Metallic iron in sediments at the Mesozoic-Cenozoic (K/T) boundary

D. M. Pechersky

Received 19 July 2008; accepted 22 August 2008; published 18 September 2008.

Thermomagnetic analysis was performed on sediments close to the Mesozoic-Cenozoic (K/T) boundary in the following sections: Gams (Austria), Tetritskaro (Georgia), Klyuchi and Teplovka (the Volga Region, Russia), and Koshak (Turkmenia). Positive correlation is found between the contents of terrestrial magnetic minerals (Fe-hydroxides, titanomagnetite, magnetite) and extraterrestrial metallic iron, i.e., between the minerals of different origin and with different pre-accumulation history. The observed different values of positive correlation between the content of the above listed minerals depend from variation in redeposition rate. The correlation is absent altogether because of different provenance and the character of sedimentation as it is observed for the boundary layer and some sections (Gams, the sections from the Volga region). In contrast, stronger correlation is found if redeposition is important (Tetritskaro, Koshak).

INDEX TERMS: 1029 Geochemistry: Composition of aerosols and dust particles; 1512 Geomagnetism and Paleomagnetism: Environmental magnetism; 1594 Geomagnetism and Paleomagnetism: Instruments and techniques; 2129 Interplanetary Physics: Interplanetary dust; KEYWORDS: cosmic dust, metallic iron, sediments, magnetic minerals, K/T boundary.


Introduction

Cosmic dust particles, in particular of metallic iron and nickel, are often found by satellite measurements in dust clouds, atmosphere, ice cores from Antarctica and Greenland, and oceanic pelagic sediments. On average, about 40,000 tons of cosmic dust is thought to fall annually on the Earth. This amount did not vary more than two-fold either for the last 30 Ky judging by a study of an Antarctic ice core or for the last 80 My as indicated by osmium and iridium isotopes in pelagic sediments in the Pacific. Two jumps up to 500,000 tons/year at ~25 Ma and ~65 Ma from a single column 596 DSDP [Peucker-Ehrenbrink, 1996] are exceptions. Numerous discoveries of metallic iron, usually as spheres and sometimes as flakes are well known. The spatial and temporal distribution and amount of the particles of metallic iron and nickel, however, are poorly known because only the “direct” methods are used for detecting such particles. An opportunity of obtaining vast and rapid information on metallic iron distribution has been missed.

Thermomagnetic analysis (TMA) is widely used as a part of paleo- and petromagnetic (rock-magnetic) studies of various geologic objects, sediments and sedimentary rocks of different geologic age. As the primary goal of such studies was to characterize the carriers of the natural remanent magnetization, the maximum temperature of TMA was not higher than the Curie point of hematite, i.e. maximum about 700°C. Therefore, any information on composition and concentration of metallic iron particles was completely excluded from the consideration!

In order to trace metallic iron we systematically used the TMA up to 800°C in petromagnetic studies of sediments at the K/T boundary [Grachev et al., 2005; Pechersky et al., 2006]. This paper is the first attempt to review TMA data on the distribution of metallic iron in several sections [Adamia et al., 1993; Grachev et al., 2005; Molostovsky et al., 2006; Pechersky, 2008; Pechersky et al., 2006a, 2006b]; (D. M. Pechersky et al., in press, 2008a,b).

Let us review these results from two points of view: 1) What the spatial distribution of metallic iron is in coeval sediments close to the K/T boundary; and 2) How metallic iron is distributed through time. In both cases, the main attention will be paid to the lithological characteristics and to the relationship with other magnetic minerals like Fe-hydroxides, magnetite, titanomagnetite, which formation and accumulation are of terrestrial provenance, in contrast to metallic iron.

The concentration of magnetite, titanomagnetite, iron and goethite was evaluated by determining the contribution of each mineral $M_i$ in the $M_i(T)$ plots with subsequent nor-
Spatial Distribution of Metallic Iron at the K/T Boundary

[7] The distribution of metallic iron was studied in the narrowest time interval that is represented by the transitional clay layer at the K/T boundary, which had been accumulating for several thousand years [Grachev et al., 2005; (D. M. Pechersky et al., in press, 2008a,b)]. The content of metallic iron in this layer from the five separated sections varies widely: it is absent or, more precisely, has not been detected by TMA, in 19 samples out of 28 studied and varies from 0.0001 to 0.002% in the remaining nine samples [Grachev et al., 2005; Molostovsky et al., 2006; Pechersky, 2008; Pechersky et al., 2006a, 2006b]; (D. M. Pechersky et al., in press, 2008a,b). A detailed imbedded study of the boundary layer from the Gams section showed that metallic iron is present only in the upper and lower parts of this layer (Figure 1). Spherules of metallic nickel were also found in the upper part of the Gams section [Grachev et al., 2005]. The correlation between main magnetic and paramagnetic components of sediments from the boundary layer is presented in Figure 2. (It is worth noting that this and the follow-
ing figures use the logarithmic scale as this notation better suits the approximately lognormal distributions of concentrations of minerals, elements, etc.). The points in Figure 2 form two groups thus highlighting the lack of correlation between metallic iron on one hand and Fe-hydroxides, magnetite, and titanomagnetite on the other and reflecting their different provenance and accumulation history: a) samples where metallic iron, Fe-hydroxides, magnetite, and titanomagnetite are present, and b) samples without metallic iron but with Fe-hydroxides and/or magnetite and titanomagnetite. Thus, certain regularity can be traced: while boundary layer of clay and Fe-hydroxides was accumulating close to the K/T boundary for several thousand years, metallic iron did not accumulate. In contrast, the maximum of cosmic dust accumulation straddles this boundary in sediments from column 596 DSDP in the Pacific [Peucker-Ehrenbrink, 1996]. Therefore, our data on metallic iron presence in the boundary layer disagree with cosmic dust accumulation close to the K/T boundary. It is worth to ponder on this controversy. The annual global fall of interplanetary dust of ∼40×10^9 g corresponds to accumulation rate of ∼0.08×10^-9 g cm^-2. The accumulation rate of pelagic sediments is 1–2 mm ky^-1. A sample of several millimeters in thickness that is needed for TMA had been forming for several thousand years at least. During this interval, the total of ∼0.3×10^-6 g will accumulate, while the total value for the anomalous sample from the K/T boundary will be by an order of magnitude more, i.e., ∼10^-5 g. As exemplified by the Gams data, the concentration of metallic iron generally increases close to the K/T boundary and varies from zero to ∼0.002%, ~0.001% on average, over an interval of ∼20 ky (±20 cm from the boundary, Figure 4). This corresponds to ∼10^-6 g for a TMA sample of 0.1–0.2 g. In the upper part of the boundary layer, the sum of metallic iron and nickel is not less than ∼0.005%, which is close to 10^-5 g [Grachev et al., 2005]. Available data indicate that fragments of chondrites, particles of silicates as well as glass with inclusions of metals and sulfides clearly predominate in the interplanetary dust, while metallic iron and nickel are much rarer. Thus the controversy disappears if a sample with anomalous content of cosmic dust belongs from the boundary clay layer. Note, however, that two adjacent samples of sediments from the hole 596 DSDP show the elevated concentrations of cosmic dust too. It is most likely that a long time interval is averaged during preparation of the probe for analysis. If so, this may partly account for the stability of cosmic dust flux to the Earth over geological time that was noted by many researchers. In contrast to publications on cosmic dust, TMA data provide a much more detailed pattern. For instance, 28 and 50 measurements of metallic iron content were made on the boundary layer alone and within ±20 cm from the K/T boundary, respectively (Figure 4), whereas there are just 19 analyses of cosmic dust in pelagic sediments over the huge interval of 80 My (Figure 3) [Peucker-Ehrenbrink, 1996]. Let us consider the ±20 cm interval around the K/T boundary, which is likely to better match averaged data on the Pacific sediments. The concentration of metallic iron varies by one to two orders of magnitude and more for four sections that are 1000 to 5000 km from each other. There are intervals where metallic iron is absent (not determined), for instance, in Danian sediments of the Teplovka and Klyuchi sections; in contrast, metallic iron content reaches 0.004% in uppermost Maastrichtian deposits of the Teplovka section. Therefore, the distribution of metallic iron over the Earth surface was very non-uniform close to the K/T boundary.

**Temporal Distribution of Metallic Iron**

[8] Let us consider the behavior of iron over an interval of hundred of thousand – few million of years around the K/T boundary. Within each section (that is through the time), the concentration of iron varies from zero to 0.002% in the Gams section and to 0.004% in the Teplovka section; its concentration does not exceed 0.0002% in the Tetritskaro and Koshak sections (Figure 4). Note that the maximums of this parameter are found at different levels and are not coeval. Hence the enrichment by metallic iron was not synchronous. Besides, a certain lithological control appears to exist as higher iron concentrations are found in Danian terrigenous sediments of the Gams section, while the lowest ones are from carbonaceous sediments of the Tetritskaro and Koshak sections. On the other hand, the samples where iron...
is absent are more common in terrigenous sediments; first of all, it is true for the boundary layer.

[9] Thus very high non-uniformity in distribution of metallic iron in both space and time appears to be present. This may be accounted for in three different ways: “primary extraterrestrial” due of accumulation of metallic iron particles both from cosmic dust and from ablation of meteorites; “primary terrestrial” due of accumulation of metallic iron particles of terrestrial origin; and “secondary” as a result of subsequent oxidation of metallic iron particles with formation of Fe-hydroxides and hematite. Large variation in concentration of metallic iron in sediments is not compatible with steady influx of cosmic dust to the Earth surface. First and foremost, I connect this variation with different amount of information; also, the concentration of metallic iron in cosmic dust is low, and its distribution is not neces-

Figure 4. Examples of distribution of metallic iron in sediments close to the K-T boundary (red line).

Figure 5. Correlation between paramagnetic magnetization ($M_p$) and concentration of ferromagnetic Fe-hydroxides (goethite), magnetite, titanomagnetite, and metallic iron in sediments. The data for the Gams, Koshak, Klyuchi, Teplovka, Tetritskaro, and Khalats sections are combined [Molostovsky et al., 2006; Pechersky et al., 2006a, 2006b; Pechersky, 2008]; (D. M. Pechersky et al., in press, 2008a,b).
sarily proportional to the total influx of the dust. Besides, it is possible that the main source of metallic iron is meteorite falls and not the cosmic dust.

Correlation Between the Content of Metallic Iron and Fe-Hydroxides, Magnetite, and Titanomagnetite

[10] As noted above, tight positive correlation between the total iron content as determined by chemical analyses, the intensity of paramagnetic magnetization \( M_p \), and the amount of ferromagnetic Fe-hydroxides (goethite) was found in sediments close to the K/T boundary in all sections studied; this observation was accounted for by prevailing role of Fe-hydroxides in the intensity of paramagnetic magnetization \( M_p \) [Pechersky, 2008]. This \( M_p \)-goethite correlation is well illustrated in Figure 5, where the data for five sections close to the K/T boundary and the Khalats sedimentary section (age 17–3 My) are summarized. When the values of \( M_p \) and goethite are compared with concentrations of magnetite, titanomagnetite and metallic iron, two main groups of data points are found (Figure 5): (a) the first group reveals clear positive correlation between accumulation of magnetite, titanomagnetite and metallic iron, in contrast to what is observed in the boundary layer (Figure 2); (b) the second zero-correlation group, where no magnetic minerals is detected but, naturally, \( M_p \) is measurable. The coefficients of linear correlation are computed both for each pair of observed values and their logarithms.

[11] First of all, I would like to pay attention to the steady increase of correlation coefficients when the values are replaced by their logarithms; this observation points to the decisive role of lognormal distribution of the analyzed magnetic characteristics. This is well illustrated by Figure 6,
Figure 7. Correlation between paramagnetic magnetization ($M_p$), concentration of ferromagnetic Fe-hydroxides (goethite), magnetite, titanomagnetite, and metallic iron in sediments from the Gams section [Pechersky et al., 2006a, 2006b; Pechersky, 2008]; (D. M. Pechersky et al., in press, 2008b).

where the rows of measured characteristics and their logarithms are presented in Figure 6a and 6b, respectively. The rows for the values differ greatly, even the general trends showing the similarity just for some intervals (Figure 6a); whereas, the rows for the logarithms are similar in all cases, as well as the general trends (Figure 6b). The strongest correlation is found between the logarithms of paramagnetic magnetization, i.e., the concentration of paramagnetic Fe-hydroxides, and the goethite content. The weaker, but still noticeable, correlation exists between the logarithms of paramagnetic magnetization and titanomagnetite content, whereas the weakest correlation between the logarithms of paramagnetic magnetization and magnetite content. Rather high and practically the same positive correlations are between the logarithms of metallic iron, paramagnetic magnetization, and the goethite content, while the correlation between the logarithms of metallic iron and magnetite + titanomagnetite is much weaker.

Let us see if this pattern is observed on the regional level on the base of data on the studied sections (Figures 7–10). For comparison, the results are presented on the Khalats section (Figure 11), where the age of sediments is noticeably younger than the K-T boundary. A common feature for all sections is that all points form two groups, similarly to the case of the boundary layer (Figure 2): Group A where metallic iron, Fe-hydroxides, and titanomagnetite are present, and Group B, or zero-group, without metallic iron but with Fe-hydroxides and/or titanomagnetite. Emphasize that the range of values is similar in both groups. In contrast to the boundary layer, where no correlation between the components of Group A is found, perceptible positive correlation is present between these components (Figures 7–

Figure 8. Correlation between paramagnetic magnetization ($M_p$), concentration of ferromagnetic Fe-hydroxides (goethite), magnetite, titanomagnetite, and metallic iron in sediments from the Klyuchi and Teplovka sections [Molostovsky et al., 2006; Pechersky, 2008].
Figure 9. Correlation between paramagnetic magnetization \( (M_p) \), concentration of ferromagnetic Fe-hydroxides (goethite), magnetite, titanomagnetite, and metallic iron in sediments from the Koshak section [Pechersky et al., 2006a, 2006b; Pechersky, 2008].

11), which is described for each object separately.

[13] For the Gams section (Figure 7), weak correlation between MT+TM and \( M_p \) and MT+TM and iron is observed, while no correlation is found between \( M_p \) and iron as well as between goethite and iron.

[14] For the Klyuchi and Teplovka sections (Figure 8), no correlation is observed, except for weak correlation between MT+TM and \( M_p \).

[15] For the Koshak (Figure 9), Tetritskaro (Figure 10), and Khalats (Figure 11) sections, all components of the Group A reveal relatively weak correlation.

[16] Therefore, the common feature is expressed by the presence of two groups A and B on the plots; note that the values on the abscissa axis have similar ranges, and the values in the Group B are often higher than in the Group A. In the latter, the characteristics are variably correlated. Hence, the degree of the connection between concentrations of Fe-hydroxides, titanomagnetite and iron varies from highly positive correlation to the lack of it. More high correlation is found in the carbonaceous Koshak and Tetritskaro sections, whereas much slight or no correlation is found in the sections with high terrigenous input. Among all correlations between separate characteristics, the weakest one is between goethite and Fe, and the strongest one is between MT+TM and \( M_p \), except for correlation between goethite and \( M_p \) (Table 1). The latter pair, in difference to the others, does not have the “zero” Group B (Figure 5), which is mainly due to the fact that \( M_p \) strongly depends upon Fe-hydroxides that are nearly omnipresent in all studied sediments [Pechersky, 2008]. It is likely that the connection between MT+TM and \( M_p \) is predictable and reflects the largely terrigenous provenance of magnetite and titanomagnetite in sediments, although both minerals, in particular titanomagnetite as indicated by its composition, had been originally produced by basaltic volcanism. It is worth recalling that a rather large “zero” Group B is found for all pairs, when one component of a pair is absent, while the other one is abundant. Such a two-ways connection excludes the “secondary” origin of the correlation between iron and titanomagnetite, magnetite, and Fe-hydroxides. It is possible to assume that the degree of oxidation of iron to hydroxides is approximately equal and thus to account for positive correlation between goethite and iron; in other words, the higher is the iron content, the higher is the concentration of its oxidized part. The concentrations of iron and goethite, however, differ by three orders of magnitude, and, therefore, the original concentration of iron had to be as high as several percent. A reverse dependence has to exist too, when iron particles approach the fully oxidized state. This is in sharp contrast to the observed pattern, when the Group B is distinct and comprises a large number of samples where metallic iron is absent altogether. Moreover, large Groups B and A coexist within similar range of TM+MT in the plot of MT+TM versus Fe, which cannot be attributed to secondary oxidation of iron for the correlation between titanomagnetite and iron. Really, titanomagnetite is definitely unrelated to oxidation of metallic iron, as the particles of metallic iron, nickel, and their alloys do not contain large amounts of other elements, titanium in particular.

[17] So the correlations (Figures 5–11) are of primary, either terrestrial or extra-terrestrial, origin. Different degree of correlation between components is to be expected for very different conditions of accumulation of Fe-hydroxides, magnetite + titanomagnetite and metallic iron. Indeed, the most interesting features are high correlations between metallic iron in sediments.

### Table 1. Coefficients of linear correlation

<table>
<thead>
<tr>
<th>Pairs</th>
<th>Coefficients</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_p )-goethite</td>
<td>0.85</td>
<td>0.91</td>
</tr>
<tr>
<td>( M_p )-titanomagnetite</td>
<td>0.71</td>
<td>0.83</td>
</tr>
<tr>
<td>( M_p )-magnetite</td>
<td>0.29</td>
<td>0.58</td>
</tr>
<tr>
<td>( M_p )-magnetite+titanomagnetite</td>
<td>0.66</td>
<td>0.71</td>
</tr>
<tr>
<td>( M_p )-iron</td>
<td>0.36</td>
<td>0.74</td>
</tr>
<tr>
<td>goethite – iron</td>
<td>0.61</td>
<td>0.79</td>
</tr>
<tr>
<td>magnetite+titanomagnetite – iron</td>
<td>0.21</td>
<td>0.6</td>
</tr>
</tbody>
</table>
iron and Fe-hydroxides and between metallic iron and titanomagnetite. As the secondary origin of the observed correlations is ruled out, the common way accumulation for the above listed minerals becomes evident. It would not be surprising if the particles of metallic iron are of terrestrial origin. In principle, authigenic metallic iron may be formed in sediments. A review of publications, however, revealed that this is exceptionally rare, while, according to our data, metallic iron is omnipresent in sediments, albeit in tiny amount. Hence metallic iron can be of terrigenous origin only, and its source is most likely to be magmatic rocks most likely of basaltic composition. However, we fail here again, as the grains of metallic iron in basalts are exceptionally rare. Therefore, metallic iron has en masse to be of extraterrestrial origin, which is in full accord with numerous publications. Although some grains may be of terrestrial origin, their share is negligible on the global scale. If so, the strange and enigmatic correlation between accumulation of the particles of very different provenance and origin, i.e., Fe-hydroxides, magnetite, titanomagnetite, and metallic iron, remains unexplained.

[18] It is worth mentioning that, irrespective of the origin of metallic iron, its accumulation may result from erosion of older rocks and subsequent redeposition. This is similar to formation of placers, similarly to the recent (Quaternary) gold placers in Northeast Asia that were formed by erosion of gold-bearing rocks of mainly Cretaceous age. However, such “far-reaching” erosion is not necessary. Several millen-
niums or even less will suffice; it is important that a positive correlation must appear between heavy iron minerals that are extracted from rocks and accumulate in sediments under the study. So it can be concluded that the observed variable positive correlations between concentrations of Fe-hydroxides, magnetite, titanomagnetite, and metallic iron stems from changeable role of redeposition in accumulation of these minerals in sediments.

Conclusions

[19] 1. Analysis of TMA data on sediments, which ages are close to the K-T boundary, revealed an unexpected positive correlation between Fe-hydroxides, magnetite, titanomagnetite, on one hand, and metallic iron on the other, that is a correlation between the minerals with very disparate origin and provenance. Of several explanations of this phenomenon (primary extraterrestrial, primary terrestrial, secondary oxidation), the extraterrestrial origin of metallic iron is the most likely one, and the observed pattern of variable positive correlations between the accumulation of Fe-hydroxides, magnetite, titanomagnetite, and metallic iron results from the different role of redeposition in accumulation of these minerals. If redeposition is not important, any correlation is absent because of the difference in provenance and character of accumulation (e.g., the boundary layer, the Gams section, and the sections from the Volga Region). This is in a contrast to the objects where redeposit material is important (e.g., the Tetritskaro and Koshak sections).

[20] 2. Taking the above into account, it is necessary to discriminate the cases of redeposition from primary accumulation of iron directly from the space. To achieve this goal, the distribution of iron in parallel sections is to be studied as well as the correlation between concentrations of metallic iron and Fe-hydroxides, magnetite, titanomagnetite and the magnitude of paramagnetic magnetization.

[21] Acknowledgments. The author thanks A. A. Lyubushin for help in mathematical treatment of the data and A. F. Grachev for careful reading and editing of the manuscript.

References


D. M. Pechersky, Schmidt Institute of Physics of the Earth, Russian Academy of Sciences, 10 B. Gruzinskaya, 123995 Moscow