ISSN 1069-3513, Izvestiya, Physics of the Solid Earth, 2008, Vol. 44, No. 3, pp. 232–238. © Pleiades Publishing, Ltd., 2008.
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Enrichment of Sediments in Iron Hydroxides at the Mesozoic–Cenozoic Boundary: A Synthesis of Petromagnetic Data

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Received September 26, 2006

Abstract—Results of petromagnetic studies of epicontinental sediments at the Mesozoic–Cenozoic (K/T) boundary are generalized. Their analysis shows that an abrupt rise in the concentration of iron hydroxides is confined to this boundary. Their concentration is highest at the base of the boundary layer and drops by more than two times at it top. As distinct from iron hydroxides, other magnetic minerals were variously accumulated, depending on their origin and local deposition conditions of terrigenous material (for example, accumulation of particles of metallic iron and nickel, aerial transport of titanomagnetite grains of volcanic origin, and deposition of terrigenous particles of magnetite and ilmenite).

PACS numbers: 91.25.F-

DOI: 10.1134/S1069351308030063

INTRODUCTION

According to numerous data, the Mesozoic–Cenozoic boundary is fixed by a higher magnetic susceptibility of oceanic and marine deposits. Analysis of oceanic continuous sedimentary sections including the K/T boundary [Pechersky and Garbuzenko, 2005] showed that a peak of the magnetic susceptibility χ is often noted at this boundary. Large values of the peak often coincide in space with epicenters of active plumes. Accumulation of magnetic material in sediments is extended in time, from a few tens of years (more often) to a few hundred thousand years, and, wherever this process can be observed, this interval includes the K/T boundary and lies mostly above it. Researchers usually relate the susceptibility increase to inflow of terrigenous material into sediments, which implies that larger values of the magnetic susceptibility of oceanic sediments should be expected near continents. However, the χ peak is often completely absent in sedimentary cores closest to continents.

Until recently, only the susceptibility behavior in sediments at era boundaries was studied, while other magnetic properties were not examined. Accordingly, almost nothing was known about the origin of the susceptibility peak at era boundaries. This significant drawback is compensated by detailed magnetolithologic and magnetomineralogical studies of epicontinental sediments near the K/T boundary outcropping on land and accessible to direct examination. In particular, the sections studied are Koshak (Mangyshlak) [Pechersky et al., 2006a], Gams (Austria) [Grachev et al., 2005; Pechersky et al., 2006b], Teplovka (Volga region) [Molostovsky, 1986], and Tetritskaro (Georgia) [Adamia et al., 1993].

Methods used in petromagnetic studies of these sections are described in detail in the papers cited. We focus only on determinations of magnetic mineral concentrations and paramagnetic magnetization.

Data of thermomagnetic analysis of sediments of the aforementioned sections point to the presence of iron hydroxides (of the goethite type), hemoilmenite, magnetite, and titanomagnetite and metallic iron. In order to estimate their concentrations from the curve $M_i(T)$, the contribution of a given magnetic mineral to the magnetization M_i was determined and this value was divided by the specific saturation magnetization of this mineral. We accepted the following values of M_s [Bagin et al., 1988; Nagata, 1961]: ~90 A m^2/kg for magnetite and titanomagnetite, ~200 A m^2/kg for iron, 4 A m^2/kg for hemoilmenite with T_C above 300°C and 10 A m^2/kg for hemoilmenite with $T_C \approx$ 250–260°C, and 0.25 A m^2/kg for goethite (the latter value is the average specific saturation magnetization of goethite, varying from 0.02 to 0.5 A m^2/kg, depending on the aggregate state of the mineral). The obtained analyses of the magnetic mineral concentrations are rather tentative, but their relative variations reflect real patterns.

The total paramagnetic–diamagnetic part of magnetization was determined from the curve of isothermal magnetization above the saturation field at room temperature. If the paramagnetic magnetization is known at room temperature, the Curie–Weiss law allows one to calculate the paramagnetic susceptibility at 800°C. The diamagnetic magnetization is virtually independent of

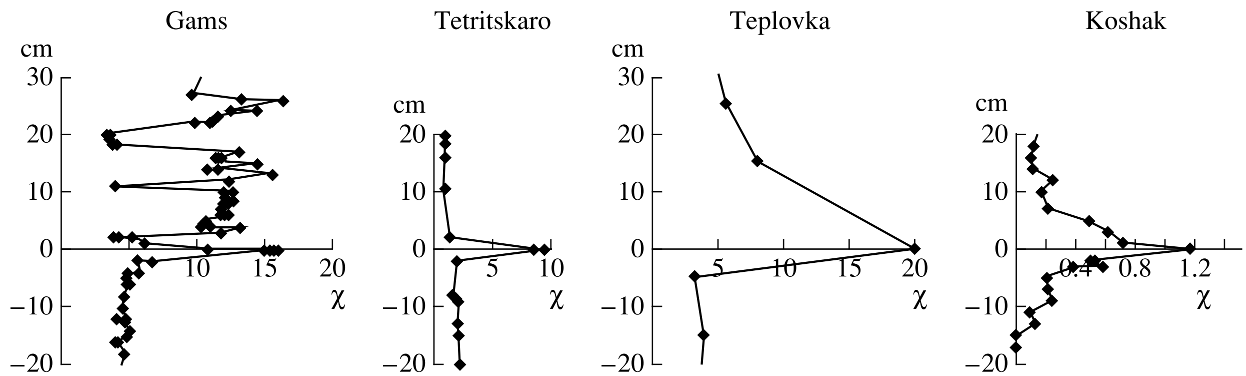

Fig. 1. Behavior of the magnetic susceptibility χ (in 10^{-9} m^3/kg) in the Gams, Tetritskaro, Teplovka, and Koshak sections.

temperature [Vonsovskii, 1971]. Considering that all measurements were made in the same external magnetic field or were reduced to this field (in such cases we accepted a linear field dependence of paramagnetic and diamagnetic magnetizations), the following simple equations can be used for calculating the paramagnetic magnetization at room temperature M_p:

$$M_p + M_d = M_{20},$$

$$M_p/3.644 + M_d = M_{800},$$

where M_d is the diamagnetic magnetization at room temperature, M_{20} is the paramagnetic–diamagnetic magnetization determined from the curve of isothermal magnetization of a sample at room temperature above the saturation field of magnetic (magnetically ordered) minerals present in the sample, and M_{800} is the sample magnetization measured in the same field as M_{20} at 800°C. The value 3.644 is the temperature ratio 1075 K/295 K. These equations yield

$$M_p = 1.378(M_{20} - M_{800}).$$

In fact, the paramagnetic magnetization is determined by the total content of iron, in our case concentrated in paramagnetic and weakly ferromagnetic minerals (mostly minerals of the goethite group) and clayey minerals.

RESULTS OF PETROMAGNETIC STUDIES

As noted in the Introduction, many researchers have fixed a magnetic susceptibility peak at or near the K/T boundary in epicontinental, marine, and oceanic sediments. Among the known continuous sections of oceanic sediments, one-third of cores yield an increase in the magnetic susceptibility near the K/T boundary varying from a very narrow peak to a rise encompassing many hundreds of thousands of years (the time of iron enrichment in sediments) [Pechersky and Garbuzenko, 2005]. Anomalous susceptibility behavior in the K/T boundary layer is widespread in epicontinental sediments at least regionally (and possibly at a global level), reflecting specific features of accumulation of iron and magnetic minerals in sediments. This behavior is of the two following types depending on the section lithology. (1) Carbonate sediments of the Maastrichtian are overlain by sandy–clayey sediments of the Danian; the susceptibility sharply increases in the boundary layer and its values in the Danian sediments remain elevated as compared with the Maastrichtian sediments. Sections of this type are, for example, Gams (Austria) [Pechersky et al., 2006b], Teplovka (Volga region) [Molostovsky, 1986], and Kubalach (Crimea) [Yampolskaya et al., 2004]. (2) Carbonate sediments near the K/T boundary including clay interbeds (in particular, at the boundary itself) are characterized by a sharp peak of susceptibility in the boundary clay bed; examples of such sections are Koshak (Mangyshlak) [Pechersky et al., 2006a], Tetritskaro (Georgia) [Adamia et al., 1993; Pechersky et al., in press], and Abat (Oman) [Ellwood et al., 2003]. Most researchers interpret the χ peak as a result of terrigenous washout and accumulation of magnetic minerals [Molostovsky, 1986; Ellwood et al., 2003; Yampolskaya et al., 2004; and others]. Actually, a susceptibility jump is fixed at the K/T boundary in all sections analyzed (Fig. 1). However, the contributions of magnetic minerals are different and the contribution of a paramagnetic mineral is generally predominant, as is evident from the correlation of the magnetic susceptibility with paramagnetic magnetization (Fig. 2). The distribution of magnetic minerals clearly demonstrates the along-section distribution of the saturation remanence (Fig. 3), primarily controlled by the total concentration of magnetic minerals in sediments; the saturation magnetization behaves in a similar way. As seen from Fig. 3, the M_{rs} value distinctly localizes the boundary layer only in the Tetritskaro section, where the susceptibility is dominated by the contribution of paramagnetic minerals. It is interesting that the values M_{rs} and M_s in the Koshak section do not resolve the boundary layer at all, whereas both M_{rs} and M_s (i.e., the concentration of magnetic minerals) sharply increase in the clay bed lying 60 cm above [Pechersky et al., 2006a]. Thus, the only feature that is undoubtedly common to K/T boundary layers of all aforementioned sections is a sharply increased paramagnetic magnetization (Fig. 4), primarily determined by the content of iron hydroxides in all cases. As seen

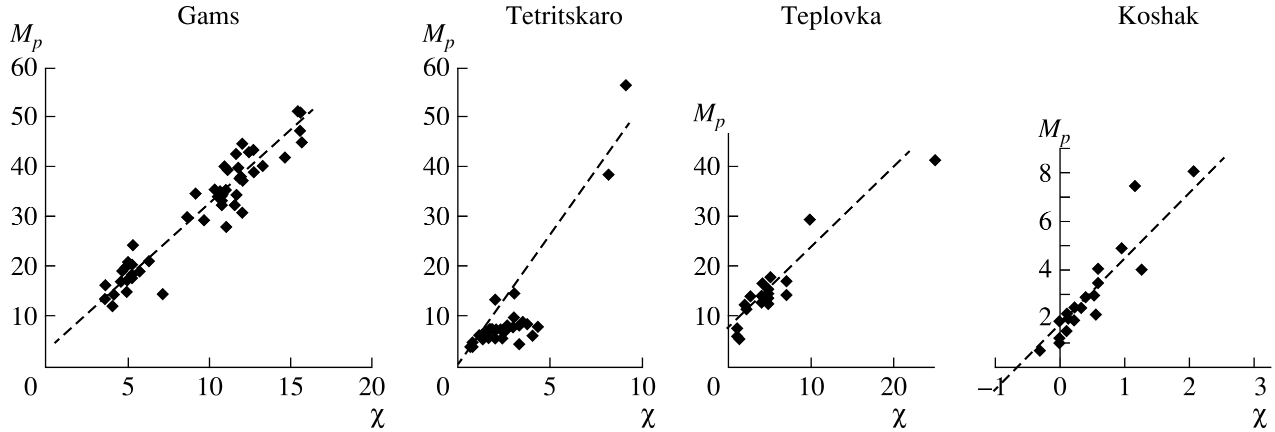

Fig. 2. Correlation between the magnetic susceptibility χ (in 10^{-9} m^3/kg) and the paramagnetic magnetization M_p (in 10^{-3} A m^2/kg) in the Gams, Tetritskaro, Teplovka, and Koshak sections.

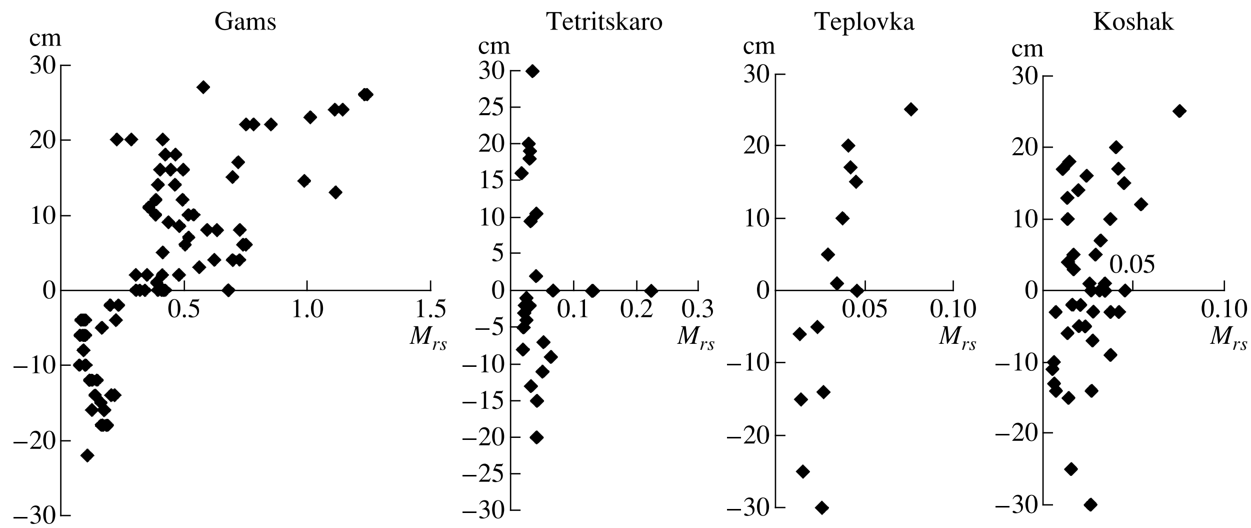

Fig. 3. Behavior of the saturation remanence M_{rs} (in 10^{-3} A m^2/kg) in the Gams, Tetritskaro, Teplovka, and Koshak sections.

from Fig. 4, the concentration of iron hydroxides in the sections varies weakly. In the boundary layer, the paramagnetic magnetization is highest in its lower part, reaching 0.06 A m^2/kg (the Gams and Tetritskaro sections), and drops in the upper part of the layer by more than two times; i.e., the sedimentation at the K/T boundary starts with abrupt enrichment in paramagnetic hydroxides of iron.

Below, we consider the behavior of various groups of magnetic minerals in the aforementioned sections.

Goethite (Fig. 5). In all sections, the behavior of goethite matches the behavior of the paramagnetic magnetization and the iron concentration (Fig. 4). The goethite concentration and paramagnetic magnetization were determined independently, the former from the contribution of the magnetic phase with T_C = 100–150°C (the goethite value) to $M_i(T)$, and the latter from M_{20} and M_{800} (see the Introduction); therefore, such a correlation is evidence for their close relation. This is also supported by the close positive correlation between the paramagnetic magnetization and the bulk concentration of iron in Gams sediments from data of chemical analysis; this information is absolutely independent of petromagnetic estimates. Hence, we may suggest that the paramagnetic material consists mostly of iron hydroxides. Therefore, enrichment in iron hydroxides of both paramagnetic and weakly magnetic types actually occurred at the K/T boundary.

Hemoilmenite (Fig. 6). Hemoilmenite of the studied sediments is present in the form of thin lamellae in ilmenite [Pechersky et al., 2006b]. Its concentration differs in different sections, reflecting different degrees of ilmenite oxidation (different local conditions of hemoilmenite formation). The hemoilmenite concentration sharply increases only in the boundary layer of the Tetritskaro section, where it reaches 0.3%, while its values are less than 0.05% in the remaining part of the section.

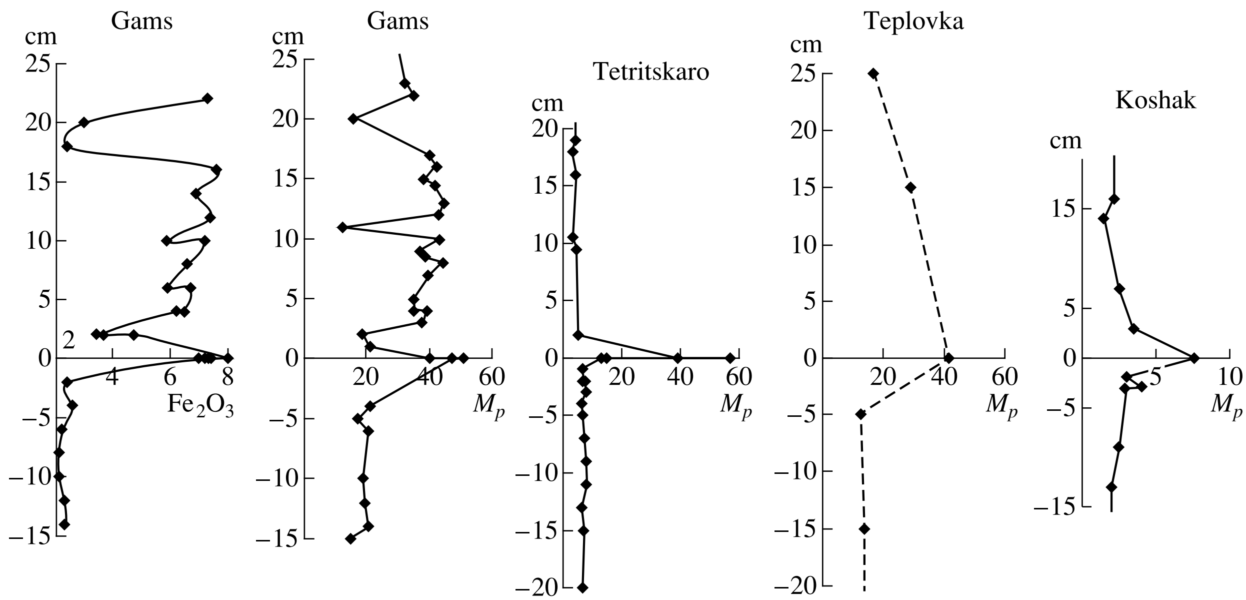

Fig. 4. Behavior of the paramagnetic magnetization M_p (in 10^{-3} A m^2/kg) in the Gams, Tetritskaro, Teplovka, and Koshak sections and the variation in the bulk concentration of iron in the Fe_2O_3 form along the Gams section from chemical analysis data [Grachev et al., 2005].

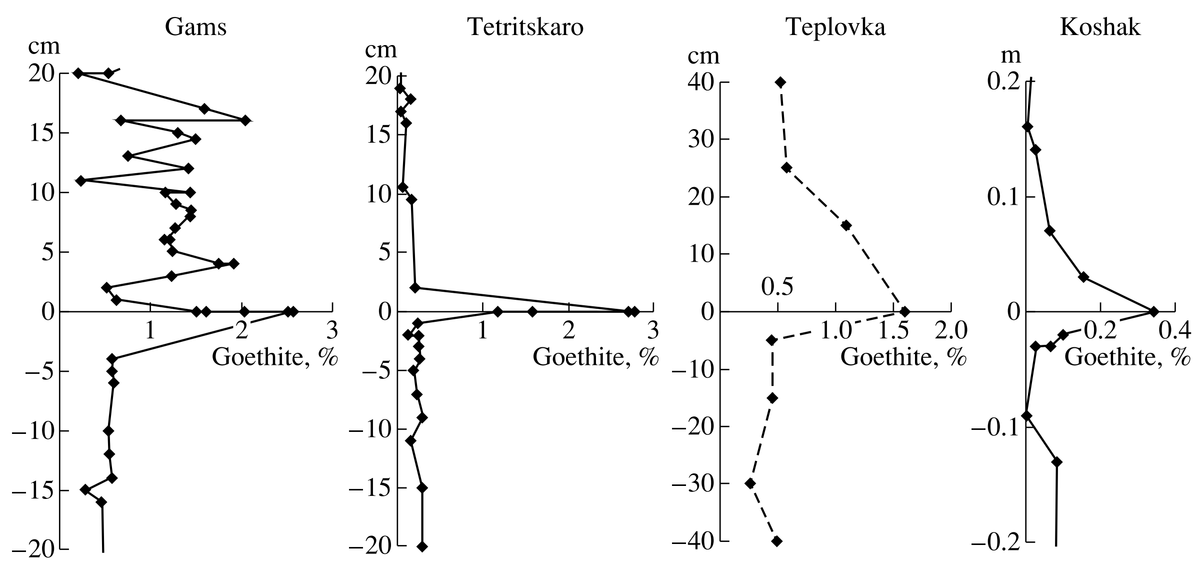

Fig. 5. Behavior of goethite in the Gams, Tetritskaro, Teplovka, and Koshak sections.

Magnetite (Fig. 7). The magnetite concentration varies within wide limits, approximately from 0.0005 to 0.02%, and this is in part due to the lithology of the sections: higher concentrations are observed in sandy–clayey sediments. The magnetite concentration is relatively higher in the boundary layers of the Tetritskaro and Koshak sections. Overall, as in the case with hemoilmenite, the magnetite concentration cannot serve as an indicator of the K/T boundary.

Titanomagnetite (Fig. 8). The lithologic control of accumulation of titanomagnetite grains is even weaker. The titanomagnetite concentration strongly varies from section to section. Thus, titanomagnetite is not discovered in sediments of the Teplovka section; in the Tetritskaro and Koshak sections, its concentration is less than 0.001% in Maastrichtian sediments and the mineral is absent in Danian sediments; in the Gams section, its concentration varies from less than 0.001 to 0.01% without any relation to the lithology. Evidently, titanomagnetite is of volcanic origin, and its composition is typical of basalts [Grachev et al., 2005].

Metallic iron (Fig. 9). The metallic iron concentration varies within wide limits from section to section. Thus, its concentration is less than 0.0002% in the Tetritskaro and Koshak sections and varies from less than 0.0001 to 0.0015% in the Gams section; the distri-

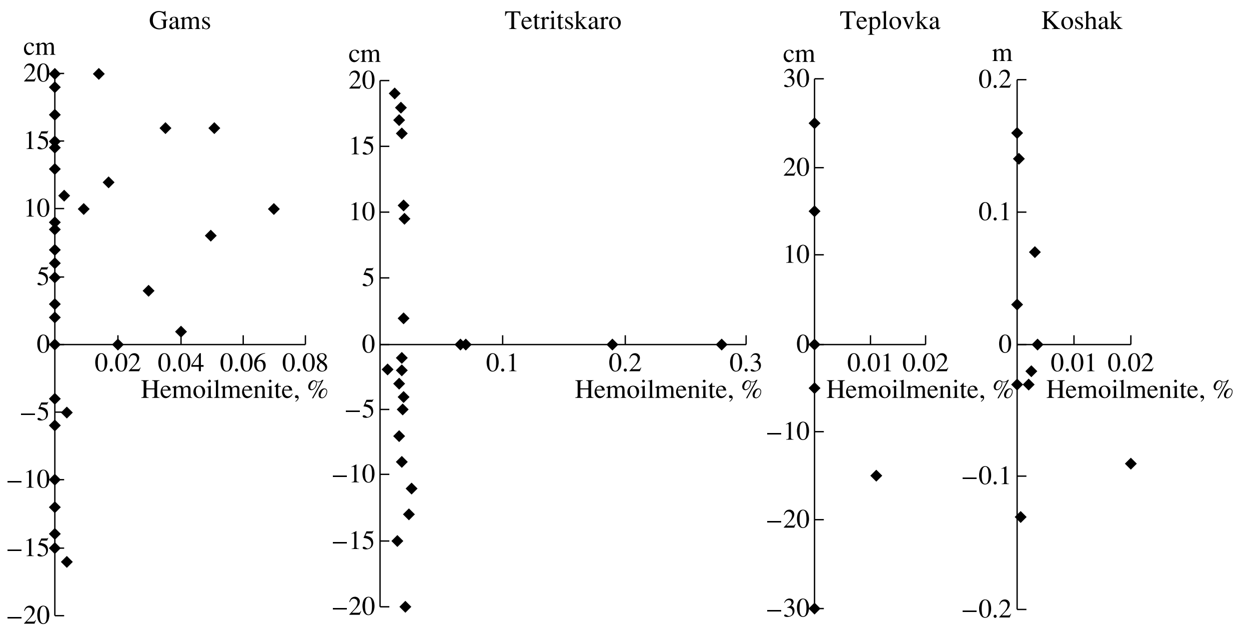

Fig. 6. Behavior of hemoilmenite in the Gams, Tetritskaro, Teplovka, and Koshak sections.

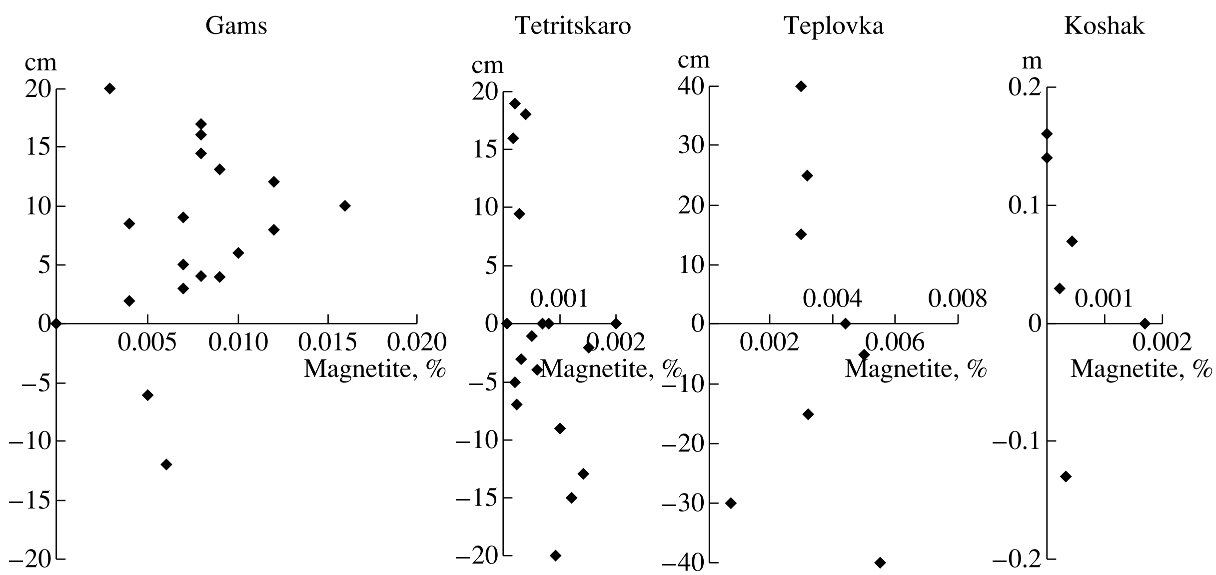

Fig. 7. Behavior of magnetite in the Gams, Tetritskaro, Teplovka, and Koshak sections.

bution of iron in these three sections is rather uniform, whereas its concentration reaches ~0.004% near the K/T boundary in the Maastrichtian sediments of the Teplovka section and no titanomagnetite is discovered in the Danian sediments. Thus even metallic iron does not exhibit any general pattern in its distribution; in particular, no correlation with the K/T boundary is observed. The metallic iron particles in the studied sediments are evidently of cosmic origin.

Metallic nickel and its alloy with iron. Like metallic iron, metallic nickel and its alloy with iron in the upper part of the boundary layer in the Gams section are most likely of cosmic origin. In other sections, nickel is not discovered; i.e., at present, this phenomenon is unique.

Thus, only enrichment in iron hydroxides can be regarded as a global, generally observed phenomenon related to the K/T boundary. All other magnetic minerals reflect the origin of these minerals (for example, cosmogenic particles of metallic iron and nickel or volcanogenic titanomagnetite grains) or local conditions of accumulation of terrigenous material (for example,

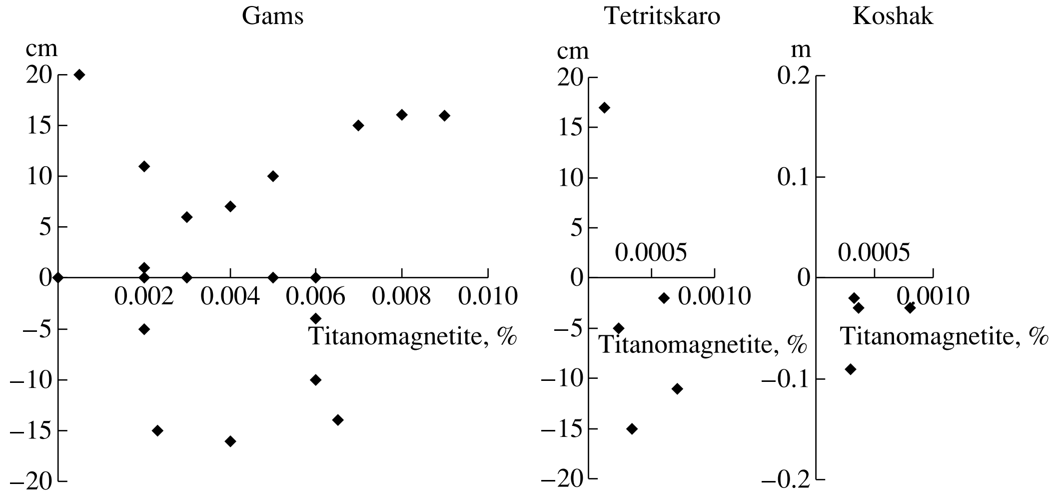

Fig. 8. Behavior of titanomagnetite in the Gams, Tetritskaro, and Koshak sections.

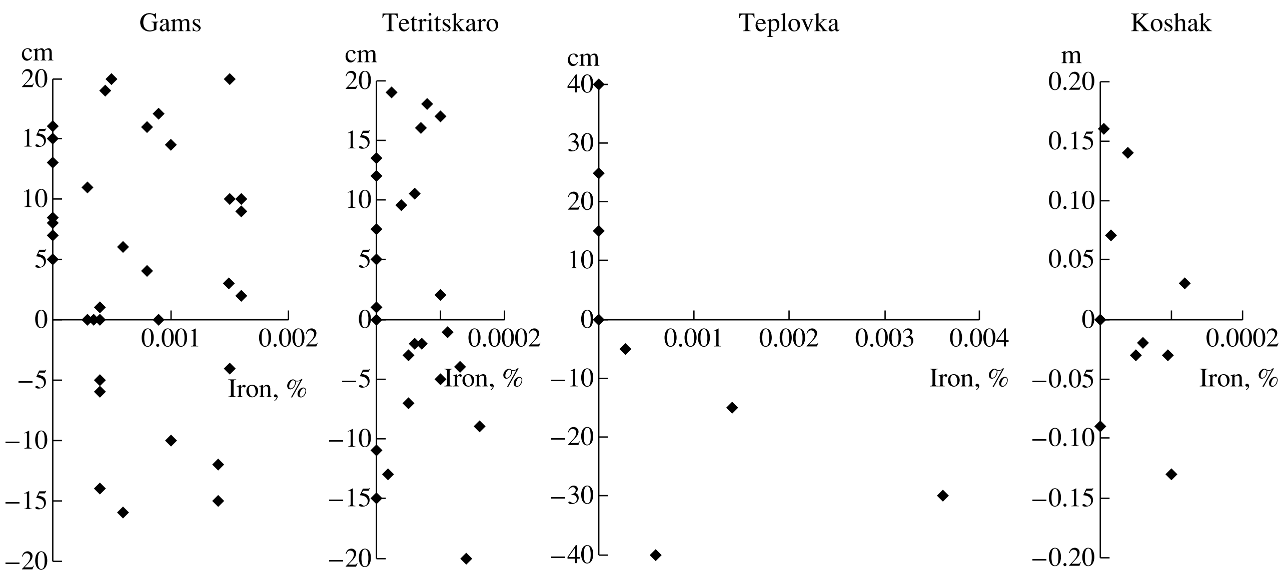

Fig. 9. Behavior of metallic iron in the Gams, Tetritskaro, Teplovka, and Koshak sections.

supplying magnetite and ilmenite); the magnetic layered fabric of the sediments indicates detrital accumulation of both iron hydroxides and other minerals [Pechersky et al., 2006b].

CONCLUSIONS

The synthesis of petromagnetic results from four sections of epicontinental sediments has led to the following conclusions.

(1) A sharply enhanced accumulation of iron hydroxides took place at the K/T boundary; this phenomenon is most likely global and unrelated to local physiographic conditions of accumulation of terrigenous material in sediments. "Global" means here that this effect is widely developed both on land and in the ocean rather than that iron hydroxides everywhere accumulated at the K/T boundary. Moreover, the iron hydroxide accumulation took place not only at the boundary between the Mesozoic and Cenozoic, but this pattern is regular at the K/T boundary. Iron hydroxide accumulation is similar to formation of metalliferous and ferruginous microconcretions as a result of volcanic and hydrothermal activity [Gurvich, 1998]. This process differs significantly from the terrigenous accumulation of magnetic minerals. The global nature of iron oxide accumulation is corroborated by the synchronism of this phenomenon, at least within Europe, as is evident from magnetostratigraphic data: the K/T boundary lies at nearly the same level within the magnetochron C29r in the sections Gubbio (Italy) [Rocchia

et al., 1990], Gams (Austria) [Mauritsch, 1986], and Tetritskaro (Georgia) [Adamia et al., 1993].

(2) As distinct from iron hydroxides, accumulation patterns of other magnetic minerals are different, evidently reflecting their origin (cosmogenic particles of metallic iron and nickel or volcanogenic titanomagnetite grains) or local conditions of terrigenous material accumulation (for example, magnetite and ilmenite); the layered magnetic fabric of the sediments is evidence for detrital deposition of iron hydroxides and other magnetic minerals.

(3) The base of the K/T boundary layer is enriched in fragments of volcanic titanomagnetite; possibly, the coinciding times of titanomagnetite and iron hydroxide accumulation indicate a common source; namely, titanomagnetite was accumulated due to fragments of volcanic eruptions transported through air, while iron hydroxides are products of hydrothermal activity associated with the same volcanism (a kind of metalliferous sediments); the eruptive activity is a short-term process, while the iron hydroxide accumulation is a process more extended in time.

(4) The jump in the iron hydroxide accumulation in the boundary layer has no relation to impact events. Thus, features indicative of an impact event in the Gams section (the presence of nickel in metallic form and as an alloy with iron, as well as an anomaly in the iridium concentration) are present in upper parts of the K/T boundary layer, whereas the jump in the accumulation of iron and titanomagnetite is fixed at the base of this layer; the iridium anomaly in the Tetritskaro section is confined to lower parts of the boundary layer. Moreover, a sharp rise in the concentration of iron hydroxides is noted in all of the aforementioned sections, while metallic nickel was discovered only in the Gams section. Enrichment in particles of cosmogenic metallic iron at the K/T boundary is not discovered in any of the sections studied. Thus, any evidence of an impact event at the K/T boundary is absent.

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