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Diagenetic Migration of Sulfides in Sediments Accumulated in Different Sedimentation Settings

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Abstract—Migration and accumulation of sulfides at the contact of lithologically and geochemically different layers are considered. The possible mechanisms (gravitational, diffusion, elision, and electrogeochemical) for sulfide transportation during diagenesis are discussed. Data are presented to explain the localization of sulfide minerals at the boundary of reduced and oxidized sediments. The paper considers examples of stratiform sulfide concentrations of not only ore grade, but also lower grade, which, however, are of great significance for understanding the formation conditions of some geochemical anomalies. Link between the diagenetic migration of sulfides and the formation of iridium anomaly is substantiated.

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INTRODUCTION

Sharp boundaries between lithologically and geochemically different sediments often serve as levels of the accumulation of diverse (carbonate, sulfide, siliceous, redox-sensitive elements, and some others) components of sediments. In fact, these boundaries are geochemical barriers related to significant variations in sedimentation regime. Issue of the interaction of lithologically and geochemically different sediments during diagenesis and various aspects of diagenetic migration were considered by Strakhov during the development of his theory of diagenesis (Strakhov, 1953, 1959, 1962). Diverse manifestations of the migration of diagenetic sedimentary components were also described in (Berner, 1969; Gavrilov, 1977, 1982; Kizil'shtein, 2007; Timofeeva, 1959; Volkov and Ostroumov, 1957; Zaritskii, 1971; and others). The migration scale was sufficiently great to form large accumulations (up to ore concentrations) of iron and manganese carbonates and diverse sulfides.

In this work, we consider issues of the diagenetic migration of sulfide matter and its accumulation as both ores and as relatively weak manifestations, which, however, are of great significance for the interpretation of past geological events.

EVIDENCE FOR THE DIAGENETIC MIGRATION OF SULFIDE MATTER

The phenomenon of diagenetic migration of sulfide matter is well known. Large sulfide (pyrite) concretions (up to 725 kg in weight) were described by A.E. Fersman in quartz sandstones intercalating with clays and coals in the Moscow coal basin as early as 1915 (Fersman, 1952).

P.V. Zaritskii (1962, 1971) believed that the formation of numerous FeS_2 concretions at the contact of coal with adjacent beds (Dnepropetrovsk brown coal basin), as well as the complete cementation of sandy lenses and interbeds in the coal by iron disulfide, were related to the influx of iron disulfide from peatbogs into terrigenous sediments. The consideration of morphology and bedding of iron sulfides in mudstones of the Donets Basin revealed that sulfide matter was mobile in the weakly compacted sediment during early diagenesis (Kizil'shtein and Nastavkin, 2003).

While considering issues of the diagenetic migration of matter in sediments, Strakhov (1962) reported data on sulfide layer at the base of the Lower Ordovician carbonaceous shales (termed as dyctionemic shales due to numerous imprints of Dyctionema graptolites) of the Baltic region as the most remarkable example of sulfide migration. This bed extends with some intervals over almost 150 km.

We also repeatedly noted traces of sulfide migration in the Mesozoic and Cenozoic sequences of the Greater Caucasus and Russian Plate. In particular, we observed droplike concretions (Fig. 1) in the Middle Miocene sediments of the eastern Cis-Caucasus region near the contact of virtually OM-barren quartz sandstones, whereas the overlying clayey sediments contained up to $n\%$ C_{org} (Gavrilov, 1982). The sulfide material (presumably, hydrotroilite) obviously formed in the reduced setting of organic-rich clay sediments, migrated in the underlying sandy sediments, and precipitated there as concretions. If a clay interbed was developed in the sandstones, it prevented sulfide migration and pyrite concretions were accumulated at its surface. We also noted that the organic-rich Middle Miocene clayey sediments lack sulfide concretions,

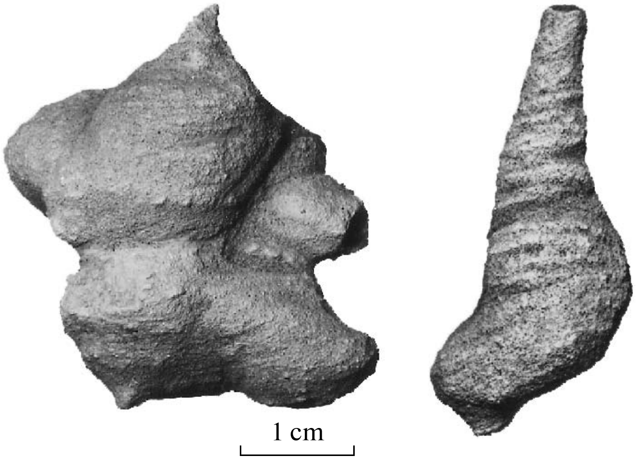

Fig. 1. Drop-shaped pyrite concretions from the upper part of sandstone bed located beneath organic-rich clayey sediments: Middle Miocene (Chokrak), Elistanzhi River section, Chechnya, northeastern Caucasus (Gavrilov, 1982).

Fig. 2. Organic-rich dyctionemic shales located within sandstones; coastal exposures of the Baltic Sea in the Paldiska area, Estonia. (1) Obolus sandstones, (2) dyctionemic shales, (3) glauconite sandstones. Arrows show positions of the lowermost and uppermost sulfide beds. All photos hereinafter were taken by the author.

but they contain lenslike sandy–silty material cemented by pyrite (as in the case described by P.V. Zaritskii). We observed a similar pattern in the section of carbonaceous sediments accumulated at the Russian Plate during the Early Aptian anoxic event (OAE 1a). In this sequence, sulfide minerals apparently confined to thin sandy–silty interbeds (Gavrilov et al., 2002) were virtually absent in the host clayey sediments.

Migration of the sulfide substance during diagenesis is also noted in Quaternary sediments of modern seas.

Arkhangel'sky (1934) noted the diffusion of H_2S and the migration of colloidal monosulfide (hydrotroilite) from organic-rich sediments of the ancient Black Sea into the underlying Neoeuxinian beds with an extremely low content of organic matter. Diffused H_2S interacted with Fe^{2+} of interstitial waters to form additional portions of hydrotroilite, resulting in the formation of the hydrotroilite bed "suspended" to the bed of Old Black Sea sediments at the top of the Neoeuxinian sequence (Arkhangel'sky, 1934; Strakhov, 1963, 1976; and others). Later, issues related to the formation of sulfide horizon in the Neoeuxinian sequence of the Black Sea were discussed in (Jørgensen et al., 2004; Neretin et al., 2004; and others).

The formation of pyrite-rich interbeds in the Quaternary sediments (protosapropels) of the Eastern Mediterranean beneath the sapropel horizons was considered in many works (Passier et al., 1996, 1997, 1999; and others). Mechanism of H_2S diffusion from sapropel into protosapropels and its reaction with sedimentary iron (i.e., mechanism similar to that proposed by A.D. Arkhangel'sky) was applied to explain the conditions of pyrite formation. However, the role of gel-type hydrotroilite, which migrated from sapropel sediments, in the formation of pyrite interbed cannot also be ruled out in this case.

CONDITIONS OF THE FORMATION OF SULFIDE ACCUMULATIONS AT THE CONTACT BETWEEN LITHOLOGICALLY DIFFERENT ENVIRONMENTS

It is reasonable to consider the conditions of early diagenetic accumulations of sulfides at the boundary of lithologically different environments based on the study of sulfide horizon at the base of the Ordovician dyctionemic shales of the Baltic region.

Both the existence of this layer, but also some details of its structure are interesting. Therefore, we present below a corresponding description of this bed. We studied this horizon on the coastal cliffs near the town of Paldiska (Estonia) and in the core samples of numerous boreholes.

The organic-rich dyctionemic shales (4–5 m thick) are observed as dark brown sediments (Fig. 2) mainly represented by a well-sorted and finely elutriated clay material. Some sections contain very fine silty admixture as thin (usually lenticular) interbeds. The shales are marked by fine foliation, which is particularly well expressed in weathered varieties. Traces of bioturbation in shales are absent, but they are abundant in the underlying and overlying sediments. No remains of benthic fauna were found. It should be noted that despite abundance of OM in the sediments, authigenic minerals (in particular, sulfides) are very rare.

The dyctionemic shales discordantly overlie the coarse-grained sandstones identified as Obolus sandstones due to the presence of Obolus brachiopod

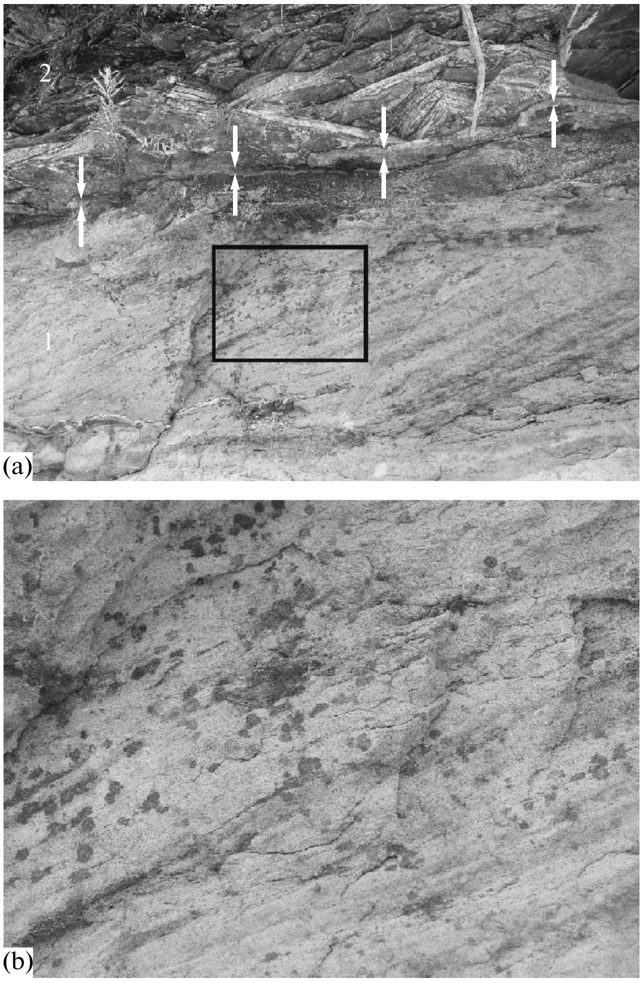

Fig. 3. Obolus sandstones and dyctionemic shales at the contact zone: (a) contact of (1) obolus sandstones and (2) dyctionemic shales (arrows show the sulfide bed); (b) sulfide concretions in cross-bedded sandstones at the contact zone with clay shales. Box shows the position of Fig. 3b in Fig. 3a.

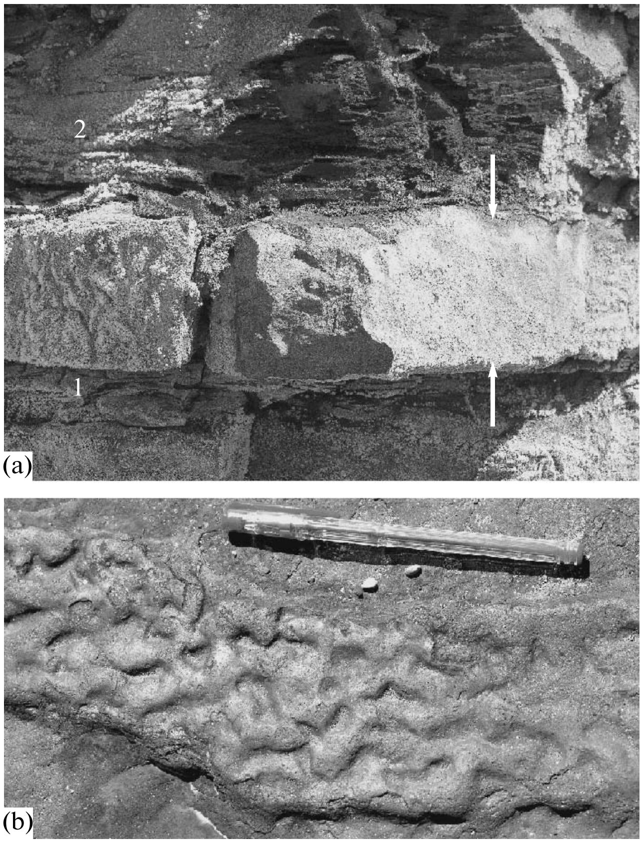

Fig. 4. Sulfide bed at the contact of sandstones and shales. (a) Sulfide bed (10–12 cm, shown by arrows) localized between (1) obolus sandstones and (2) dyctionemic shales; (b) layer at the sulfide bed roof (view from top) with traces of the diagenetic redistribution of sulfide (gel-type) matter (thickness of the layer with traces of redistribution is ~1.5 cm).

shells. Unidirectional cross bedding is observed at several levels of sandstones (Fig. 3).

A sandstone bed (up to 10–15 cm thick) cemented by sulfide minerals (mainly pyrite) is observed immediately beneath the contact with the dyctionemic shales (Figs. 3–5). As compared to the underlying loose sandstones, this bed is very dense and hard. The underlying sandstones contain numerous concretions (~1 cm across) of sulfide minerals, which are now oxidized to iron hydroxides. With increasing distance from the contact, the amount of concretions decreases and they disappear after 1 m (Fig. 4).

A lenticular bed (1–2 cm) of pure pyrite with a hummocky surface rests on the sulfide-cemented sandy bed (Fig. 4b).

In terms of all lithogeochemical parameters typical of the Obolus sandstones, the wide development of sulfides in them was impossible because of the lack of OM, whereas the dyctionemic shales provided favorable conditions. Thus, like sediments of other ages, this section demonstrates an apparently strange pattern: the clayey (finely elutriated) organic-rich sediments with HS^-, Fe^{2+}, and gel-type hydrotroilite lack pyrite concretions, which often occur in the adjacent sandy rocks virtually devoid of C_{org}.

Strakhov (1962) suggested that the sulfide bed was formed due to the migration of gel-type sulfide mass (hydrotroilite) from carbonaceous sediments because of gravitational. The sulfide cement was mainly developed at the contact of sandstones.

In general, Strakhov's mechanism of the migration of sulfide material is sufficiently persuasive. Iron disulfide (pyrite), crystalline monosulfides (mackinawite and greigite or melnikovite), and amorphous iron monosulfide (hydrotroilite) were found in the modern marine sediments. The latter mineral can migrate during diagenesis from one portion of the sediment to another.

However, some issues related to the diagenetic migration need to be discussed.

First, whether gravity factor was the single mechanism responsible for the migration of sulfide material or components therein and the subsequent precipitation of iron disulfide? Second, why hydrotroilite, which forms in carbonaceous sediments and migrates into sediments with oxidizing conditions, produced here pyrite mineralization?

Reality of the existence of gravitational migration of sulfide matter was repeatedly noted in sediments of different (terrigenous, carbonate, and siliceous) compositions. In our opinion, it was the main mechanism for sulfide migration. At the same time, sulfide migration can also be controlled by diffusion influx of HS^-, and Fe^{2+} from organic-rich sediments into adjacent beds, where they could form pyrite. It should also be noted that organic-rich clayey sediments were strongly compacted during diagenesis. Estimation of the compaction degree of sediments of this type shows that their initial thickness could be reduced by five and more times (Gavrilov, 1977, 1982). The compaction was accompanied by the squeezing of interstitial waters containing products of early diagenesis. Together with the squeezed out waters, HS^- and Fe^{2+} could migrate in the neighboring (both underlying and overlying) beds. Thus, the gravitational factor, diffusion, and elision processes could provide the migration of sulfide matter or its components from the parental sediments into the adjacent beds, where their formation was virtually impossible. However, the gravitational factor promoted downward migration, whereas two other factors fostered both upward and downward migration.

We should also note the electrogeochemical factor, which can affect the migration of matter during lithogenesis (Khairetdinov, 1982; Khairetdinov et al., 1997; and others). Electrogeochemical processes during lithogenesis are based on the interaction of two different-charge masses. For example, genetically different sediments can occur between positively charged masses (oxidized mass with high oxidizing potential) and relatively negatively charged (reduced sediments with low oxidizing potential). In such case, electrical potential difference can appear at the contact of sedimentary beds and significantly affect the migration of diagenetic components of sediments.

The main mechanism of sulfide migration (gravitational movement, diffusion, transportation with the squeezed out interstitial waters, or electrogeochemical factor) is unclear so far. It was presumably a combination of diverse mechanisms, though the degree of their participation in this process was different. We believe that the main role belonged to the gravitational transfer, whereas the role of other processes was variable.

Thus, it is evident that migration of matter formed during early diagenesis can be controlled by several mechanisms. But it is unclear why sulfide substance (hydrotroilite and other minerals), which formed in carbonaceous sediments and migrated in sediments with oxidizing conditions, was concentrated as pyrite mineralization?

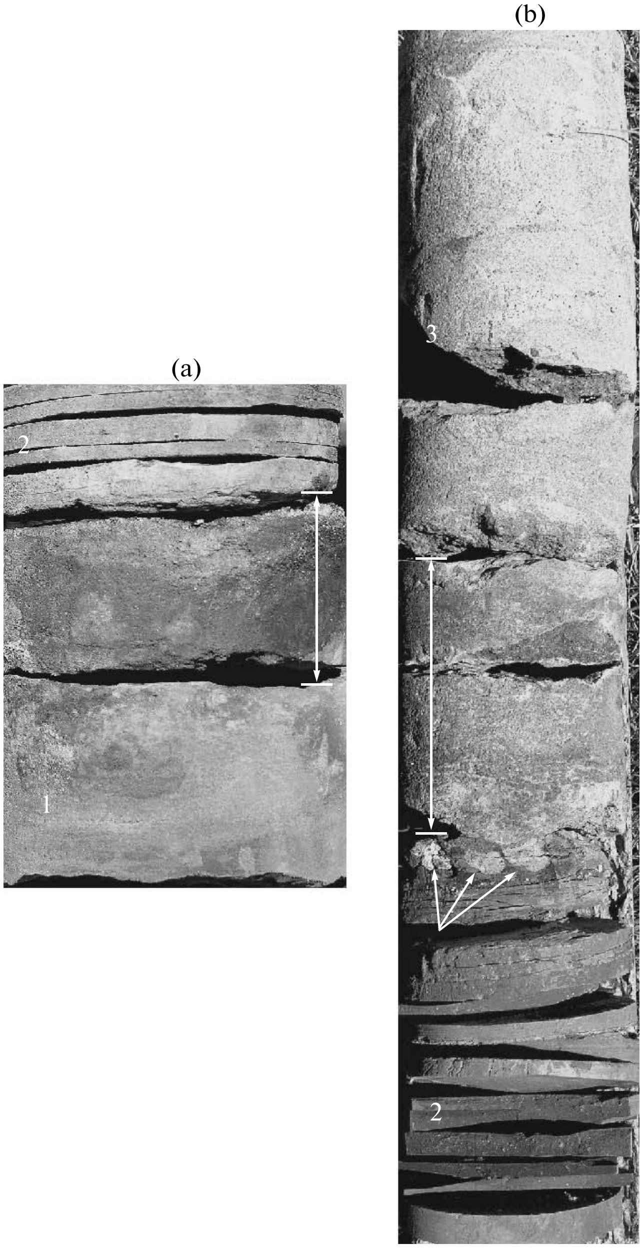

Fig. 5. Sulfide interbeds at the lower and upper contacts of dyctionemic shales with the underlying and overlying sandstones in the borehole core. (a) Sulfide bed at the contact of (1) obolus sandstones and (2) dyctionemic shales (core diameter ~20 cm); (b) layer with sulfide mineralization at the base of (3) glauconite sandstones (core diameter ~10 cm). Triangle shows traces of bioturbation at the upper bed of shales.

Considering issues of the formation of diagenetic sulfides in marine sediments, Rozanov and Morozov (Morozov, 1984, 1994a, 1994b; Rozanov and Morozov, 1983; and others) noted that since pyrite sulfur is more oxidized (oxidation degree I) than sulfide sulfur (oxidation degree II), the formation of pyrite should involve the participation of polysulfide sulfur (S_n^{2-}) or an oxidizer providing the following reaction: $2S^{2-} - 2\bar{e} \longrightarrow S_2^{2-}$. Ferric iron, oxygen, and elementary sulfur could serve as such oxidizers in natural sediments. W should emphasize an important role of oxygen for the transformation of mobile gel-type monosulfide into disulfide (pyrite). This fact elucidates the hardly explainable appearance of sulfide mineralization in some ancient sediments.

We believe that the scenario of sulfide mineralization in the Ordovician sediments of the Baltic area is as follows.

The accumulation of obolus (mainly quartzose) sandstones under oxidizing conditions after some interval was followed by a rapid transgression, accumulation of organic-rich sediments, and development of a strongly reduced environment. As a result, significant gradients in Eh, pH, and concentrations of diagenetic components in interstitial waters appeared at the contact of geochemically different sediments.

Gravitational and other factors mentioned above (diffusion, elision, and electrochemical) facilitated the migration of mobile components formed during diagenesis and their accumulation at the contact of heterogeneous environments (organic-rich clayey and sandy layers). Most part of sulfides was precipitated at the boundary between sandy and clayey sediments, resulting in the formation of pyrite cement in the contact zone of sandstones.

Owing to compaction and diffusion, the interstitial waters of clay sediments containing dissolved OM penetrated the neighboring sandy layer and fostered replacement of the oxidized environment by a weakly reduced one. Owing to this process, a part of sulfide material bypassed the near-contact layer at the initial stage of migration and penetrated the deeper beds of sandy sequence down to a depth of no more than approximately 1 m, resulting in the formation of individual (up to 1–2 cm) sulfide concretions. Further cementation of boundary sandstone bed gradually led to the loss of permeability and the formation of a very dense monolithic bed. New portions of sulfide gel extracted from the carbonaceous sediments could not overcome this boundary. Spreading of the gel over the surface of the pyrite-cemented sandstone produced a sulfide bed (1–2 cm) without the sandy admixture and with the characteristic hummocky surface (Fig. 4b).

Migration of sulfides from the carbonaceous clayey sediments is also supported by the following facts. As was mentioned above, clayey sediments rarely contain sulfide concretions. However, if very thin (a few millimeters thick) silty lenses and beds are present, they include sulfide material as chains of lenslike pyrite concretions. It should be emphasized that the sulfide cementation zone in the underlying sandstones in these cases is significantly reduced or virtually absent; i.e., the sulfide material did not leave the clayey sediments and was localized in them. Thus, the sulfide-generating sequence became the sulfide-bearing one.

One more very interesting feature of sulfide distribution in these sequences is the appearance of a sulfide mineralization zone in some borehole sections in the basal layer of glauconite sandstones that overlay the dyctionemic shales (Figs. 2, 5). As compared to sulfide horizon at the base of dyctionemic shales, the zone is thinner (only a few centimeters). The pyrite cement is not continuous, and the rock is relatively loose. If sandstones were precipitated immediately after the carbonaceous sediments, the formation of this sulfide bed could be easily explained, since interaction of geochemically different beds could be very intense (except for gravitational factor). However, sedimentation of dyctionemic shales and glauconite sandstones was separated by a significant hiatus. The upper contact of sulfide mineralization adjoins and sometimes even penetrates the shales, suggesting that sulfides were derived from the carbonaceous sediments. Obviously, the gravitational factor, which played a leading role in the sulfide bed formation beneath the dyctionemic shales, did not operate in this case. Thus, the formation of the upper zone of sulfide mineralization should be attributed to other factors (elision, diffusion processes, and electrogeochemical factor) that could affect the migration of matter.

It should also be admitted that migration capacity of sulfide substance (at least as hydrotroilite) could be preserved for a long time in the lithologically monotonous organic-rich clayey sediments. This scenario needs the monotonous composition of clayey sediments and the absence of sandstone interbeds, which can serve as pathways for the removal of interstitial water from inner parts of the carbonaceous sequence or, in contrast, as conduits for the penetration of geochemically different solutions. Physicochemical conditions of diagenesis were likely conserved in a closed system of dyctionemic shales for a long time because of a significantly stronger compaction of marginal parts of the clay horizon as compared to its central parts, which is a phenomenon common of alternating clayey–sandy sequences (Magara, 1974, 1978; and others). Consequently, the central parts of clay horizon were less permeable for the penetration of oxygen and other materials from the adjacent beds.

During the hiatus after the accumulation of dyctionemic shales, their roof (surface of horizon) was presumably exposed to an oxic environment prior to their burial under sediments of the following stage, resulting in oxidation of the upper beds of the shales. However, the upper beds of the dyctionemic sequence were eroded during the subsequent transgression, and glauconite sandstones were deposited on the relatively fresh (least oxidized) sediments, which contained reactive OM and mobile sulfide matter. Therefore, the bottom part of sediments overlying the carbonaceous shales represented a favorable medium for sulfide mineralization.

Plausibility of the proposed formation scheme of the upper sulfide bed is confirmed by the study of Cretaceous black shales from the Demerara Rise in the Atlantic Ocean (Arndt et al., 2006). Data reported in this work showed that the geochemical activity of organic-rich sediments is preserved for a fairly long time (tens of million years) after their formation.

Thus, we can note the following specifics of sulfide formation in the Ordovician sediments of the Baltic area. The accumulation of organic-rich clayey sediments was accompanied by the appearance of highly negative Eh values in sediments. At the same time, diagenetic processes in the almost OM-free underlying and overlying sandy sediments proceeded under positive Eh conditions. Significant geochemical differences in the diagenetic settings provided prerequisites for the formation of sharp geochemical boundaries at the contact zones of clayey and sandy sediments. Intense formation of sulfide substance (gel-type hydrotroilite, sulfide ion, and so on) in the clayey sediments was accompanied by its migration in the adjacent sandy beds and the formation of pyrite-rich beds at the contact of geochemically heterogeneous sediments. Sulfide migration could be caused by a variable contribution of gravitational (for lower sulfide bed), diffusion, elision, and electrochemical factors. Sulfide localization at the contact of environments with sharply different Eh values was strongly governed by the following fact: pyrite (disulfide) sulfur was a more oxidized form than hydrotroilite (monosulfide) sulfur; i.e., the formation of pyrite (already immobile form) requires an oxidizer (oxygen), which was abundant in sandy sediments.

MANIFESTATION OF THE DIAGENETIC MIGRATION OF SULFIDES IN SEDIMENTS OF DIFFERENT FACIES ENVIRONMENTS

Let us present some examples of the localization of sulfide deposits in the lithologically different sediments, where sulfides were formed due to the diagenetic migration of sulfide material.

Sulfide horizons in the Lower Paleozoic sediments of China. Sometimes, sulfide migration is more extensive than in the Baltic dyctionemic shales. For example, a horizon of Lower Cambrian black shales is developed over a huge territory of South China and Korea (Coveney et al., 1992; Fan et al., 1973, 1984, 1992; Jiang et al., 2007; Sozinov, 2008; and others). The base of this horizon host a sulfide bed several decimeters thick and many hundred kilometers long with extremely high contents of Mo, Ni, Se, As, Ag, Au, Hg, PGE, and so on. The sulfide bed is often underlain by a lenticular bed with phosphorite concretions, the geological setting of which points to their redeposition. In other areas, the sulfide bed rests on the Precambrian crystalline schists, which are significantly weathered in their upper part. In general, geochemical setting during the sulfide bed formation was similar to that in the Baltic carbonaceous sediments. Osmium isotope data indicate that sulfides were enriched in Re and PGE during the diagenesis of sediments in the Early Precambrian (Horan et al., 1994).

Some researchers attribute the formation of this sulfide bed to hydrothermal activity (Sozinov, 2008; and others). However, its diagenetic origin seems to be more preferable. Examples of the localization of ore sulfide bed beneath (rarely above) the carbonaceous sediments can be supplemented by the carbonaceous sequence and ore occurrences in Canada (Hulbert et al., 1992; and others), Africa, and other regions.

Bentonitic interbeds in the Eocene sequences of southern Russia. Numerous bentonitic interbeds of the centimeter and decimeter scale in thickness formed after the products of ash eruptions are observed within some intervals in the Paleogene (mainly Eocene) sediments of Northern Caucasus, in particular, in its eastern part. Bentonites in the sediments of well-aerated paleobasins are represented by light gray (with yellowish tint) homogenous clayey rock of the smectite composition without traces of the diagenetic authigenic mineralization. Bentonitic interbeds in sediments of the anoxic Oligocene–Early Miocene Maikop basin and especially Bartonian Kuma basin have a different appearance. Bentonitic interbeds of the Kuma Formation acquire a dark gray color and are saturated with pyrite concretions, which are virtually absent in the host clayey–carbonate sediments. We suggest that association of pyrite concretions with bentonites of this sequence is related to the following fact: ash material contained a significant amount of oxygen (in absorbed and oxide forms) after atmospheric transportation; therefore, when this material precipitated on the anoxic basin floor, it formed an oxic interbed, whereas the host sediments were characterized by sharply reduced environments. Consequently, sulfide components in the organic-rich background Kuma sediments could migrate, reach ash interbeds, and precipitate there as pyrite concretions in the presence of some amount of oxygen. Sometimes, their amount was sufficiently high to form ore horizon. Similar phenomenon was observed in the bentonitic interbeds from the Lower Oligocene sediments of the Maikop anoxic basin (sections of the Belaya River, Adygeya, and other areas).

Sulfide horizons in sediments of the Maikop Group. Similar mechanism of sulfide migration and localization could also produce ore-bearing horizons of a different type. It is known that sediments of the Maikop (Oligocene–Early Miocene) anoxic basin contain horizons of bone breccias associated with abundant sulfide mineralization (Stolyarov and Ivleva, 1989, 1991, 2004; Stolyarov and Kochenov, 1995; Kochenov and Stolyarov, 1996; and others). The formation of these horizons could be interpreted as follows. The bone breccia horizons were formed by the washout of

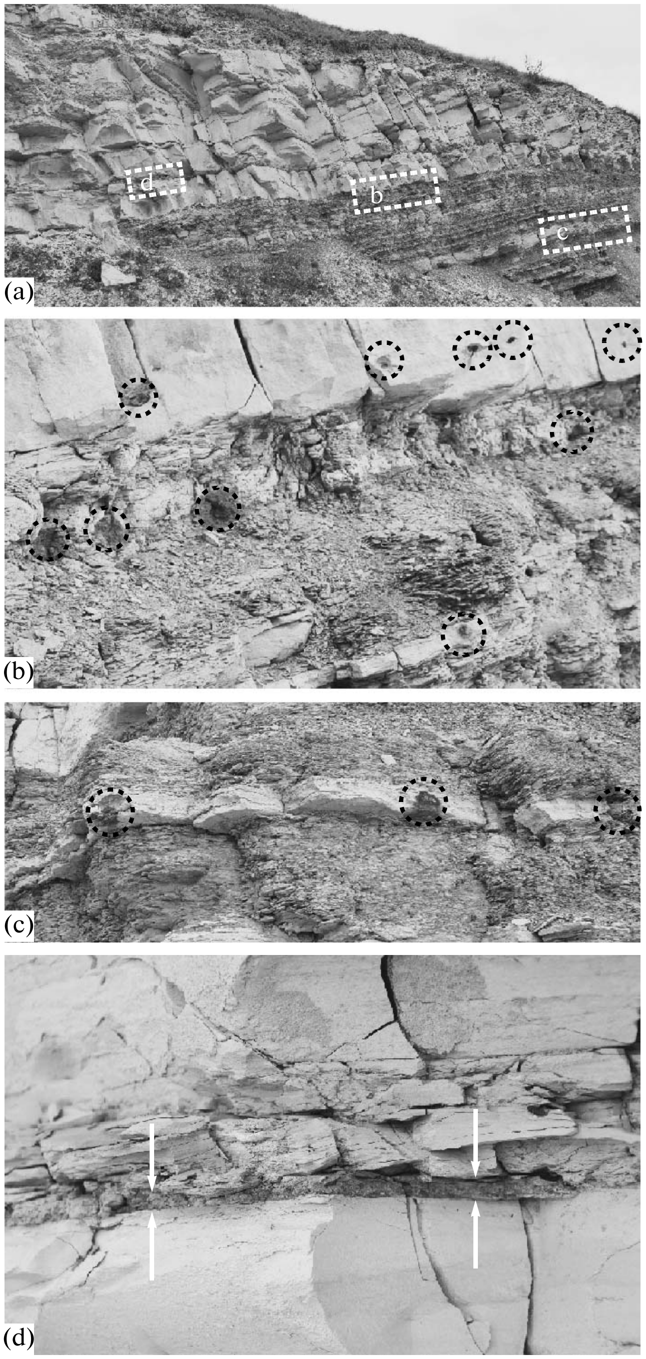

Fig. 6. Sulfide concretions in limestones intercalated with organic-rich clayey sediments. (a) General view of the upper part of the Albian and Cenomanian sediments, Levashi area, Dagestan. Boxes with letters show the exposures demonstrated in photos 6b–6d; (b, c) sulfide concretions in limestone intercalations (concretions are in circles); (d) thin interbed (0.5 cm) enriched in iron hydroxides (products of sulfide oxidation) at the contact of clayey marls (~ 15 cm) with limestone interlayer.

older sediments, which were distinctly reduced in the Maikop basin. It is difficult to reconstruct at present processes responsible for these washouts: temporal near-bottom currents, extremely strong storms that displaced sediments accumulated below the wave erosion basis, run-off of powerful floods from the land, turbidite flows, earthquakes, or other phenomena. However, they were formed in all cases due to the sharp intensification of hydrodynamic activity in a certain part of the basin. In all these cases, oxic waters were mixed with anoxic waters of the basin, resulting in an appreciably lesser oxygen deficit. Therefore, fragments of bones and their terrigenous cement were accumulated in more oxidizing (or weakly reduced) conditions and characterized by the presence of oxygen in free, absorbed, or hydroxide forms. In addition, while bone breccia lied on the surface, all elements with an affinity for phosphorus (U, REE, Sc, and so on) were absorbed by bone phosphate remains from the near-bottom waters. When hydrodynamics in this part of the basin became less intense later, terrigenous (mainly clayey) sediments were accumulated under prominent reduced conditions. As a result, reduced muds contained horizons with a much higher Eh value as compared to the host sediments. Correspondingly, the processes of sulfide formation in the reduced muds were accompanied by sulfide migration toward the horizons of bone breccias, retained there, and transformed into an immobile pyrite form (as in the cases described above). Mineralization of the breccias began during the erosion of sediments and was significantly enforced during diagenesis, i.e., the process occurred in several stages.

It should be noted that signs of the diagenetic migration of sulfides are widespread in nature and often noted during geological studies. While studying the Cretaceous sediments of Dagestan, we often observed the confinement of pyrite concretions to white limestone interbeds, which are localized among the organic-rich dark gray (sometimes almost black) marls (Fig. 6). It is fairly evident that sulfide matter was formed in the carbonaceous clayey–carbonate sediments under reduced conditions. However, this matter was accumulated as pyrite concretions in almost OM-free limestones.

In addition to geochemical characteristics of sediments, the amount of sulfides mobilized from the carbonaceous sediments also depends on the thickness of carbonaceous sediments. Sulfides mobilized from the sufficiently thick (at least several meters) horizons of carbonaceous sediments can yield an almost uninterrupted sulfide bed. Thin layer of organic-rich sediments (less than 1 m) produces a lesser amount of sulfides and only a thin sulfide-rich layer. While studying the Cenomanian carbonate sediments of Dagestan, we observed a thin (no more than 15 cm) dark clayey marl interbed with a sharp lower boundary and vague gradual upper boundary. The sulfide-rich layer (about 0.5 cm thick) is located at the base of this clayey interbed (Fig. 6d). The formation of this bed can be regarded as a miniature model for more extensive processes described above.

IRIDIUM ANOMALIES AT THE BOUNDARIES OF GEOCHEMICALLY DIFFERENT SEDIMENTS

Numerous data mentioned above indicate that intense sulfide migration could occur at the contact of highly carbonaceous sediments with organic-free rocks, i.e., at the contact of sediments with very different geochemical (and electrogeochemcial) parameters. The question arises as to the gradient range required for this process. The lithogeochemical analysis of sedimentary sequences containing geochemical anomalies showed that they could be formed at the contact of reduced and oxidized sediments, and intense organic enrichment is not required. Let us consider the best known examples of such anomalies.

One of the results of diagenetic migration and accumulation of sulfides at the contact of geochemically and lithologically diverse sediments could be geochemical iridium (Ir) anomaly. Its formation is often attributed to impact events. According to the proponents of this hypothesis, such events caused sharp biotic changes on the Earth. Like the examples of sulfide mineralization considered above, iridium anomalies are typically restricted to the contact between reduced clayey (sometimes marly) and carbonate sediments accumulated in oxidized sediments (in some cases, oxidized during a hiatus), i.e., to the boundary of sediments formed in different redox conditions. Sometimes, they occur at the contact of sediments of different compositions, for instance, siliceous and carbonate rocks, coal seams, sandstones, and so on. In most cases, iridium anomalies are restricted to thin interbeds containing sulfides or products of their oxidation, e.g., iron hydroxides, which imparts a reddish color to these beds.

Iridium anomalies established in the sediments of different ages ranging from Phanerozoic to Precambrian have been described in numerous works (Alekseev et al., 1988; Alvarez et al., 1980, 1982; Christensen et al., 1973; Dupuis et al., 2001; Hurley and Van der Voo, 1990; Love et al., 1989; Olsen et al., 2002; Orth et al., 1986, 1988; Playford et al., 1984; Preisinger et al., 1986; Rochia et al., 1990; Schmitz and Asaro, 1996; Schmitz et al., 1997; Wang et al., 1991, 1993a, 1993b; Zakharov et al., 1993; and many others).

Iridium anomalies differ in terms of the degree of accumulation of Ir and other elements, assemblage of elements typical of a certain anomaly, configuration of variation curves of the elements, spatial position in host layers, number of peaks of anomalous concentrations of elements, and other parameters.

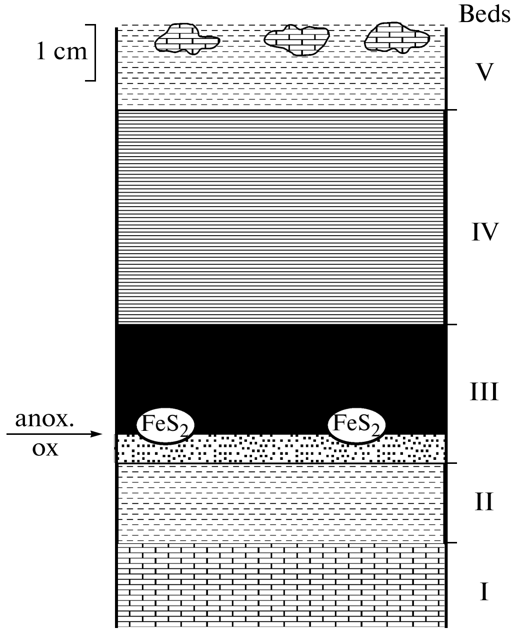

Fig. 7. Schematic structure of the Cretaceous–Paleogene boundary sediments (fish clays) in the Stevns Klint section, Denmark (Schmitz, 1985). Numbers of beds according to (Christensen et al., 1973). (I) Bryozoan chalk; (II) transitional chalk-clay; (III) black marls with fish scales (red clayey bed with oxidized pyrite spheroids at the base); (IV) dark and light gray bedded marls with upward increasing $CaCO_3$; (V) transitional marl chalk deposits. (anox/ox) boundary between sediments with reduced and oxidizing settings.

The most characteristic feature of iridium anomaly is a sharp increase in the content of Ir and associated elements as compared to those in the underlying rocks and rapid (but relatively gentle) decrease in the contents of these elements in the overlying sediments. This can be exemplified by one of the most known K/T boundary sequences of North Europe with iridium anomaly, i.e., the Stevns Klint section in Denmark (Fig. 7). The geochemical features of sediments in this section studied by many researchers (Alvarez et al., 1980, 1982; Christensen et al., 1973; and others) are considered most comprehensively in (Schmitz, 1985), which reports the results of analysis for a wide spectrum of elements. It was shown that the brick-red bed at the base of the organic-rich "fish clay" bed containing oxidized pyrite microspherules demonstrates a sharp increase in the content of many elements. In particular, the proportions of elements in the underlying rocks and fish clay are as follows Fe, in %; other elements, in ppm: Fe 0.37–10.5, Co 10–180, Ni 62–1500, Cu 9.7–110, Zn 73–1500; the Ir content in the fish clay bed is high and reaches 28 ppb in the red bed (Schmitz, 1985). Schmitz assumed that correlation of the highest contents of elements with the basal bed of fish clay indicates that metals were supplied from the underlying rather than overlying (carbonaceous) sediments, as suggested in our model. In any case, the geochemical anomaly is of diagenetic rather than impact origin, as suggested in (Alvarez et al., 1980, 1982; and others). In this context, we should note the following point. According to the impact hypothesis, Ir is transported with some material mobilized during the impact event and the material must differ in com-

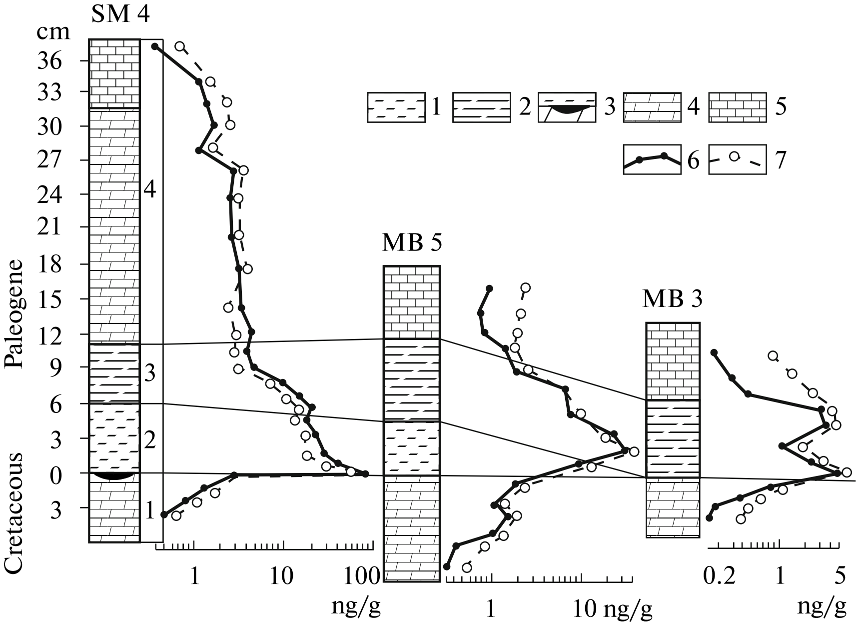

Fig. 8. Distribution of Ir concentrations in the K/T boundary sediments of Turkmenistan. (CM 4) Section on the right bank of the Sumbar River near the Kara-Kala settlement; (MB 3, MB 5) sections in an anonymous canyon east of the Kuidzhik Spring, Lesser Balkhan. (1–5) Sediments: (1) brown clays, (2) green clays, (3) pocket at the roof of Maastrichtian marls filled with ferruginous material with a large amount of gypsum crystals, (4) marls, (5) limestones; (6) Ir content; (7) Ir/Al ratio.

position from the adjacent beds formed during background sedimentation. However, detailed studies of mineral composition of clays in the Stevns Klint section revealed no difference between the clay bed containing Ir anomaly and the overlying clays (Drits et al., 2004); i.e., the lower clay horizon exhibits no signs of alien (extraterrestrial) origin.

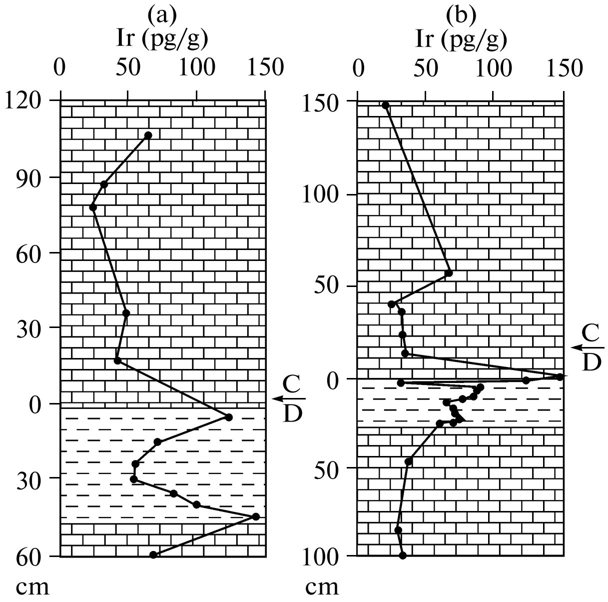

Fig. 9. Iridium anomaly in the Devonian/Carboniferous boundary sediments (Wang et al., 1993a). (a) Carnian Alps, Austria, (b) Montagne Noire, France.

According to (Alekseev et al., 1988), significant Ir enrichment (66 ppb) was found in the geochemical anomaly in the K/T sediments of the Sumbar River valley in southern Turkmenistan (Fig. 8). In these sediments, lenses of iron hydroxides, i.e., products of pyrite oxidation, are observed at the bottom of Paleogene section at the contact between Maastrichtian limestones and a brown clay bed. In addition to Ir, these lenses are enriched in Fe, S, Ni, Co, Cu, Zn, Au, and some other elements. In general, this geochemical anomaly (as many other anomalies) is similar to that of the Stevns Klint section in terms of element spectrum.

In nature, some iridium anomalies confined to considerable geological boundaries contain two (rather than one) Ir peaks. Among them is the Devonian–Carboniferous boundary at the Carnian Alps, Austria (Fig. 9) (Wang et al., 1993a). In this area, an elevated Ir content is observed in the black shale bed (~45 cm), with the highest contents found both at the bottom and roof of the bed. Such an Ir distribution is difficult to explain in terms of the impact event, whereas the inferred mechanism of diagenetic redistribution of sulfides and related Ir explains the formation of anomalies of such configuration (similar to that in the dyctionemic shales of the Baltic area). It is noteworthy that the bed of the same stratigraphic level (~20–25 cm) in the Montagne Noire, South France, contained two Ir peaks, but the upper peak was stronger than the lower one (Wang et al., 1993a) (Fig. 9).

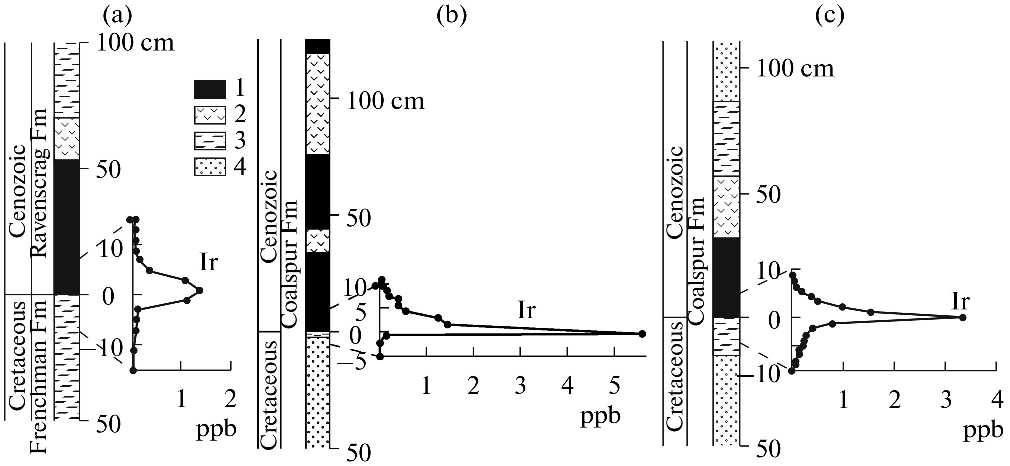

Fig. 10. Iridium anomaly in the Cretaceous/Paleogene boundary sediments of western Canada (Lerbekmo et al., 1987). Sections: (a) Frenchman Valley; (b) Scollard Valley; (c) Red Deer Valley. (1) Coal; (2) bentonite; (3) clayey sediments; (4) sandstones.

Two Ir peaks were also noted in some Cretaceous/Paleogene boundary sections (Fig. 8) of the Lesser Balkhan in Turkmenistan (Alekseev et al., 1988) and in other sections.

Anomalies of the considered type are observed not only in the organic-rich clayey rocks, but also in limestones. In particular, geochemical anomalies in the K/T boundary sections in New Zealand (Brooks et al., 1984, 1986; Hollis et al., 2003; and others) were found in the essentially siliceous and carbonate–siliceous sediments, although they are in contact with beds differently enriched in OM.

Fairly intense iridium anomalies (Fig. 10) occur at the base of coal seams (Lerbekmo et al., 1987). In these cases, the mechanism of their formation, in general, does not differ from the mode considered above, except for an increasing role of metal migration with the squeezed interstitial waters (probably as metallorganic complexes) due to compaction, which can be sufficiently significant (ten and more times higher) in coal seams.

Of special interest are anomalies in the coal seam. One of the most known manifestations of iridium anomaly is the section of boundary K/T sediments of the Moody Creek Mine in New Zealand. In this area, the K/T boundary lies within a coal seam (15–20 cm thick) localized among siltstones (Fig. 11) (Vajda et al., 2001). Such confinement of iridium anomaly to a bed appears to be inconsistent with the proposed mechanism of its formation. However, despite the apparently homogenous composition of coal seam, the spore-and-pollen analysis revealed significant differences between its lowermost and uppermost parts (Vajda et al., 2001). Such changes could not be instantaneous, and accumulation of the lowermost and uppermost portions was presumably separated by some hiatus. During this hiatus, the lowermost part of the coal seam (more exactly, accumulated mass of plant remains) was subjected to variable oxidation. The younger plant mass should be formed in much more reduced conditions than the underlying portion. Thus, the lithologically common bed comprised two units formed under different redox conditions. In this case, as in the examples considered above, conditions favorable for the development of boundary geochemical anomaly arose during sedimentation.

One can suggest that the iridium anomalies located within lithologically homogenous (not coal) beds in other cases are also confined to the boundary between materials of different oxidation states.

Commonly, contents of Ir and associated elements gradually increase, reach maximum, and then gradually decrease (Figs. 8, 10a, 10c). It is hardly possible to interpret this pattern in terms of impact hypothesis, whereas diagenetic mechanism may easily explain the nonstandard configuration of the anomaly. compaction of the organic-rich clayey sediments leads to the squeezing of interstitial waters with the dissolved organic components into the adjacent beds, providing reduced conditions in the boundary zones of these layers. Owing to this process, elements are not retained (partly or completely) at sharp lithological boundaries, but penetrated into neighboring beds and precipitated or scattered there. If the dissolved OM migrated intensely, the initially strong redox boundary could cease to serve as a geochemical barrier, and elements would not be accumulated there.

Such interaction of beds can be exemplified by the organic-rich black clayey bed at the Paleocene/Eocene boundary sediments in the section of the Chirkei hydroelectric power station in Dagestan (Fig. 12). This bed (present-day thickness 0.25 m) occurs among reddish brown marls and adjoins gray marls (a few tens of centimeters thick) from above and below. Transition of the gray marls to the reddish brown variety is gradual. The gray border of black bed

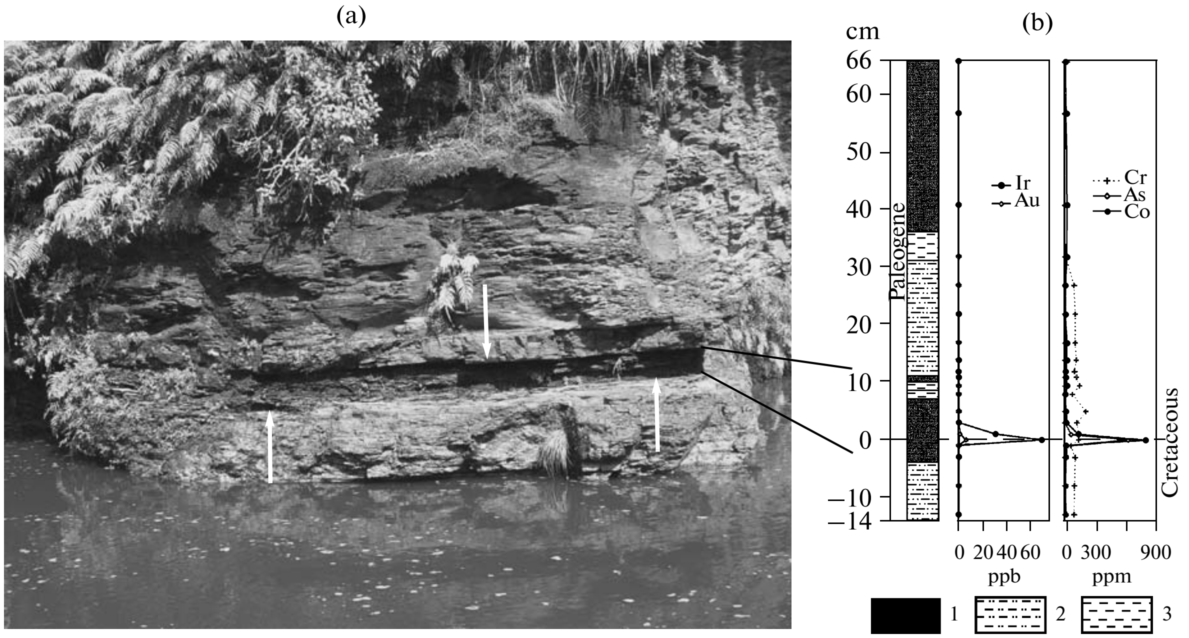

Fig. 11. K/T boundary sediments in the Moody Creek Mine section, New Zealand. (a) Photo of K/T sediments (arrows show a coal seam); (b) lithological column and distribution of elements according to (Vajda et al., 2001). (1) Coal; (2) sandy siltstones; (3) clayey rocks.

is related to migration of the dissolved OM with interstitial waters, which caused the transition of iron oxide species contained in marls to the reduced species. Consequently, the development of reduced environments in the sediments adjacent to the sapropel bed smoothed out the initial sharp geochemical differences, and the boundary ceased to serve as a barrier for the migrating sulfides. Consequently, boundary between the sapropelite and underlying rocks lacked sulfides, which are rather abundant in other Paleocene/Eocene boundary sections of the Northern Caucasus (Gavrilov et al., 1997).

Since we attribute the formation of high-Ir beds to sulfide migration, the mode of occurrence of Ir (and other PGE) in these beds is an interesting point. Note that iridium typically does not form its own sulfide minerals, and mode of its incorporation in sulfides is unknown. It is difficult to answer this question using natural samples from real sections, because pyrite microaggregates are typically oxidized and observed now as clots of iron hydroxides, which imparted the reddish rusty brown color to these beds. Important information for estimating the modes of sulfide and iridium coexistence can be obtained from experimental data. Sulfides of Fe, Cu, Pb, and Zn synthesized in the presence of Ir did not contain this element (Zhmodik et al., 2004). However, Ir is concentrated at the surface of individual crystals or polycrystalline aggregates. Inner parts of the crystals and aggregates lacked Ir. Therefore, the authors of experiments concluded that Ir was accumulated at the surface of growing crystals and polycrystalline aggregates. Beds with iridium anomalies showed the same distribution pattern: Ir was concentrated at the surface of pyrite microconcretions (microframboids) formed in sediments at the diagenetic stage.

Such a pattern of Ir localization is likely responsible for the low Ir content in relatively large sulfide concretions and its much higher content in beds containing numerous small spheroids (and significant total area of the surface). In addition, intense sulfide formation and growth of large pyrite concretions can be accompanied by the effect of dilution. Since background Fe contents in clayey sediments are several orders of magnitude higher than the Ir content, the formation of iron sulfide-rich bed could lead to relative decrease in the Ir content, although it was mobilized from the overlying sediments and accumulated in the lower boundary layer.

This situation can be exemplified by a horizon of the Paleocene/Eocene boundary sediments in the Paleogene section along the Kheu River, Kabardino-Balkaria, Northern Caucasus. This horizon is represented by OM-rich (C_{org} up to 10%) clayey sediments, which discordantly overlie the greenish gray marly clays. Numerous pyrite concretions (up to 5–7 cm across) are confined to this boundary. Analysis of sulfide material of these concretions did not reveal elevated contents of PGEs at the base of the black clay horizon, although all prerequisites for their accumulation at the boundary of geochemically different sediments were present. Thus, high intensity of the early diagenetic processes accompanied by large-scale sulfide formation and redistribution of sulfides did not promote the localization of Ir and other elements in the boundary layer. Moderately intense processes of diagenesis and sulfide formation in sediments with the C_{org} content of no more than 2 % are likely most favorable for the iridium anomaly formation.

Study of different sections showed that the sediments (typically clayey or marly) with iridium anomalies at the base and/or roof are enriched in Ir, relative to the underlying and overlying rocks often represented by limestones. What is the reason for such difference in the Ir content between these sediments? Study of the Ir sorption and desorption by coastal marine sediments showed that the components of terrigenous sediments (detrital silicate minerals, sulfides, and OM) are good accumulators of Ir, whereas carbonate sediments have very low sorption capacity with respect to Ir (Dai et al., 2000). Close association of Ir and clay minerals was noted at the well-known Cretaceous/Paleogene boundary in the Gubbio area of Italy (Rocchia et al., 1990) and other areas.

At the same time, clay beds containing relatively elevated C_{org} can accumulate PGEs due to their interaction with some OM components. Experimental study of the sorption of these elements on humic acids (extracted from both peat and marine sediments) revealed a high sorption capacity of both groups of humic acids with respect to ions of many PGEs (Varshal et al., 1999, 2000; and others).

Sedimentation environments favorable for the formation of geochemical anomalies. Comparison of geochemical (iridium) anomalies of different age shows that they are formed during the accumulation of a certain sequence of lithologically and geochemically different sediments, which were formed under different redox conditions.

We believe that the formation of such layer sequence is caused by rapid and relatively short-term transgressions after regression events (Gavrilov, 1994; Gavrilov and Shcherbinina, 2004; Gavrilov et al., 1997, 2002, 2003). Essence of the proposed mechanism is as follows. At the regression stage, areas liberated from sea were marked by the rapid formation of soils and lacustrine-swampy landscapes that accumulated solid and dissolved OM, as well as compounds of biophile (P, N, Fe, and so on) and other elements. When regression gave way to transgression, the invading sea interacted with these landscapes and extracted biophile elements, resulting in the outburst of bioproductivity of mainly lower biotic forms (bacterioplankton, organic-walled dinoflagellates, and so on) and the accumulation of muds variably enriched in OM. The coastal landscapes also delivered solid, colloidal, and dissolved forms of plant OM and as metallorganic compounds, which also took part in the formation of carbonaceous sediments and promoted the concentration of PGE and other elements.

During transgression, the sea destroyed and obliterated traces of terrestrial landscapes. However, accumulations of terrestrial OM were preserved, buried, and later transformed into coal seams under some favorable conditions (Collinson et al., 2003; Lerbekmo et al., 1987; Vajda et al., 2001; and others).

Fig. 12. Organic-rich sapropelite bed (1) at the Paleocene–Eocene boundary (event PETM, section exposed at the Chirkei hydroelectric power station, Dagestan) localized among brick-red marls (3); the underlying and overlying sediments (2) changed their color into bluish gray during diagenesis owing to the influx of organic-rich interstitial waters as the result of compaction of sapropelite sediments and reduction of iron hydroxides.

It should be noted that lowstand episodes in relatively small epicontinental seas during regressions intensified hydrodynamic activity, resulting in the partial erosion of older sediments and intense oxidation of their uppermost layers. Rapid transgression after regression was accompanied by the accumulation of organic-rich sediments. Consequently, sediments strongly oxidized during regression or initially lacking significant amounts of OM were overlain by intensely reduced sediments. The appearance of such lithological contacts created favorable conditions for the formation of aforementioned geochemical anomalies at the boundary between them. Since sea level fluctuations were eustatic rather than regional, compositionally similar rock sequences were accumulated in different parts of the World Ocean. For instance, instable sedimentation conditions near the Cretaceous/Paleogene boundary were mainly governed by eustatic fluctuations in sea level (Keller et al., 1993, 2009; and others).

In rare cases, when sediments with iridium anomaly lack visible traces of sulfides, its formation could be related to the diffusion of metallorganic compounds into adjacent beds or their transport with the squeezed interstitial waters. During this process, organic component of these compounds could be oxidized and decomposed, resulting in the precipitation of PGEs (including Ir) at the boundary between the reduced clayey (or marly) sediments with the more oxidized sediments (typically limestones). This mechanism was likely responsible for the formation of iridium anomaly in the sulfide-free Zumaya section, Spain (Schmitz et al., 1997). However, absence of sulfides in rocks with the iridium anomaly is a rare situation. In contrast, confinement of sulfides or products of their oxidation to the bed with elevated Ir concentrations is common.

It should be noted that evidence for the absence of link between iridium anomalies and certain impact events has been reported by many authors. For instance, study of the Maastrichtian/Danian transitional beds in Texas revealed that impact event, which produced the Chicxulub Crater in Central America, took place 300 ka before the Cretaceous/Paleogene boundary event (Keller et al., 2007; and others).

The formation of iridium and other similar anomalies is a natural process typical of certain sedimentation–geochemical environments. We suggest that such geochemical anomalies should be widespread in nature. Further investigations of contact zones between sediments with sharply different geochemical parameters should confirm this assumption.

CONCLUSIONS

(1) Diagenetic migration of sulfide matter in sediments is widespread in nature. Manifestations of sulfide migration are common in sedimentary sequences that comprise alternation of sediments formed during diagenetic stages under sharply different redox conditions due to significant differences in the OM content.

(2) Migration of sulfides could be provided by the gravitational influx of colloidal substance (hydrotroilite), diffusion, and transfer of matter with the squeezed interstitial waters. Migration of charged particles in sediments could also be affected by electrical potential difference at the boundary of lithologically and geochemically different sediments. Diverse elements could migrate in various forms with sulfides.

(3) The scale of sulfide migration differed under various sedimentation environments and ranged from the formation of sulfide beds extending over tens and hundreds of kilometers to the appearance of a weak sulfide mineralization at the bed contacts. However, the mineralization promoted the accumulation of PGE and other elements (iridium anomaly and others).

(4) Sulfides accumulated during diagenesis can be interesting not only for paleoecological and palegeographical reconstructions, but also for ore geology. It seems reasonable to revise the existing formation models for some types of stratiform ore deposits.

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