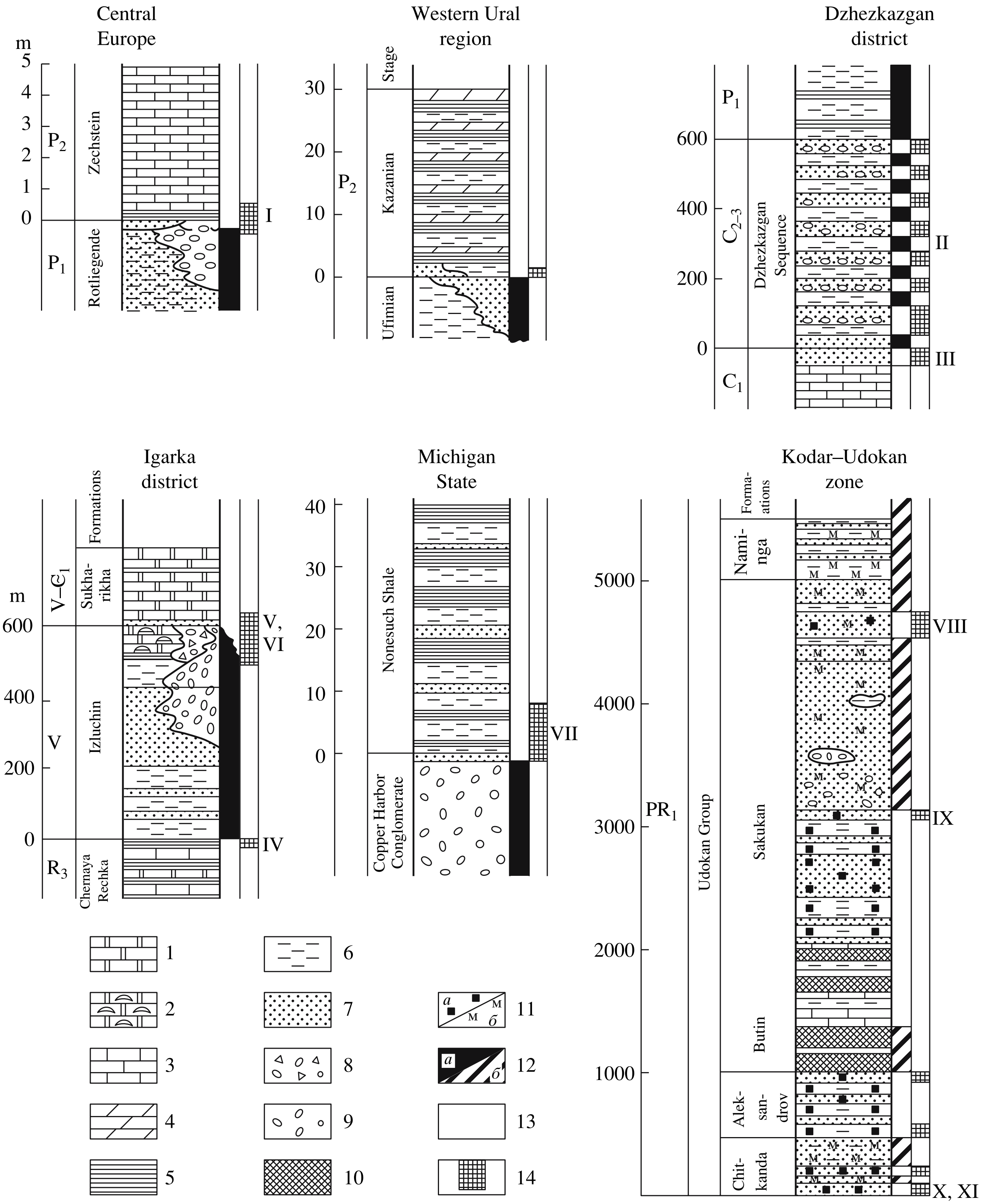

Fig. 1. Relationship of cupriferous sandstones and shales with red rocks. (1) Dolomites; (2) stromatolitic dolomites; (3) limestones; (4) marls; (5) mudstones and shales; (6) siltstones; (7) sandstones; (8) breccia and conglobreccia; (9) conglomerates; (10) albitites; (11) authigenic indicator-mineral of the redox potential of rocks in the metamorphosed Udokan Group: (*a*) pyrite and pyrrhotite, (*b*) hematite and magnetite; (12, 13) rock color: (12) red: (*a*) observed, (*b*) reconstructed; (13) gray; (14) copper mineralization. (I–XI) deposits and ore occurrences: (I) Mansfeld, Sanderhausen, Lubin-Sieroszowice, and others; (II) Dzhezkazgan; (III) Northern group deposits; (IV) Horizon A; (V) Horizon B; (VI) Graviika; (VII) White Pine; (VIII) Udokan; (IX) Unkur; (X) Krasnoe; (XI) Pravyi Ingamakit.

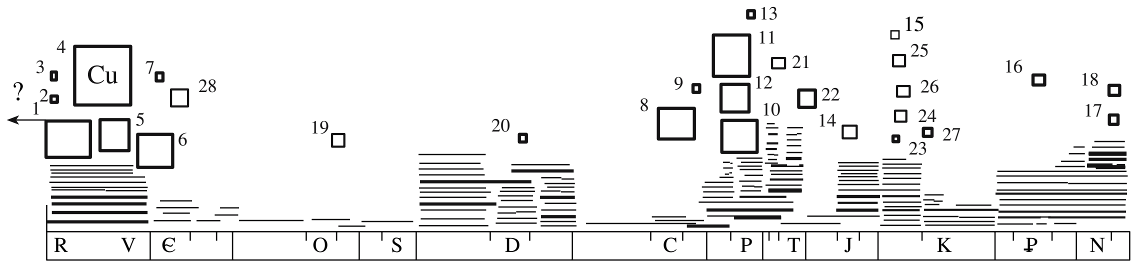

Fig. 2. Red rocks and large copper deposits in sandstones and shales. Length of horizontal lines corresponds to the age range of red rocks. Bold lines show the thickest red sequences. Data on the red rocks are adopted from (Anatol'eva, 1978) and modified. (1–18) Deposit numbers as in the table; (19–28) numbers of deposits and districts omitted in the table due to the lack of information: (19) Mount Lyell cupriferous shale deposit (Australia), (20) Altai–Sayan cupriferous province, (21) Weiniya and Milichan ore districts (China), (22) Happy Jack deposit (United States), (23) Seboruco deposit (Venezuela), (24) Kashueiras deposit (SW Africa), (25) Merja deposit (North African province), (26) Heili ore district (China), (27) Beni Mellal cupriferous district (North African province), (28) Timna deposit (Israel). Box size corresponds to the reserve of deposits.

formed in arid climate. Such rocks are abundant in the Phanerozoic. Precambrian red rocks are mainly developed in the Riphean and Vendian, e.g., Ushakov Formation and Oselkov Group (southern framing of the Siberian Platform), Izluchin Formation (Igarka district), Lower Roan (Africa), and others. Older red rocks are represented by the Early Proterozoic Lorain Formation (Canada), Jatulian Group (Karelia), and others.

Phanerozoic and Precambrian red rocks formed in different settings. The Phanerozoic red rocks are markers of arid climate. Climate did not play any significant role in the Precambrian because of the absence of land vegetation. According to (Cloud, 1973; Melezhik, 1987; and others), formation of the Precambrian red rocks is related to the vital activity of cyanobacteria that promote the photosynthesis of oxygen. Based on reliable findings of stromatolites and microfossils beginning from 3.5–3.3 Ga (Notre Pol, Australia; Onvervaxt, South Africa), Krylov (1983) suggested that the atmospheric oxygen content was close to the present-day one by the initial Proterozoic owing to the vital activity of organisms.

Thus, researchers do not doubt the presence of favorable conditions for the formation of red rocks and their existence in the Precambrian. However, it is rather difficult to identify them in the Precambrian metamorphosed sequences. We proposed mineral–geochemical criteria for the identification of primary red rocks in the Precambrian metasediments, which lost the red color in the course of metamorphism (Gablina, 1990).

As was mentioned, red and gray rocks in the unmetamorphosed sediments are distinguished by the FeO/Fe_2O_3 ratio, the mineral form of Fe, and the C_{org} content. Based on these criteria, we reconstructed the primary color of rocks of the Udokan Group, the metamorphism of which varies from the greenschist to the epidote–amphibolite facies. Thus, we deciphered rock complexes (with the primary gray color) formed in the reducing environment and primary red rocks formed in the oxidizing environment. The first type is characterized by the prevalence of Fe^{2+} ($FeO/Fe_2O_3 > 1$), abundance of authigenic pyrite (or pyrrhotite) dissemination, and high content of the residual C_{org} (up to 1.11%, average 0.4%). The primary red rocks are marked by low values of C_{org} (<0.1%, on average) and FeO/Fe_2O_3 (average 0.5), as well as the presence of newly formed hematite and magnetite. Validity of this reconstruction is supported by positions of cupriferous levels in the section. Like in unmetamorphosed sequences, high Cu concentrations in the metamorphosed sequences are controlled by geochemical barrier zones: boundaries of the replacement of primary red rocks by gray rocks or sectors of primary gray rocks within the red complexes (Fig. 1). The present-day gray color of metasedimentary primary red continental rocks is related to the selective recrystallization of fine-dispersed hematite and its transformation into magnetite under the influence of high temperatures and reduction of oxidative potential during metamorphism.

Such reconstruction can also be accomplished for other continental molassic rocks. For example, rocks of the Katanga system in the Copper Belt of Africa are metamorphosed to different degrees. According to F. Mendelsohn, the metamorphism grade increases from the north to south and southwest (*Geology…*, 1961). At the northernmost margin (Shaba province, Zaire), where the Katanga rocks are not metamorphosed, sandstones and conglomerates beneath the ore horizon have preserved the red color. Pigment in them is represented by goethite and hematite. In the southern part of the Copper Belt, increasing grade of metamorphism leads to replacement of the red coarse-clastic rocks beneath the ore horizon by the gray variety with crystalline hematite and magnetite in the cement (Roan Muliashi syncline).

Geochemical Setting of the Formation of Red Rocks

From the point of view of physical chemistry, red rocks represent the stability region of Fe^{3+}. The Eh–pH diagram (Fig. 3) shows that this region includes all (bivalent, monovalent, metallic, and sulfide) species of

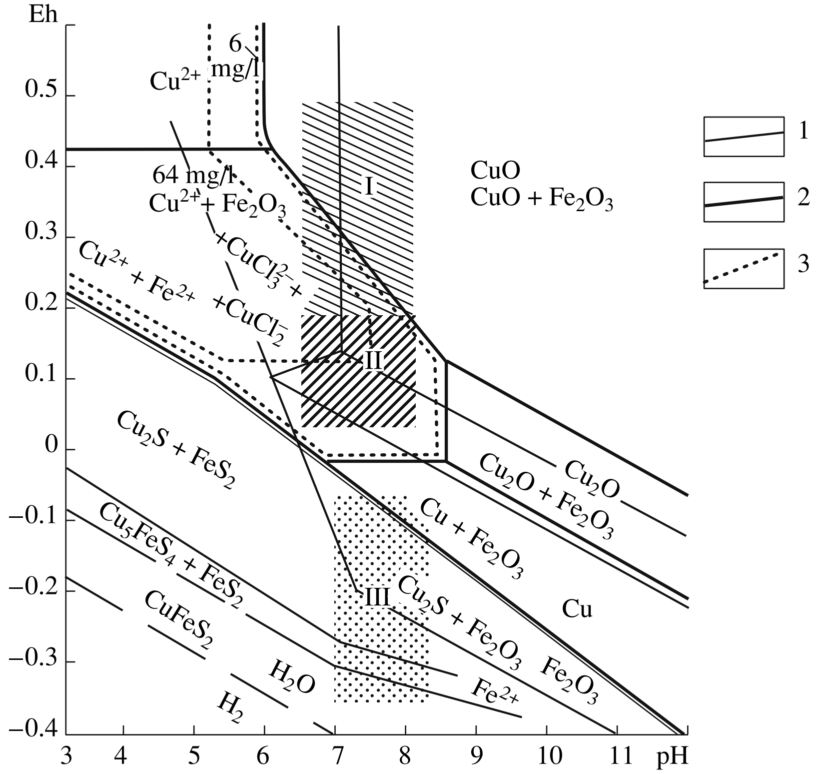

Fig. 3. Diagram showing the stability of copper compounds and geochemical settings of Cu migration and concentration. Based after (Lur'e, 1988). (1) Cu–Fe–S–O–H system at $T = 25°C$, total $P = 1$ atm, and $\Sigma S = 10^{-4}$ mol; (2) Cu–S–O–H–Cl system at $T = 25°C$, $\Sigma S = 10^{-4}$ mol, and $Cl^- = 0.5$ mol (as NaCl); (3) isolines of the Cu content in the NaCl solution. (I–II) Geochemical settings: (I) in sedimentary waters during the accumulation of continental red sediments in the course of active water exchange, (II) in formation waters during peneplanation and retarded water exchange (formation of ore-bearing solutions during catagenesis), (III) in the reducing geochemical barrier zone (sulfide formation period).

Cu known in nature. At the same time, their stability fields replace each other sequentially during the drop of redox potential. The Fe^{3+}/Fe^{2+} boundary is located in the stability field of copper sulfides.

Enrichment of rocks with Cu is atypical of red rocks. The Cu content in rocks is close or slightly lower than the clarke value (Borisenko, 1980; Perel'man and Borisenko, 1962). Depending on the Eh and pH values of solutions, the Cu content in ground (interstitial and formation) waters of red rocks can exceed 50 mg/l (Pushkina, 1965; Shcherbakov, 1968). It is now commonly accepted that Cu and other nonferrous metals are mainly transported in water solutions as complex compounds. Sedimentation waters of continental red rocks are characterized by high oxidizing potential and nearly neutral medium (Fig. 3, field I) during sedimentation. Subsidence and consumption of oxygen for oxidizing reactions lead to decrease in the Eh value of pore solutions and development of an oxidation-to-reduction transitional medium (Fig. 3, field II). Under such conditions, the bivalent Cu is reduced to the monovalent state (Lur'e, 1988). Formation waters of continental red rocks usually contain Cl ion, which makes up water-soluble complexes with Cu^+. Compounds of Cu^{2+} are less mobile. In nearly neutral natural waters typical of the formation waters of red rocks, the Cu^{2+} content is very low and varies from $n \times 10^{-3}$ to $n \times 10^{-4}$ (Goleva et al., 1968; Perel'man, 1968; Shcherbakov, 1968; and others).

Proterozoic continental red rocks do not contain reducers (Yanshin, 1972). In contrast, their Phanerozoic counterparts represent more complex compounds owing to the appearance of higher plants on continents. They often contain relicts of organic remains testifying to the incomplete process of oxidation. Therefore, Lur'e (1988) distinguishes two basically different (ore-generating and barren) types of red rocks. In the ore-generating rocks, Cu occurs as the mobile Cu^+ ion with Eh value corresponding to field II in Fig. 3. In the barren red rocks, the Eh value can be higher (field I in the Cu^{2+} stability field) or lower (field III in the sulfide Cu stability field). In the latter case, new insoluble (sulfide and native) forms of Cu are formed. With respect to the Cu occurrence mode, these red rocks do not differ from the gray variety (Cu in them is inert). Therefore, their role as a source of Cu is negligible. The barren type includes Devonian red rocks in the northwestern Russian Platform, Permian and Triassic rocks in middle Pechora, Neogene rocks in Karakum, and others (Borisenko, 1980). In fact, only two (Late Precambrian

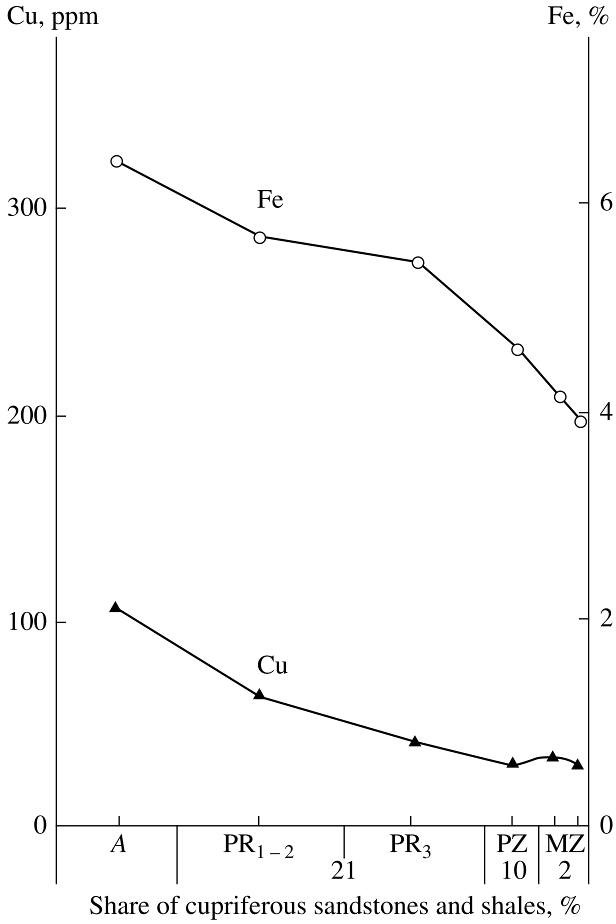

Fig. 4. Variation in the average content of Fe and Cu in shales along the stratigraphic scale. Modified after (Ronov, 1983).

and Permian–Carboniferous) epochs of the wide development of arid red rocks coincide with the maximum Cu accumulation in sedimentary rocks (Fig. 2). The Devonian period can serve as example of reverse relationships: intense development of red rocks in the Devonian is not accompanied by the formation of any significant deposits of cupriferous sandstones and shales. The absence of reducers in the Proterozoic continental red rocks could foster their maximal Cu productivity.

Middle–Upper Carboniferous red rocks of the Chu-Sarysui Depression contain abundant remains of land vegetation as molds of red ocherous clays that are devoid of any signs of bleaching. Reducing environment was not developed here because of the complete oxidation of plant tissues. Hence, these sediments were unfavorable for the local precipitation of Cu and the whole reactive Cu could migrate. Such sediments are the most probable source of Cu for the Dzhezkazgan deposit. In contrast, their Permian counterparts in the western Ural region and Donbas contain abundant remains of coalified plant tissues and shales with a green rim, suggesting the reduction of Fe. These regions incorporate only small deposits, because the environment was unfavorable for the transport of large masses of Cu. Thus, mobility of Cu in Paleozoic continental red rocks also varied depending upon conditions of the burial of organic matter.

As was mentioned, the third (Mesozoic–Cenozoic) stage of Cu accumulation in the Earth's history was least productive. Decrease in the Cu accumulation during this stage could be related to variation in the formation condition of red rocks. Mesozoic–Cenozoic red rocks formed in the course of postsedimentary oxidation of primary gray rocks. Therefore, the red rocks retained the relatively low Eh values corresponding to the boundary between stability fields of bivalent and trivalent Fe species (Fig. 3). Under such conditions, mainly insoluble (sulfide and metallic) forms of Cu could be developed in the red rocks.

Deposits of the cupriferous sandstone and shale type have not been found so far in Quaternary sediments. This can be explained by the absence of Quaternary arid red rocks. According to (Rukhin, 1969), the formation of cupriferous sandstones and shales in the Quaternary period is hampered by the abundance of grass cover that was not developed in dry regions in the previous period. However, based on the study of present-day and Tertiary (alluvial, deltaic, coastal-marine, evaporitic, and eolian) sediments in the maritime desert region of northern Baja California, Walker (1967) demonstrated that several millions of years are needed for the formation of red rocks. Although such sediments were accumulated under constant facies and climatic conditions, one can see gradual change of color from gray to red during the transition from Quaternary sediments to Tertiary ones. This is related to the decomposition of Fe-bearing clastic minerals, which produce the authigenic ferruginous pigment. Migration and dispersion of Fe are caused by fluctuations of Eh and pH in pore solutions.

According to data presented in (Ronov, 1983), the Fe content in the Earth's sedimentary shell gradually decreases due to the reduction of areas with exposures of basic effusive rocks. Decrease in the Fe content is accompanied by decrease in the background Cu content (Fig. 4). Since intensity of the formation of ore solutions in red rocks allegedly influences the average Cu content therein, the gradual decrease in the Cu content should be reflected as decrease in the ore-generating potential of the red rocks.

CONDITIONS OF COPPER CONCENTRATION

Investigation of cupriferous sandstones and shales of different ages revealed that Cu was precipitated in the sulfide form. Isotope data indicate the biogenic origin of sulfide sulfur in ores. Sulfate-reducing bacterial played a crucial role in the generation of hydrogen sulfide during the formation of sulfide ores. Hence, the presence of fossil organic and sulfate-reducing bacteria is essential for Cu concentration.

Carbonaceous matter and problematic organic remains are known in sedimentary rocks since 3.8 Ga ago (Isua, Greenland), whereas undoubted stromatolites and siliceous microfossils are known since 3.5–3.3 Ga ago (Krylov, 1983). Anaerobic sulfate-reducing bacteria are likely among the oldest living organisms. Like the stromatolite builders (cyanobacteria), the anaerobic bacteria appeared more than 2 Ga ago. Results of their vital activity (iron sulfides in carbonaceous sediments) are known at the oldest levels of Precambrian sedimentation. Thus, conditions needed for the Cu concentration in sedimentary rocks appeared no less than 3 Ga ago.

Cupriferous sandstones and shales formed at syngenetic and epigenetic geochemical barriers. The syngenetic barriers are particularly interesting for investigation of the periodicity of Cu accumulation in the Earth's history. Their formation is related to the simultaneous accumulation of organic matter and sediments. Such barriers are known in the shallow-water marine, lagoonal, boggy, channel, and deltaic facies settings. The shallow-water marine and lagoonal barriers, which were typical of the entire history of cupriferous sandstones and shales, are most widespread. Sediments of the shallow-water marine facies host several Precambrian deposits, such as the majority of deposits in the Copper Belt of Africa, White Pine deposit (Fig. 5a), ore occurrences in the framing of the Siberian Platform. This facies also includes many Phanerozoic deposits (Mansfeld, Lubin-Sieroszowice, and cupriferous sandstones in the Kazanian Stage of the western Cis-Ural region). Maximal Cu accumulation in the Precambrian sedimentary sequences corresponds in time to the Middle Riphean period of blooming and rapid spreading of stromatolite builders (cyanobacteria) in the Earth (Fedonkin et al., 1987; Semikhatov, 1987). Their vital activity produced organic-rich sediments over vast areas of previous seas.

It is evident that the possibility of cupriferous solutions running against the potential geochemical barriers depends on the scale of barriers. Hence, the development of carbonaceous sediments in the terminal Precambrian over large areas provided maximal facilities for Cu concentration. The boggy and channel facies appeared only since the Devonian owing to the development of land plants. These geochemical barriers became particularly widespread since the Permian. However, fragmentary character of the burial of plant tissues in continental sediments resulted in the dispersion of Cu as numerous small ore occurrences (e.g., cupriferous sandstones in Upper Permian sequences of the western Cis-Ural region). Large Cu deposits of this type are unknown.

Epigenetic geochemical barriers appear at catagenetic stages in the course of the percolation of reducers (oil waters, bitumens, oil, and gases) in collector-rocks of red-bed associations (Fig. 5b). Such barriers are commonly represented by the clastic and coarse-clastic (deltaic, alluvial, proluvial, fan, and others) facies of red rocks with signs of local catagenetic alterations, such as bleaching, pyritization, and calcitization (Gablina, 1983), as well as bituminization in some places (Rzhevskii et al., 1988). Their formation in the Earth's history was provided by two essential conditions: the presence of organic matter and the development of carbonaceous formations near the red molassic sequences. Hence, availability of corresponding combinations of geological factors could provide the formation of epigenetic barriers and associated copper deposits without any variations over the whole time interval under consideration. The largest copper deposits of this type (and associated syngenetic barriers) are found at two stratigraphic levels coinciding with peaks of the accumulation of carbonaceous sediments, on the one hand, and the abundance of red rocks, on the other hand. The first (Riphean–Vendian) level incorporates some deposits in Zambia and separate orebodies confined to the Izluchin Formation at the Graviika deposit. The second (Permian–Carboniferous) level includes the Dzhezkazgan deposit.

Thus, conditions essential for the formation of cupriferous sandstones and shales appeared simultaneously with the origination of the first arid red rocks, which served as ore-generating formations for Cu, more than 2 Ga ago. Variation in the setting of exogenic Cu accumulation in the Earth's history is related to the evolution of living matter in our planet. Maximum Cu concentration in the Riphean–Vendian corresponds in time to the blooming period of cyanobacteria. Appearance of land plants in the Phanerozoic promoted the formation of barren red rocks and the facies diversity of sediments that served as geochemical barriers.

SPECIFIC FEATURES OF THE FORMATION OF LARGE AND UNIQUE COPPER DEPOSITS IN SEDIMENTARY SEQUENCES

Irrespective of dimension, cupriferous sandstone and shale deposits are characterized by common regularities of structure and localization. However, they can form only under the following conditions: (1) the presence of large sedimentary basins with red rocks; (2) the presence of large geochemical barriers; and (3) the long-term and unilateral development of sulfide-forming process (Gablina, 1997). In the case of deposits associated with syngenetic barriers, the first and second conditions are provided by marine transgression into foredeeps and intermontane depressions filled with red sediments (Fig. 5a).

The table shows that large and giant deposits of this type are related to large marine barriers. Local (intraformation) syngenetic barriers of the channel, boggy, and other facies formed in the continental setting incorporate small separate ore deposits and occurrences scattered over a large area (e.g., deposits of the

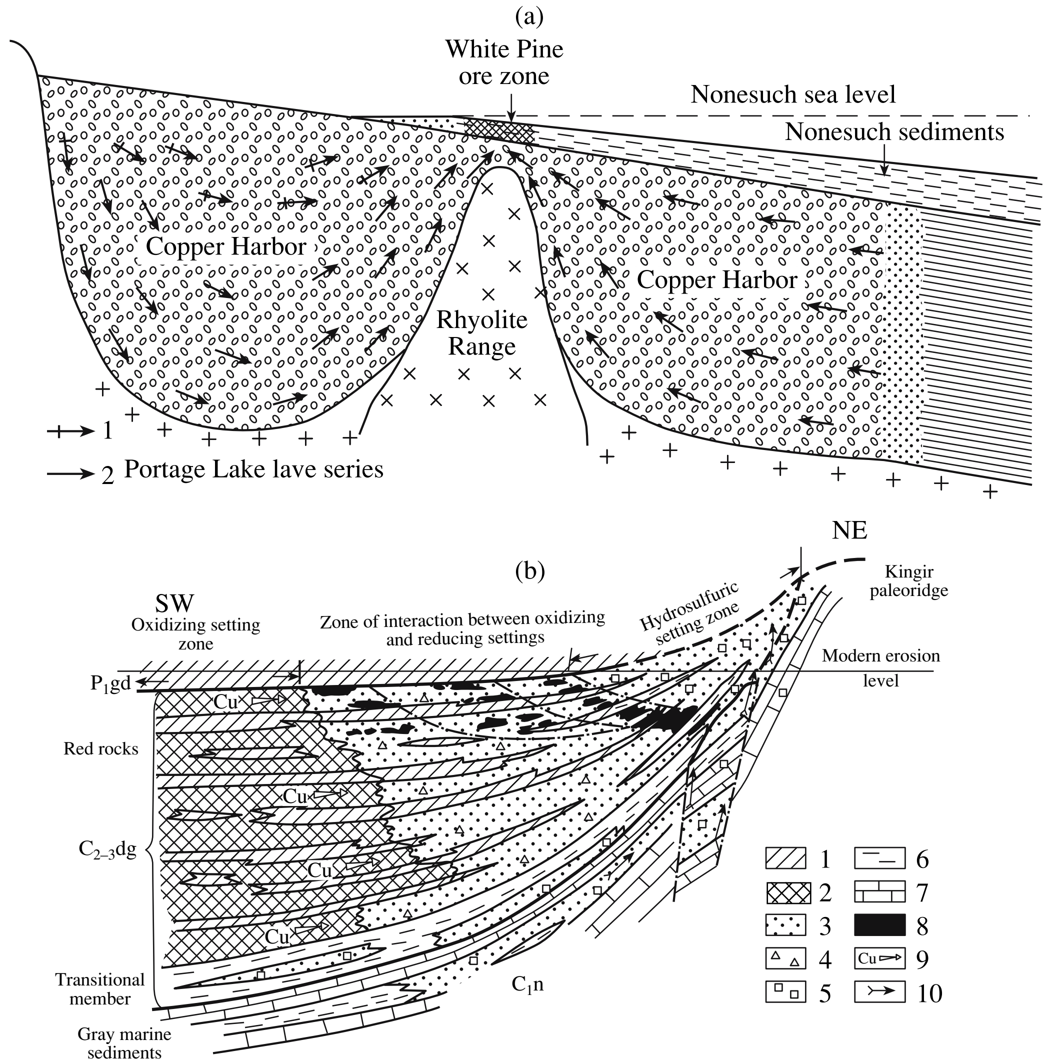

Fig. 5. Models of the formation of copper deposits in sedimentary sequences at (a) syngenetic and (b) epigenetic geochemical barriers. (a) Formation model of the White Pine deposit in H_2S-bearing bottom sediments of the marine basin (White, 1971). (1, 2) Inferred direction of groundwater motion in the underlying Copper Harbor red rocks: (1) infiltration, (2) elision. (b) Formation model of the Dzhezkazgan deposit in the rebleached collector-rocks (Gablina, 1983). (1) Red mudstones and siltstones; (2) red sandstones and conglomerates; (3) gray sandstones and conglomerates; (4) dissemination of copper sulfides; (5) pyrite dissemination; (6) gray mudstones and siltstones; (7) limestones; (8) ore lodes; (9) direction of the percolation of Cu-bearing solutions: (10) migration paths of reducers (hydrocarbons and H_2S). (P_1gd) Lower Permian rocks (Gidelisai Formation); ($C_{2-3}dg$) productive Middle–Upper Carboniferous Dzhezkazgan (red rock) Sequence; (C_1n) marine Lower Carboniferous gray sediments (Namurian Stage).

Kargalin group in the Ufimian red rocks of the western Ural region and ore occurrences in the Kartamysh Formation of the Donbas region).

However, some areas with large marine geochemical barriers incorporate only small ore deposits (e.g., ore occurrences in the Belebeev and other zones of the Kazanian Stage in the western Ural region). Although ore occurrences discussed above and cupriferous deposits in Europe (Zechstein type) formed in similar spatiotemporal settings, one can see certain differences between them. Marine Zechstein sediments overlie large troughs (depth up to 600–1000 m or more) filled with the Rotliegende. In the western Ural region, such large depressions with red coarse-clastic rocks are absent at the Kazanian seafloor and the coarse-clastic (permeable) rocks fill up only fragments of channel (up to 10-m-deep) downcuttings in the Ufimian red clayey rocks beneath the Kazanian marine sediments (Fig. 6). This feature is clearly reflected in the scale of mineralization. Low productivity is also typical of syngenetic barriers at the base of red rocks (Horizon A of the Igarka district, Northern group of copper deposits in the Dzhezkazgan district, as well as Unkur and other copper ore occurrences at the base of the Middle Sakukan Subformation and Aleksandrov Formation of the Kodar–Udokan zone), because processes of diffusion

(a)

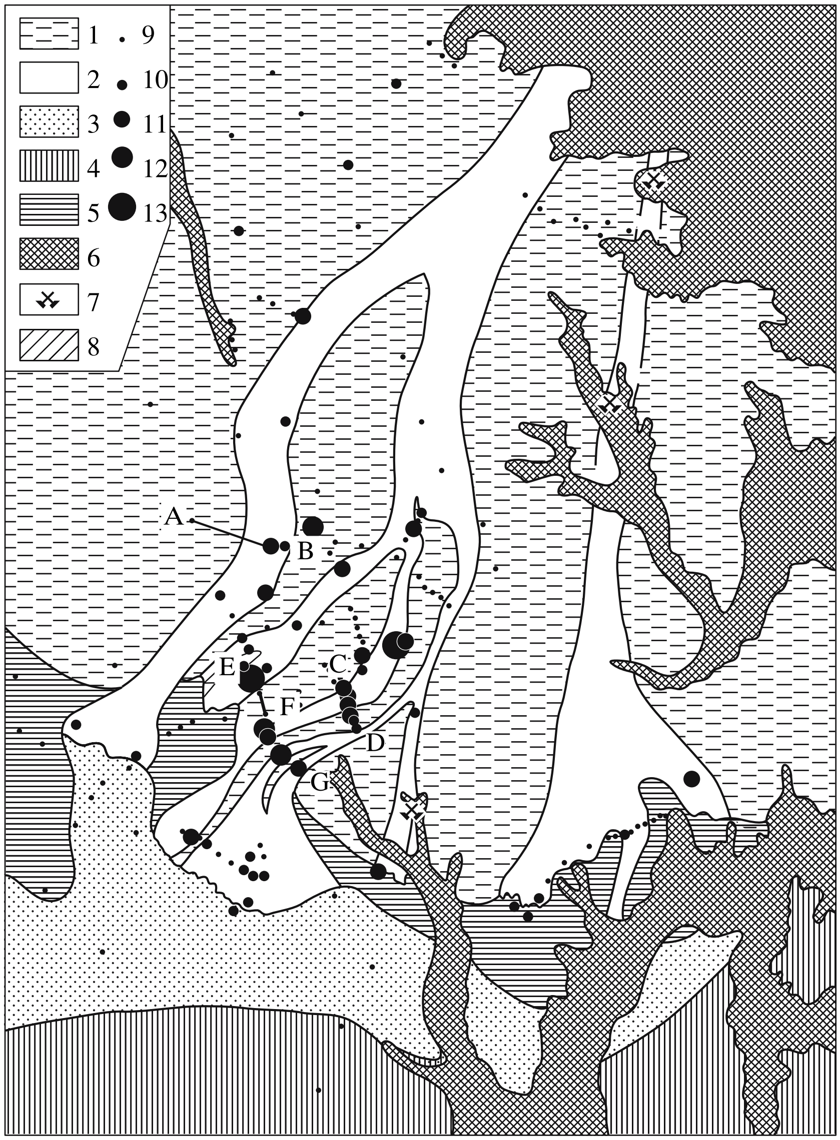

Fig. 6. (a) Paleogeographic scheme of the Belebeev sector at the end of the Ufimian Age and (b) lithofacies profiles (Lur'e and Gablina, 1972). (1, 2) Continental sedimentation settings: (1) coastal plain (primarily, red shales and siltstones), (2) channels and fans (primarily, red sandstones); (3–5) basinal sedimentation settings: (3) bars and shoals (gray sandstones), (4) sectors with elevated salinity (dolomites, gypsum, siltstones, and shales with gypsum), (5) freshened lagoons (intercalation of red shales, siltstones, and less common sandstones); (6) areas characterized by the complete erosion of Kazanian rocks; (7) abandoned deposits; (8) mineralized zones in sections (Cu > 0.1%); (9–13) Cu content at the base of Kazanian marine sediments (Linguba Member, kg/m^2): (9) <2.5, (10) > 2.5, (11) >5, (12) >10, (13) >20. Ratio of horizontal and vertical scales in the sections is 1: 10.

responsible for mineralization of this type can only produce low-grade sulfide dissemination in gray rocks at the contact with red rocks.

Large deposits can only be formed at epigenetic barriers in the case of the presence of large sedimentary basins with the elisional regime of groundwaters and synsedimentary uplifts, near which the groundwaters could discharge (Fig. 5b). Epigenetic barriers can only form under conditions of the existence of conjugated bituminous rocks (sources of reducers) and faults (or lithological windows), which could promote the hydraulic connection between geochemically contrasting solutions (fluids). These conditions were available in Dzhezkazgan located on the slope of the synsedimentary Kingir Uplift in the northern sector of the large Dzhezkazgan–Sarysui Depression filled with continental red sediments of the Dzhezkazgan Sequence. The red Dzhezkazgan Sequence is underlain by a thick Lower Carboniferous carbonate (oil- and gas-generat-

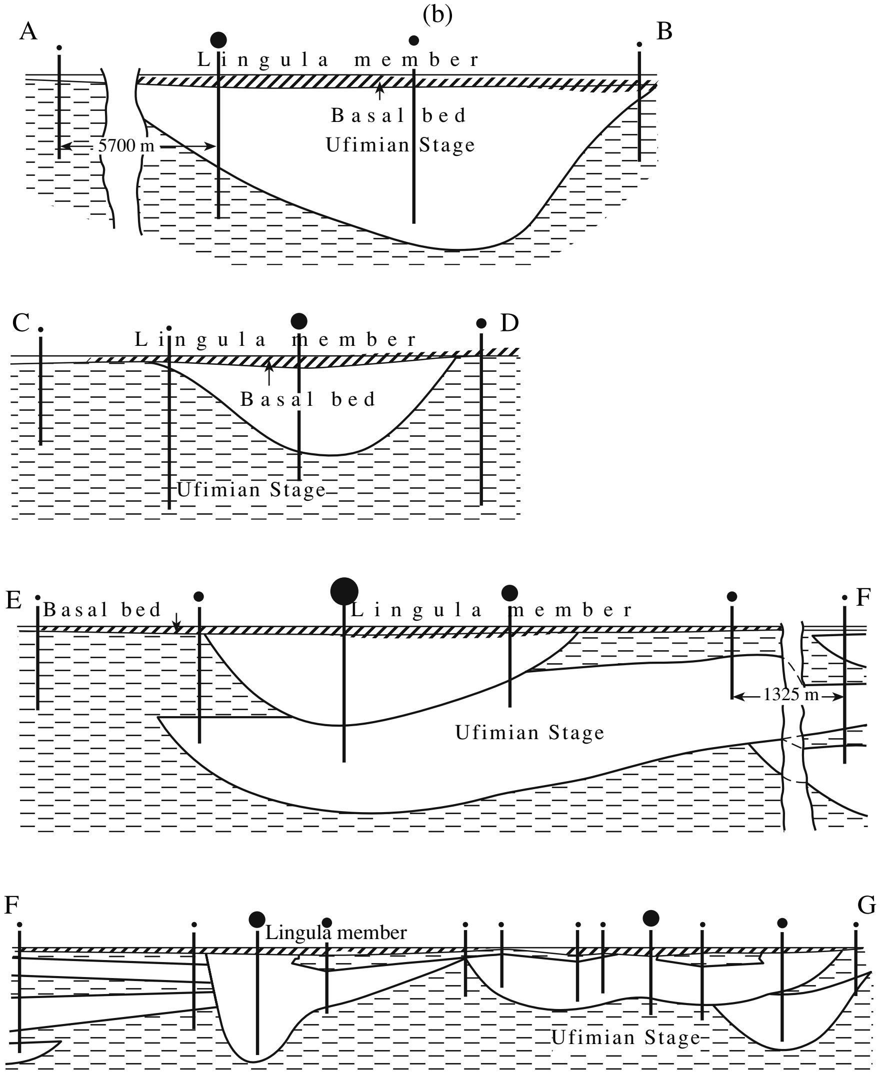

Fig. 6. Contd.

ing) sequence, which could serve as the source of reducing fluids (Fig. 5b).

Duration of mineralization plays a significant role in the formation of giant deposits. Ores of the Dzhezkazgan deposit formed in the course of catagenesis and metagenesis of enclosing sediments. The long-term evolution of these processes was provided by stability of hydrodynamic regime in the Dzhezkazgan–Sarysui Depression. An elisional groundwater regime was developed in the basin due to its long-term (Devonian–Permian) synsedimentary subsidence. Waters squeezed out from clayey sediments percolated along aquifers from the depression center to flanks and local uplifts. Ores were deposited near the synsedimentary Kingir Uplift crosscut by long-lived deep faults. Waters with contrast geochemical characteristics were discharged and mixed in this zone for a long time (Gablina, 1983, 1997).

Formation of the giant Lubin-Sieroszowice deposit was related the activity of a syngenetic barrier at the boundary between the organic-rich basal Zechstein layers and the underlying Rotliegende. This process continued during syngenesis, diagenesis, and catagenesis of enclosing rocks. At initial stages, Cu was delivered to nonlithified Zechstein sediments during the discharge of slightly oxidizing elision waters from the underlying red rocks located at the Zechstein seafloor. Oxygen-bearing waters were delivered to lithified Zechstein rocks along the same conduits (permeable layers of the Rotliegende) in a different hydrodynamic setting of the later stage. Their long-term influence fostered the oxidation, redeposition, and considerable enrichment of primary copper ores, as well as the input of new ore elements (Gablina, 1997; Ermolaev et al., 1996; Wodzicki and Piestrzynski, 1986). Rocks of the Udokan Sequence were initially mineralized during diagenesis and catagenesis of enclosing rocks at the

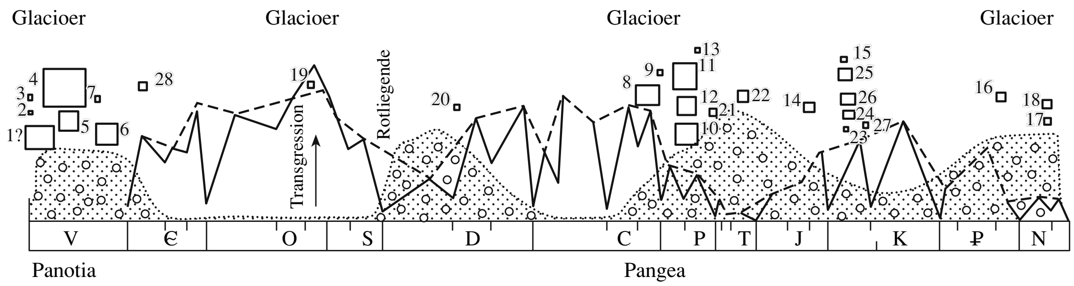

Fig. 7. Copper deposit in shales against the background of very intense global alterations. Dots show red rocks according to (Anatol'eva, 1978). Deposit numbers are as in Fig. 2.

syngenetic barrier (members of primary gray pyrite-bearing rocks in a thick red sequence). The present-day appearance of the Udokan deposit was developed in the course of the whole (Proterozoic–Recent) history of ore-enclosing rocks. In this process, the Cu concentration was significantly controlled by superimposed processes related to the regional and contact metamorphism and hypergenesis (Gablina, 1997; Gablina and Mikhailova, 1994).

PERIODICITY IN THE FORMATION OF CUPRIFEROUS SANDSTONES AND SHALES

The stratigraphic distribution of cupriferous sandstones and shales lack any explicit periodicity (table). One can only see an irregular distribution of ore deposits in the stratigraphic scale.

However, periodicity in global changes is well known, e.g. the formation and breakup of supercontinents (Wilson Cycle); Bertrand Cycle (~180 Ma); periodic fluctuations of the World Ocean level; periodicity of glacioeras, biospheric rhythms, and so on. The formation of ore deposits should also be associated with these processes. We should investigate cupriferous sandstones and shales against the background of global changes in order to unravel the hidden periodicity in their accumulation. This approach reveals a clear link of unique and large deposits with the Panotia and Pangea supercontinents (Fig. 7). Large deposits of the Copper Belt of Africa, White Pine (Lake Superior, United States), and Ainak (Afghanistan), and, probably, the unique Udokan deposit were formed in the Panotia supercontinent. Existence of Pangea fostered the formation of very large deposits of the Dzhezkazgan group (Kazakhstan), copper deposits confined to the Rotliegende and Zechstein rocks of Europe (Mansfeld, Sangerhausen, Reichelsdorf, and others in Germany), and the giant Lubin-Sieroszowice deposit (Poland).

This pattern of the formation of cupriferous sandstones and shales is natural from the point of view of the model described above. The existence of thick sequences of ore-generating red rocks and carbonaceous geochemical barriers is essential for the formation of large deposits. The formation of thick continental red sequences is related to climatic features of supercontinents. Their environment was most favorable for the formation of giant ice sheets and specific climatic conditions characterized by virtual absence of the humid tropical belt (Zharkov, 2004). Onset of the breakup of the supercontinents was dominated by the continental arid climate at their lower and middle latitudes, as suggested by the Permian and Triassic paleogeography of Pangea (Zharkov, 2004).

Lowstand of the World Ocean during the onset of extension of the Earth's continental crust promoted the accumulation of huge masses of red rocks in the newly forming grabens. The specific type of atmospheric and oceanic circulation related to glaciation was retained after the degradation of glaciers. For example, a humid tropical belt appeared only in the Albian (Chumakov, 2004) almost 100 Ma after the degradation of glaciers. Therefore, accumulation of red rocks coupled with sandstones and shales is not drastically terminated but gradually decreased. For example, the Middle–Upper Cambrian level incorporates only one moderate-size deposit (Timna, Israel) and some small ore occurrences in the West Arabian cupriferous zone, southern framing of the Siberian Platform, and others (Narkelyun et al., 1983). The maximum Cu accumulation in the Upper Jurassic–Lower Cretaceous related to deposits in the North African province and China (Yunnan and Heili ore districts) is much smaller than the Permian peak.

Thus, large exogenic copper deposits were formed during glacioeras and the subsequent arid epochs. However, the prolonged (Middle Ordovician–Silurian) glacial period, which was not accompanied by strong decrease in the World Ocean level and large-scale continental glaciation, did not promote the formation of large copper deposits. In addition to small ore occurrences at the framing of the Siberian Platform, only one medium-size cupriferous clay deposit (Mount Lyell, Australia) is known in Late Ordovician rocks (Narkelyun et al., 1983). Thus, the scale of glaciation shows inverse correlation with the size of copper deposits. This regularity is also typical of all other Phanerozoic ore-bearing and petroliferous rocks (Malinovskii. 1982).

Maximums of cupriferous sandstones and shales lack any periodicity, but their minimums correspond to Early Ordovician, Early Carboniferous, and Late Cretaceous. Interval between the minimums is approximately 180 Ma (Bertrand period). These epochs are characterized by the minimal accumulation of red and carbonaceous rocks, the maximal World Ocean level, and the maximal expansion of humid tropical zones. The latter process also continued at the beginning of glacioeras.

Transition from warm eras to glacial epochs is apparently paradoxical, because the maximal warming is abruptly replaced by the glacial process against the background of highstand of the World Ocean and the maximal reduction of arid zones. As is known, such periods are characterized by reduction of the Earth's reflectance (albedo) and increase of the solar energy input. Transition from glacioeras to warm epochs is no less surprising: drastic cooling is suddenly replaced by warming in the course of the maximal development of continental glaciation and climate aridization when the Earth's surface can only consume a minimal portion of solar energy. Degradation, for example of the Permian ice sheet, took place without any change in the position of Pangea (Zharkov, 2004). Such paradoxical scenario can testify to self-oscillating nature of the phenomenon (Malinovskii, 2007). Such self-oscillations took place in the biosphere, that according to V.I. Vernadsky, the process of natural oscillation includes living matter, hydrosphere, troposphere, and upper part of the lithosphere. What is their possible mechanism?

The water column of the present-day World Ocean is mainly stratified by temperature. Temperatures of deep and intermediate waters are approximately 2.5°C, on average. According to (Huber et al., 2000), the temperature of deep waters of the Late Cretaceous ocean varied from 7–11 to 20%C before the onset of glacioera and the waters were stratified by salinity. They flowed from equators to poles (Kuznetsova and Korchagin, 2004). In contrast, the present-day water current is directed from poles to equator. Following (Lisitsyn, 1989), we can accept that all glacioeras were characterized by T-circulations, whereas warm eras were characterized by S-circulations. The T-circulation is formed by "natural refrigerators" near poles, whereas the S-circulation is related to the sink of warm saline waters in arid zones. The T-circulation creates the "cold ocean," while the S-circulation creates the "warm ocean." However, Lisitsyn believes that the climate of continent only depends on the type of its new climatic zone. The S-circulation is much weaker than the T-circulation, as suggested by the absence of contourites at the bottom of the Cretaceous ocean. The point is that water circulation should be weak in the Cretaceous (particularly, Late Cretaceous) when the water was almost completely stratified by salinity.

The T-circulation comes to a standstill when the entire ocean becomes cold. Consequently, surficial warm currents of the Golf Stream type do not operate and heat is not transferred to poles. Thus, the environment becomes favorable for the maximal glaciation and aridization of climate. This process leads to the formation of heavy (high-salinity) warm waters at low latitudes of the ocean. After the accumulation to a certain limit, the waters sink to deep zones and flow to poles. Thus, the currents drive the interoceanic conveyer and destroy the glaciation. This scenario is typical of the first (carbonaceous) phase of biospheric rhythms (Malinovskii, 2007) that can be compared with the global upwelling. The atmosphere is concentrated with CO_2 owing to the upwelling and the input of biogenic elements into the oceanic photosynthesis zone. Ultimately, this process is accompanied by the augmentation of bioproductivity and the emission of carbon in both marine and continental ecosystems (Malinovskii, 1982, 2007). Thawing of glaciers fosters the rise of the World Ocean level. Carbonaceous sediments of the first phases of biospheric rhythms overlie the ore-generating red rocks formed during the "calcic" phases of previous rhythms, resulting in the formation of syngenetic geochemical barriers.

Consumption of the high-salinity warm waters is accompanied by the retardation of oceanic currents, resulting in the gradual onset of the second ("calcic") phase of biospheric rhythms. This phase goes on for a more prolonged period (relative to the carbonaceous phase) until the accumulation of the next critical mass of waters at low latitudes. The process can be initiated near critical states by external forces (fall of space bodies, earthquakes, and so on). Thus, the S-circulation responsible for the warm ocean also represents a rhythmic process (biospheric rhythms). Heating of all waters of the ocean is followed by the gradual attenuation of the S-circulation, resulting in expansion of zones with the humid tropical climate, termination of the process of accumulation of high-salinity waters in the interoceanic conveyer, and cessation of the delivery of heat to poles (Malinovskii, 2007).

Such conditions existed in the Early Ordovician, Early Carboniferous, and Late Cretaceous. These epochs were characterized by the low amount of carbonaceous sequences, minimal accumulations of sedimentary deposits, and maximal deposits of carbonates. Stratification of waters of the "warm climate" and the consequent weak functioning of the interoceanic conveyer against the background of warm humid climate provoked continental glaciation in the Middle Ordovician, Middle Carboniferous, and Paleogene. Portions of cold and denser waters accumulated near the polar "refrigerators" were transported to the equator in deep zones of the ocean, resulting in the T-circulation and biospheric rhythms. Biospheric rhythms of both T- and S-circulations have a similar structure: the first phase has the carbonaceous composition, whereas the second phase has the calcic composition. The first phase promotes a short-period humidification of climate, whereas the second phase is often terminated by the formation of salts. The well-known triad (carbonaceous sediments–carbonates–salts) represents biospheric rhythms (Malinovskii, 2003).

Cupriferous sandstones and shales occupy a certain position in the biospheric rhythms at the boundary between the "calcic" phase and the "carbonaceous" phase of the next rhythm. The "carbonaceous" phase of biospheric rhythm begins drastically and gradually gives way to the "calcic" phase. During glacial epochs, the carbonaceous phase is accompanied by the ocean level rise due to the periodic melting of ice. Therefore, carbonaceous sediments can more often overlie the continental red sequences formed during the calcic phase of the preceding biospheric rhythm. The "calcic" phase of biospheric rhythms is characterized by the intensification of climate aridization, which reaches the maximum degree at the end of the "calcic" phase. Consequently, the most contrasting transitions of sedimentation environment coincide with the barriers of biospheric rhythms, resulting in the development of geochemical barriers that are involved in the formation of exogenic copper deposits.

Thus, the formation of cupriferous sandstones and shales is governed by the general law of periodicity in the accumulation of petroliferous and ore-bearing sediments in accordance with the Bertrand and Wilson cycles. However, the Wilson cycle (~400–450 Ma), which is related to the maximal development of red rocks at supercontinents, plays the major role in this scenario.

CONCLUSIONS

1. Relationship of cupriferous sandstone and shale deposits with red molassic sequences is explained by the mobility of Cu (Cu^+) in a weakly oxidizing medium, which is typical of formation waters in the red sequences. Cu is precipitated as sulfides at the H_2S-rich barriers of two (syngenetic and epigenetic) types.

2. Decrease in the Cu concentration in the Earth's sedimentary shell from the Precambrian to Cenozoic can be related to the influence of the following processes: evolution of living matter in the Earth's history; decrease in the background Cu content in sedimentary rocks; and variation in the formation condition of red rocks.

3. Maximal Cu concentrations in the sedimentary shell is mainly related to the presence of large and unique deposits (reserve more than 10 Mt) that can only form under the following conditions: the presence of large depressions filled with ore-generating red rocks; the presence of large areas of reducing barriers; and the long-term process of ore formation. Therefore, the oldest copper deposits, the formation of which is still going on due to secondary enrichment in the hypergenesis zone, also often represent the largest Cu concentrators in sedimentary rocks.

4. The periodic formation of cupriferous sandstones and shales is related to global biospheric rhythms. The major epochs of copper accumulation coincide with initial stages of the rearrangement of gyres and correspond to the replacement of the calcic phase of large biospheric rhythms by the "carbonaceous" phase of the next rhythm.

5. Periodicity of the maximal Cu accumulation in the Earth's history described in our work coincides with periods of the maximal development of red rocks at supercontinents (Panotia and Pangea), the origination period of which corresponds to the Wilson cycle (400–450 Ma).

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REFERENCES

Amantov, V.A., Unresolved Problems of Proterozoic Stratigraphy in the Baikal Amur Mainline Zone, *Tr. Vseross. Geol. Inst. Nov. Ser.*, 1978, vol. 302, pp. 87–93.

Anatol'eva, A.I., *Glavnye rubezhi evolyutsii krasnotsvetnykh formatsii* (Major Boundaries in the Evolution of Red Rock Associations), Novosibirsk: Nauka, 1978.

Arustamov, A.A., Esenov, Sh.E., Parshin, G.B., and Shtifanov, V.I., *Medistye peschaniki Severnogo Dzhezkazgana* (Cupriferous Sandstones of Northern Dzhezkazgan), Alma-Ata: Nauka, 1963.

Autorenkollektiv, Litologie, Paläogeographie und Metallfürung des Kupferschiefers in der DDR, Geologie, 1968, vol. 17, no. 6/7, pp. 776–791.

Bogdanov, Yu.V., Bur'yanova, E.Z., and Kutyrev, E.I., et al., *Stratifitsirovannye mestorozhdeniya medi SSSR* (Stratified Copper Deposits of the USSR), Leningrad: Nedra, 1973.

Bogdanov, Yu.V., Kochin, G.G., Kutyrev, E.I., et al., *Medistye otlozheniya Olekmo-Vitimskoi gornoi strany* (Cupriferous Deposits in the Olekma–Vitim Mountain Region), Leningrad: Nedra, 1966.

Borisenko, E.N., *Geokhimiya gleevogo katageneza v porodakh krasnotsvetnoi formatsii* (Geochemistry of the Gley Catagenesis of Red Rocks), Moscow: Nauka, 1980.

Cailteux, J., Minerals Cuprifers et rockes encaissantes a Musoshi province du Shaba republique du Sair, *Am. Soc. Geol. Belg.*, 1973, vol. 96, no. 3, pp. 495–521.

Chumakov, N.M., Climatic Zonation and Cretaceous Climate, in *Klimat v epokhi krupnykh biosfernykh perestroek*, (Climate during Epochs of the Major Biospheric Rearrangements), Semikhatov, M.A. and Chumakov, N.M., Eds., Moscow: Nauka, 2004, pp. 105–123.

Cloud, P., Paleoecological Significance of the Banded Iron Formation, *Econ. Geol.*, 1973, vol. 68, no. 7, pp. 1135–1143.

Cony, A.G., Scott, S.D., Bellon, H., and Beaudoin, G., The Boleo Cu–Co–Zn Deposit, Baja California Sur, Mexico: The Role of Magmatic Fluids in Genesis of a Synsedimentary Deposit, in *Mineral deposits at the 21st Century*, 2001, pp. 223–226.

Eisenhut, K. and Kautzsch, E., *Handbuch für dem Kupferschiferbergbau,* Leipzig, 1954.

Ensign, K.O., Jr., White, W.S., Wright, J.K., et al., Copper Deposits of the White Pine Region in the Nonesuch Shales, Michigan State, in *Ore Deposits of the United States, 1933–1967*, Ridge, J.D., Ed., Am. Inst. Min. Metal. Petrol. Engn., 1968. Translated under the title *Rudnye mestorozhdeniya SShA*, Moscow: Mir, 1972, vol. 1, pp. 602–627.

Ermolaev, N.P., Gablina, I.F., and Bernard, V.V., Redistribution of Platinum Group Metals, Gold, and Silver in Cupriferous Sandstones and Shales (Lower Silesia, Poland), *Geokhimiya*, 1996, vol. 34, no. 9, pp. 840–851 [*Geochem. Int.* (Engl. Transl.), 1996, vol. 34, no. 9, pp. 757–767].

Fedonkin, M.A., Chumakov, N.M., and Yankauskas, T.M., The Main Biotic and Abiotic Events during Late Precambrian, Abstracts of Papers, *III Vsesoyuznyi simpozium po paleontologii dokembriya i rannego kembriya* (III All-Union Symposium on the Precambrian and Early Cambrian Paleontology), Petrozavodsk, 1987, pp. 99–101.

Gablina, I.F., *Usloviya medenakopleniya v krasnotsvetnykh kontinental'nykh formatsiyakh* (Conditions of Copper Accumulation in Continental Red Rock Associations), Moscow: Nauka, 1983.

Gablina, I.F., Mineralogical–Geochemical Criteria for the Recognition of Red Rock Associations in Precambrian Metamorphic Sequences in Connection with Their Copper Potential, *Litol. Polezn. Iskop.*, 1990, vol. 25, no. 3, pp. 95–109.

Gablina, I.F., Formation Condition of Large Cupriferous Sandstone and Shale Deposits, *Geol. Rudn. Mestorozhd.*, 1997, vol. 38, no. 4, pp. 372–386 [*Geol. Ore Deposits.*, (Engl. Transl.) 1997, vol. 38, no. 4, pp. 320–333].

Gablina, I.F. and Mikhailova, A.I., Localization Trend of Copper Mineralization at the Udokan Deposit, *Litol. Polezn. Iskop.*, 1994, vol. 29, no. 3, pp. 147–168.

Geology of the Northern Rhodesian Copperbelt, Mendelsohn F., Ed., London: McDonald, 1961. Translated under the title *Mednyi poyas Severnoi Rodezii* (The Copper Belt of Northern Rhodesia), Moscow: Inostran. Literatura, 1963.

Germanov, A.I., Hydrodynamic and Hydrochemical Formation Conditions of Some Hydrothermal Deposits, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1962, pp. 79–98.

Gipergennye okisly zheleza v geologicheskikh protsessakh (Hypergene Iron Oxides in Geological Processes), Moscow: Nauka, 1975.

Goleva, G.A., Polyakov, V.A., and Nechaev, T.N., Distribution and Migration Forms of Copper in Groundwaters, *Geokhimiya*, 1968, no. 5, pp. 586–594.

Gustafson, L.B. and Williams, N., Sediment-Hosted Stratiform Deposits of Copper, Lead, and Zinc, in *Economic Geology 75th Anniversary Volume 1905-1980*, B. Skinner, Ed., Lancaster: Econ. Geol. Publ. Co. 1981. Translated under the title *Genezis rudnykh mestorozhdenii*, Moscow: Mir, 1984, pp. 156–224.

Hoyningen-Huene, E., Zur Paläohidrologie des Oberrotligenden und Zechsteins in Harzvorland, *Ber. Geol. Ges. DDR*, 1963, no. 1, pp. 201–220.

Huber, B.T., Norris, R.D., and Macleod, K.G., Deep-Sea Paleotemperature Record of Extreme Warmth during the Cretaceous, *Geology*, 2000, vol. 30, no. 2, pp. 123–126.

Kirkham, R.V., The Distribution, Settings and Genesis of Sediment-Hosted Stratiform Copper Deposits, in *Sediment-Hosted, Stratiform Copper Deposits*, Geol. Assoc. Can. Spec. Pap., 1989, no. 36.

Kossovskaya, A.G. and Sokolova, T.N, *Graywackes from Red Rock Associations in the Orenburg Sector of the Ural Region*, in *Grauvakki* (Graywackes), Moscow: Nauka, 1972, pp. 232–284.

Krylov, I.N., Precambrian Organic Kingdom and Its Influence on Sedimentary Processes, Abstract of Papers, *Biogeokhimicheskie aspekty formirovaniya osadochnykh porod i rud* (Biochemical Aspects of the Formation of Sedimentary Rocks and Ores), Leningrad, 1983.

Kuznetsova, K.I. and Korchagin, O.A., Global Expansion of Planktonic Foraminifers: Triassic, Jurassic, and Cretaceous, in *Climat v epokhi krupnykh biosfernykh perestroek* (Climate during Epochs of the Major Biospheric Rearrangements), Semikhatov, M.A. and Chumakov, N.M., Eds., Moscow: Nauka, 2004, pp. 124–148.

Lisitsyn, A.P., Evolution of Oceans, in *Evolyutsiya geologicheskikh protsessov. Dokl. sovetskikh geologov na XXVIII sessii MGK* (Evolution of Geological Processes: Papers of Soviet Geologists at XXVIII Session of Int. Geol. Congr.), Moscow: Nauka, 1989, pp. 153–166.

Lur'e, A.M., Copper Deposits in Marine Sediments, *Sov. Geol.,* 1974, no. 1, pp. 20–29.

Lur'e, A.M., *Genesis medistykh peschanikov i slantsev* (Genesis of Cupriferous Sandstones and Shales), Moscow: Nauka, 1988.

Lur'e, A.M. and Gablina, I.F., Sources of Copper for the Formation of Mansfield-Type Deposits in the Western Ural Region, *Geokhimiya*, 1972, vol. 10, no. 1, pp. 75–88.

Lur'e, A.M. and Gablina, I.F., Principle Model of the Formation of Exogenous Copper Deposits, *Dokl. Akad. Nauk SSSR,* 1978, vol. 241, no. 6, pp. 1402–1406.

Malinovskii, Yu.M., *Sinfaznaya stratigrafiya fanerozoya* (Inphase Phanerozoic Stratigraphy), Moscow: Nedra, 1982.

Malinovskii, Yu.M., *Biosfernye osnovy litologii* (Biospheric Principles of Lithology), Moscow: RUDN, 2003.

Malinovskii, Yu.M., *Neftegazovaya litologiya* (Petroleum Lithology), Moscow: RUDN, 2007.

Melezhik, V.A., Early Precambrian Red Bed Associations: Results of the Biochemical Activity of Organisms, in Abstracts of Papers, *III Vsesoyuznyi simpozium po paleontologii dokembriya i rannego kembriya* (The 3rd All-Union Symposium on Precambrian and Early Cambrian Paleontology), Petrozavodsk, 1987, pp. 66-67.

Narkelyun, L.F., *Geologiya i orudenenie Dzhezkazganskogo mestorozhdeniya (po materialam rudnogo raiona Pokro)* (Geology and Ore Mineralization of the Dzhezkazgan Deposit: Based on Materials of the Pokro Ore District), Moscow: Akad. Nauk SSSR, 1962.

Narkelyun, L.F., Bezrodnykh, Yu.P., Trubachev, A.I., et al., *Medistye peschaniki i slantsy yuzhnoi chasti Sibirskoi platformy* (Cupriferous Sandstones and Shales in the Southern Siberian Platform), Moscow: Nedra, 1977.

Narkelyun, L.F., Salikhov, V.S., Trubachev, A.I., et al., *Medistye peschaniki i slantsy mira* (Cupriferous Sandstones and Shales of the World), Moscow: Nedra, 1983.

Perel'man, A.I., *Nekotorye voprosy geokhimii katageneza v osadochnykh mestorozhdeniyakh tipa medistykh peschanikov* (Some Problems of the Geochemistry of Catagenesis in Sedimentary Deposits of the Cupriferous Sandstone Type), Moscow: Akad. Nauk SSSR, 1959, pp. 5–21.

Perel'man, A.I., *Geokhimiya epigeneticheskikh protsessov* (Geochemistry of Epigenetic Processes), Moscow: Nedra, 1968.

Perel'man, A.I. and Borisenko, E.N., *Ocherki geokhimii medi v zone gipergeneza* (Essays on Copper Geochemistry in the Hypergene Zone), Moscow: Akad. Nauk SSSR, 1962, pp. 30–99.

Pushkina, Z.V., Pore Waters in Mudstones and Their Changes with Depth, in *Postsedimentatsionnye izmeneniya chetvertichnykh i pliotsenovykh glinistykh otlozhenii Bakinskogo arkhipelaga* (Postsedimentary Alterations of Quaternary and Pliocene Clayey Sediments in the Baku Archipelago), Moscow: Nauka, 1965, pp. 160–203.

Ronov, A.B., Chemical Composition of Sedimentary Rocks from the Most Important Zones of Continents and the Ways of Its Evolution, in *Geokhimiya platformennykh i geosinklinal'nykh osadochnykh porod i rud* (Geochemistry of Platformal and Geosynclinal Sedimentary Rocks and Ores), Moscow: Nauka, 1983, pp. 7–18.

Rose, A.W., The Effect of Cupriferous Chloride Complexes in the Origin of Red-Bed Copper and Related Deposits, *Econ. Geol.*, 1976, vol. 71, pp. 1036–1048.

Rukhin, L.B., *Osnovy litologii* (Fundamentals of Lithology), Moscow: Nedra, 1969.

Rzhevskii, V.F., Gablina, I.F., Vasilovskaya, L.V., and Lur'e, A.M., Genesis of the Graviika Copper Deposit, *Litol. Polezn. Iskop.,* 1988, vol. 23, no. 2, pp. 86–97.

Semikhatov, M.A., Precambrian Stromatolite Taxa in Space and Time, in Abstracts of Papers, *III Vsesoyuznyi simpozium po paleontologii dokembriya i rannego kembriya* (III All-Union Symposium on Paleontology of Precambrian and Early Cambrian), Petrozavodsk, 1987, pp. 87–89.

Shcherbakov, A.V., *Geokhimiya termal'nykh vod* (Geochemistry of Thermal Waters), Moscow: Nedra, 1968.

Strakhov, N.M., *Osnovy teorii litogeneza* (Fundamentals of the Theory of Lithogenesis), Moscow: Akad. Nauk SSSR, 1964, vol. 2.

Tazhibaeva, P.T., Eirish, M.V., and Safargaliev, Role of Organic Carbon in Ore Formation in the Dzhezkazgan Deposit, *Izv. Akad. Nauk Kaz. SSR, Ser. Geol.,* 1964, no. 4, pp. 91–95.

Vil'mova, E.S., First Find of Fauna and Traces of Vital Activity in the Udokan Group of the Udokan Depression, Eastern Transbaikal Region, in Abstracts of Papers, *III Vsesoyuznyi simpozium po paleontologii dokembriya i rannego kembriya* (III All-Union Symposium on Paleontology of Precambrian and Early Cambrian), Petrozavodsk, 1987, pp. 18–19.

Volodin, R.N., Chechetkin, V.S., Bogdanov, Yu.V., et al., The Udokan Cupriferous Sandstone Deposit, East Siberia, *Geol. Rudn. Mestorozhd.*, 1994, vol. 36, no. 1, pp. 3–30.

Walker, T.R., Formation of Red-Bed in Modern and Ancient Deserts, *Bull. Geol. Soc. Am.*, 1967, vol. 78, no. 3, pp. 510–521.

White, W.S., A Paleohydrologic Model for Mineralization of the White Pine Copper Deposit, Northern Michigan, *Econ. Geol*, 1971, vol. 66, no. 1, pp. 1–13.

Wodzicki, A. and Piestrzynski, A., An Ore Genetic Model for the Lubin-Sieroszowice Mining District, Poland, *Mineral. Deposita,* 1986, vol. 21, pp. 70–80.

Yanshin, A.L., Criteria for the Recognition of Geological Formations, in *Domezozoiskie krasnotsvetnye formatsii* (Pre-Mesozoic Red-Bed Associations), Novosibirsk: Nauka, 1972, pp. 5–12.

Yashchinin, S.B. and Giruval, T., The Ainak Copper Deposit (Afghanistan), *Sov. Geol.*, 1981, no. 7, pp. 78–82.

Yurgenson, G.A., Akram, M., Alami, G., et al., Mineralization Types and the Sequence of Sulfide Deposition in the Ainak Deposit (Afghanistan), *Izv. Vyssh. Uchebn. Zaved., Ser. Geol. Razved.*, 1981, no. 7, pp. 78–82.

Zharkov, M.A., Paleogeographic Events and Depositional Environments during the Permian and Early Triassic, in *Klimat v epokhi krupnykh biosfernykh perestroek*, (Climate during Epochs of the Major Biospheric Rearrangements), Semikhatov, M.A. and Chumakov, N.M., Eds., Moscow: Nauka, 2004, pp. 158–180.