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IRIDIUM ANOMALY AT THE JURASSIC-CRETACEOUS BOUNDARY IN NORTHERN SIBERIA

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Abnormally high contents of noble metals have been recognized by methods of atom-absorption analysis (AAA), neutron-activation analysis (NAA), and X-ray fluorescence analysis (XFA) in an interbed of phosphate limestone 5 to 6 cm thick at the Jurassic-Cretaceous boundary near the Berriasian bottom and in the sole of its basal zone (Chetaites sibiricus) in northern Siberia (the Nordwik Peninsula). These are up to 75.0 ppb Ir, up to 267.0 ppb Pd, up to 12.0 ppb Pt, up to 37.0 ppb Ru, up to 62.0 ppb Rh, and up to 34.4 Au. The noble metals are proven to be of cosmic origin. Their abnormally high concentration is explained by specific features of sedimentation processes: a great distance from the sourceland and corresponding undercompensation of sedimentation in the Khatanga central paleobasin.

After L. Alvares with coauthors have adviced [1] that a thin layer of clays at the Cretaceous–Paleogene boundary in the Gubbio section, Northern Italy, is enriched in Ir and other noble metals and made an attempt to relate the Ir anomaly with the impact hypothesis as a cause of mass global extinction of organisms in the late Cretaceous, the specialists in the whole world show a great interest to searching for Ir anomalies both at the same level and throughout the geochronological scale. The four-year intense searches for the anomalies at the Mesozoic–Cenozoic boundary revealed them in more than 20 localities throughout the Earth's globe on continents as well as in oceans, in marine and continental facies [2].

The investigators' attention was drawn, first of all, to the levels of mass global or semiglobal extinctions or large restructurings in biota evolution, which are usually confined to boundaries of erathems and systems, sometimes series and stages.

In the last decade, increased Ir contents were revealed at some stratigraphic levels since Precambrian. Thus, anomalous Ir contents (averaging to 15 mg/t) were established in the Kalyus argillites of the Mogilev-Podolskian series of the Upper Vendian within the Dniester region [3] and at the boundaries: Cambrian–Precambrian in the bottom of Meishucun stage in Southern China [4], Ordovician–Silurian in the persculptus zone bottom in Southern China [5] and at the Dobs-Lynn section in Scotland [6], Frasnian–Famennian in Western Australia [7], Devonian–Carboniferous in China [8], Permian–Triassic in China [9, 10] and USA, Colorado [11], Cenomanian–Turonian, Eocene–Miocene, Serravallian–Tortonian [12], Pleistocene and Holocene in Southern Urals [13].

The many of the above publications consider the high contents of Ir to play an important or crucial role in justification of impact nature of biotic crises. This made the authors of the present paper to search for anomalous contents of noble metals, iridium included, at stratigraphic levels where neither mass extinctions of organisms, nor crisic rebuildings of biota were observed in sea ecosystems [14, 15]. One of these objects is the boundary beds between the Jurassic and Cretaceous systems in northern Siberia.

MATERIALS

A continuous section of marine basin facies of the Jurassic–Cretaceous transient deposits is situated on the Nordwik Peninsula, northern Central Siberia (Fig. 1). The section is characterized by alternation of dark-brown bituminous argillites and bluish-gray condensed clays of the Upper Volgian substage and Berriasian. A complete sequence of ammonite zones and buchiazones (Fig. 2) [16]. There is a Jurassic–Cretaceous boundary layer of phosphate limestone 4–6 cm thick in the bottom of the Berriasian zone Praetollia maynci. It is constant in strike and was observed at a distance about 5 km without visible changes. Macroscopically, the layer is a thin horizontal-laminated brownish-gray rock. Dark-brown points are usually predominant in the central part of the

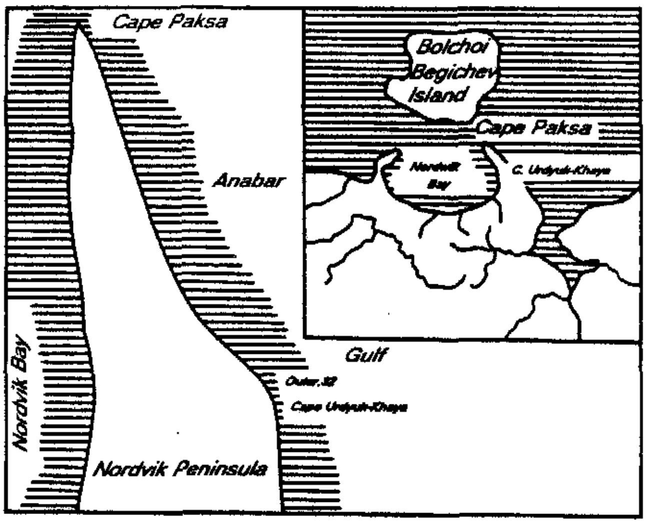


Fig. 1. Localization of the section of transitional layers at the Jurassic–Cretaceous boundary in northern Siberia.

parting. Sulfide inclusions, sometimes in the form of horizontal jets, are dispersed throughout the layer. The bulk chemical composition of specimens sampled through the phosphate limestone thickness is given in Table 1.

TECHNIQUE OF SAMPLING AND ANALYSIS OF NOBLE METALS

One-centimeter-thick plates were cut layer-by-layer with a diamond saw from a phosphate limestone 5–6 cm thick. The plates were ground, and then specimens were prepared of them for analyzing noble metals. Anticipating low (near-clarke) contents of the latter, the authors used a combination of sensitive analytical methods to obtain safe results. The used methods include: radiochemical neutron-activation analysis of silver and gold, acid opening of the specimens (3 g) in analytical autoclaves, sorption-X-ray-fluorescent, extraction-atom-absorption analyses of gold, palladium, platinum, ruthenium, iridium, and osmium [17]. Gold was also determined by the radiochemical neutron-activation method with a detection limit of 0.01 ppb. One of the most efficient methods of determination of ultralow concentrations of Ir, Os, and Ru is authors' radiochemical method using micromelting of radiated specimens to produce a Ni matte.

The weighted specimen of 0.5–1 g in mass after its radiation by a flux of $(3–5)\cdot 10^{18}$ neutron/cm^2 and two-week "cooling" was fused at 1000–1050 °C with a charge of calculated composition, specially selected for certain types of rocks and ores, in specially made refractory crucibles. In some cases, the determination of low Ir concentrations in Ni mattes interferes with radionuclides of silver, cobalt, selenium, antimony, and arsenic. Dissolution of the ground matte in concentrated saline acid yielded a pure insoluble residue containing only platinum group metals (PGM) and gold. The method precludes specimen infection with the PGE impurity

Table 1

Chemical Composition of Phosphate Limestone, wt%

No.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Ba	Ign. loss	Total
18/1	10.22	0.164	3.50	3.85	0.170	2.18	41.55	1.08	0.41	22.497	0.247	13.70	99.57
18/2	5.68	0.091	1.81	2.73	0.162	2.05	47.48	0.84	0.25	28.205	0.334	10.24	99.86
18/3	4.78	0.066	1.60	2.47	0.166	1.89	47.90	0.96	0.21	27.167	0.301	11.93	99.44
18/4	6.96	0.101	2.33	3.77	0.337	2.08	44.75	0.82	0.27	24.106	0.252	13.37	99.14
18/5	10.83	0.182	3.76	4.75	0.209	2.35	41.05	0.90	0.47	17.231	0.177	17.90	9980

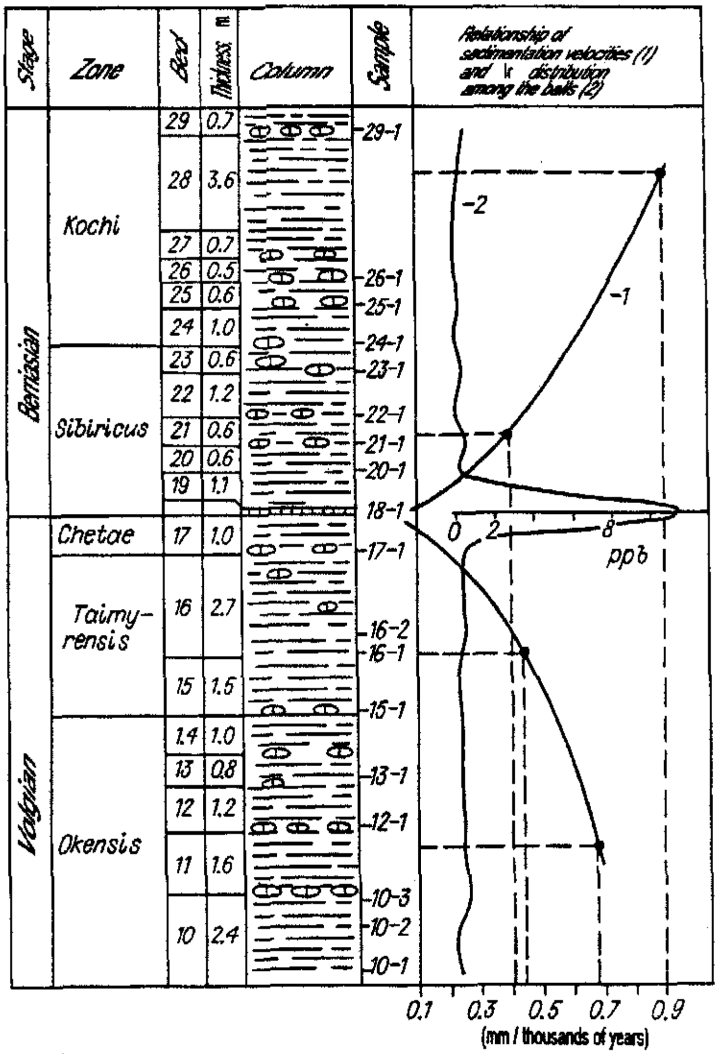


Fig. 2. Stratigraphic column of deposits at the Jurassic–Cretaceous boundary (northern Siberia, Nordvik Peninsula).

contained in charge components and lowers detection limits to $1 \cdot 10^{-12}$ g for iridium and to $1 \cdot 10^{-10}$ g for ruthenium and osmium.

Independently, V. A. Bobrov and S. V. Kiyanov have managed to detect anomalous Ir contents (more than 10 ppb) in some specimens under 24-hour expositions by means of the instrumental neutron-activation method.

GEOCHEMISTRY OF NOBLE METALS

By combining independent nuclear-physical methods, the authors have managed in obtaining commensurate values of gold and PGM for both the interlayer as a whole and layer-by-layer 1-cm-spaced sections (Table 2). Geochemical peculiarities of noble metal distribution based on data of 80 determinations are as follows.

1. Extreme variability of gold contents and PGM in the interlayer both in thickness and along the strike. Gold contents increase gradually to the sole, and PGM, especially Ir and Rh, increase drastically in the central sites of the interlayer (Fig. 3). The limit contents reach the following magnitudes (ppb): Au – 34.4; Pt – 16.0; Pd – 267.0; Rh – 62.0; Ru – 37.0 and Ir – 75.0 (see Table 2).

2. Average gold contents in the interlayer of phosphate limestones given in Table 2 are an order, while PGM several orders as high as geochemical estimates of the clarkes of the corresponding metals for sedimentary rocks [18].

Table 2

Contents of Noble Metals in Specimens Sampled from an Interlayer of Phosphate Limestone in the Cretaceous System Bottom on the Nordvik Peninsula (Cape Urdyuk-Khaya) in Northern Siberia

Sample No.	Element contents					
	Au	Pd	Pt	Rh	Ru	Ir
1/2	16.8–31.6 av. 26.3(3)	60.0–63.0	3.1	11.0–16.3	3.0–13.0	0.05–30.0
2/2	1.4–10.2 av. 6.5(3)	80.0	3.9	9.6–24.0	4.0–37.0	0.05–0.5
3/2	1.4–8.3 av. 4.1 (3)	61.0–91.7 av. 73.9(3)	16.0	62.0	33.0	0.05–0.5,
4/2	3.4–15.8 av. 8.5(4)	113.3–267.0 av. 190.0	12.0	4.3–18.5 av. 11.4	5.3	0.2–75.0 av. 23.6(4)
5/2	1.9–34.4 av. 11.3(4)	5.3-26.7 av. 16.0	2.0	0.0–0.8	5.6–32.0	0.2–25.0
6/2	2.5–4.3 av. 3.0(4)	34.6-97.0	3.6	0.0–0.8	3.1	0.1–0.7
Interlayer average	9.6±4.2 (21)	63.8±21.3 (11)	6.4 (6)	13.6 (10)	15.1 (9)	7.8±4.7 (10)

Note. **In all specimens, Os content is beyond the analysis sensitivity threshold. The number of the samples analyzed is given in parentheses. Analysts, R. D. Melnikova, S. V. Kiyanov (radio-X-ray neutron activation analysis), V. G. Tsimbalist (AAA), Institute of Geology, Siberian Division of Russian Academy of Sciences.**

3. Geochemical trends of distribution of *C1*-chondrite-normalized noble metals are gently inclined from gold to iridium for both interlayer as a whole and its separate sections (Fig. 4). Figure 4, *B* shows borrowed curves [18–20] normalized in the same way demonstrating the noble-metal distribution in cosmic dust and meteorite substance. Their similarity can be indirect evidence of possible cosmogenic nature of the anomalous contents of noble metals. Insignificant disturbances of geochemical trends of "cosmogenic" type add increased gold concentrations confined to the interlayer bottom and, probably, connected with a terrigenous source.

Similar trends of distribution and extremely nonuniform contents made us to search for carriers of noble metals and signs of cosmic dust described somewhere [19–21]. The problem was solved in two ways:

— by isolation of a heavy fraction and its subsequent microprobe and neutron-activation analysis;

— by preradiation of 1-g specimens by a flux of thermal neutrons of $1 \cdot 10^{18}$ n/cm^2 and subsequent neutron-activation analysis for Ir of separate light and heavy fractions.

The heavy fractions were isolated from 50-g specimens ground up to 1 mm and treated for 24 hours by 1N hydrochloric acid. Along with a small impurity of terrigenous minerals, there are two types of sulfide formations:

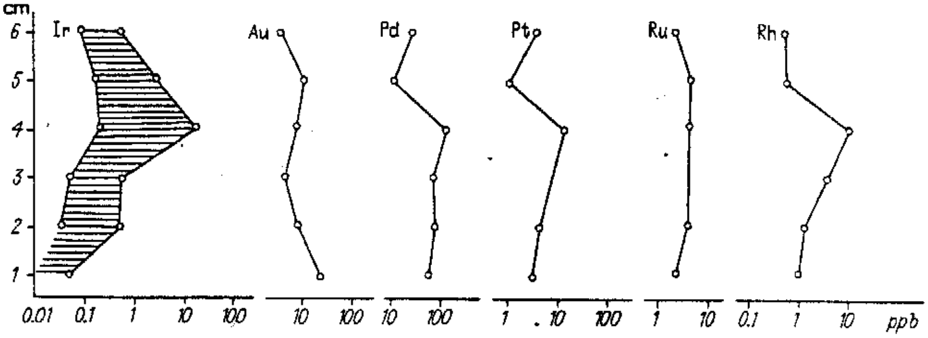


Fig. 3. Vertical profiles of distribution of Ir, Pd, Au, Pt, Ru and Rh contents (ppb) in an interlayer of phosphate limestones.

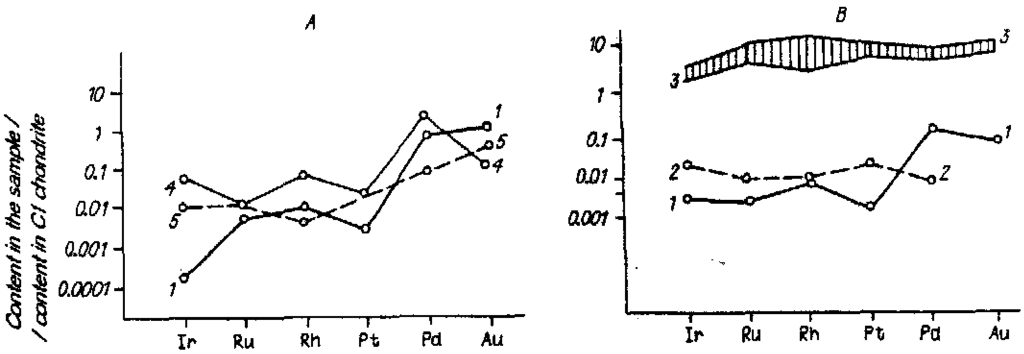


Fig. 4. Geochemical distribution trends of *C1*-normalized noble metals. *A* — In sections *1, 4, 5*; *B* — throughout the interlayer (*1*), in cosmic dust (*2*) and iron meteorites (*3*) according to [18–20].

irregular micronodules with yellowish-gray crystalline surface and perfect globules with bright silver surface. According to phase X-ray-structural investigations, both varieties are represented by pyrite with an admixture of amorphous phase. The microprobe analysis has confirmed pyritic composition of these formations and revealed increased contents of cobalt, nickel, and chrome.

According to data of 111 measurements, the globule diameters range from few to 100 μm to average 50–70 μm (Fig. 5). With scanning electron microscope magnifying 36,000 times we have observed heterogeneities of the "shrinkage crack" type, microcraters and singular cones like the tails of solidified melted drops on the globule surface. As opposed to micronodules, the globules are weakly magnetized, many of them are hollow (see phototable). In many morphological signs, the globules are like those described from the Permo-Triassic siliceous formations of Japan [21].

For the purpose of Ir neutron-activation analysis we managed to sample 493 globules of 0.11 mg in total mass and micronodules of 1.04 mg in the material of the heavy fraction isolated from a united specimen of 150.7 g in weight. The globules and micronodules were placed into quartz drots, sealed and radiated by a flux of thermal neutrons of $3 \cdot 10^{18}$ n/cm^2. After the specimens having been cooled for two weeks, we managed to determine by instrumental neutron-activation analysis the following iridium contents: 230 ppb in pyrite nodules and 1200 ppb in pyrite globules.

Thus, the pyrite globules appeared to be the most concentrated carrier of iridium. Although the micronodules contain Ir as low as a half of order, they also are an important concentrator of PGM's, as their total mass dominates over pyrite globules. The same conclusion about the connection of anomalous Ir contents with a sulfide fraction is made on the basis of a successive neutron-activation analysis of several liquid and solid monomineral fractions obtained by solving a preradiated specimen in hydrochloric acid and its later separating.

DISCUSSION

Anomalously high contents (AHC) of iridium and other noble metals in northern Siberia at the Jurassic-

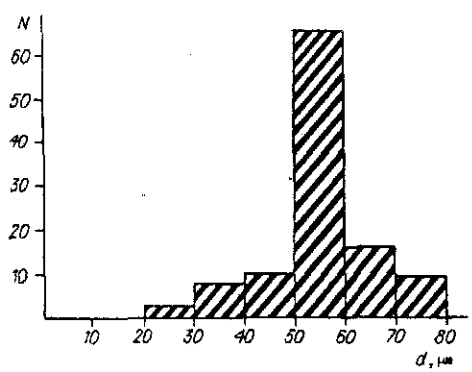
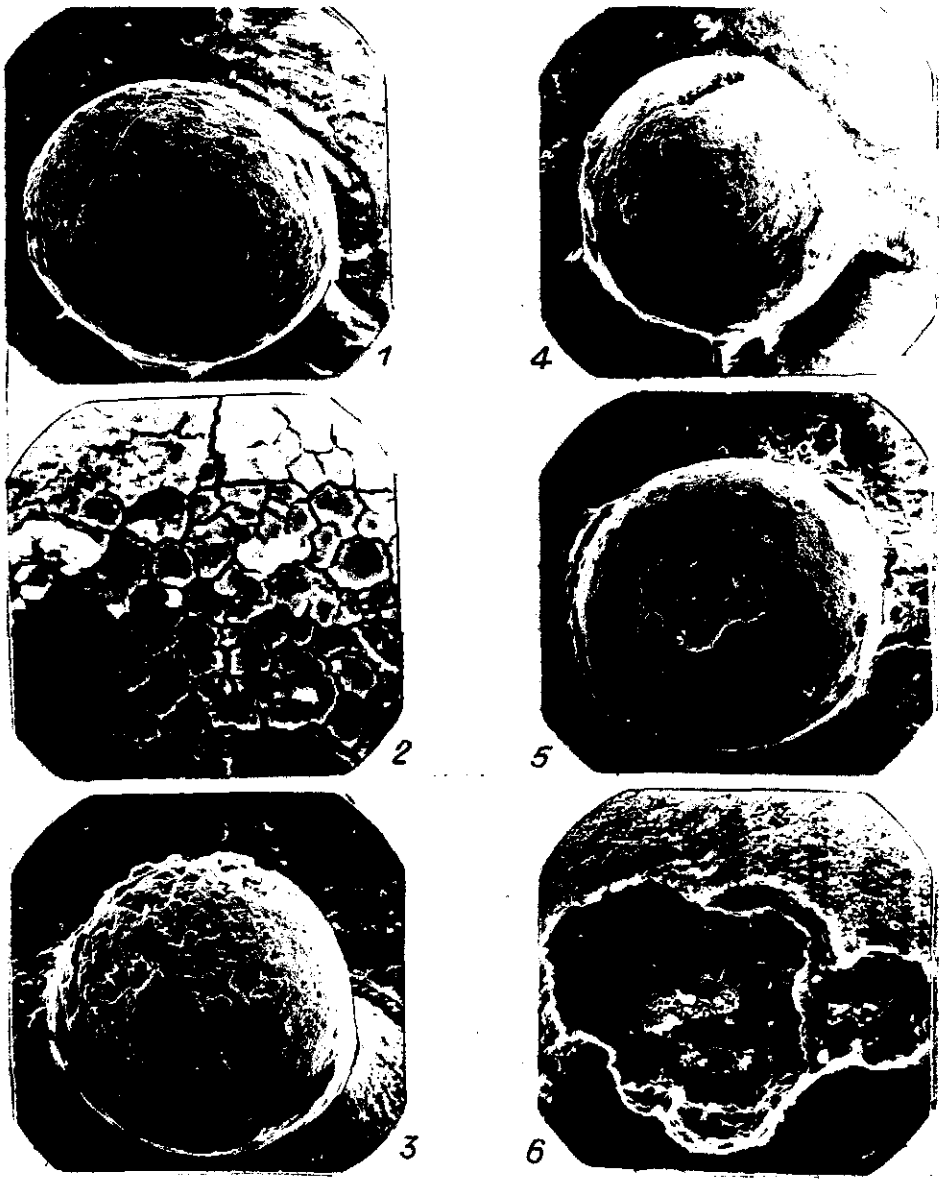


Fig. 5. **Histogram of sizing of Ir-bearing (1200 ppb) pyrite globules (μm). *N* — Number of measurements, *d* — globule diameter.**



Structure of "globule" surface under electron scanning microscope from Jurassic–Cretaceous boundary deposits in the Nordvik Peninsula (northern Middle Siberia).

Fig. 1. Sp. 33/18-1, × 5,500; a typical globule from a sample of 111 specimens.

Fig. 2. The same specimen, × 36,500; a dense net of the "shrinkage-type" cracks is seen on the globule surface.

Fig. 3. Sp. 33/18-2, × 6,000; the globule is partly corroded, probably because of possible dissolution of some part of surface substance.

Fig. 4. Sp. 33/18-3, × 400, a large globule with protrusions on the surface of the type of legs of solidified drops.

Fig. 5. Sp. 33/18-4, ×5,500; a cavern-containing globule.

Fig. 6. The same specimen, ×16,600; a hollow cavity is seen inside the cavern.

Cretaceous boundary seem to have no connection with impact of a comet or other cosmic bodies. Within the region under consideration there are no signs of volcanism or basite magmatism which could serve a source of anomalous contents of noble metals. Their correlation with biogenic processes is also ruled out, because contents of organic carbon are distinguished by their rather monotonous distribution along the section near the Jurassic-Cretaceous boundary [22].

One of possible explanations of AHC of noble metals in terrigenous deposits is based on the supposition of a drastic decrease in sedimentation rate at the Jurassic-Cretaceous boundary in the central part of the paleobasin against the background of uniform supply of cosmic dust (effect of sedimentation undercompensation).

Analysis of thicknesses of ammonite zones at the Jurassic-Cretaceous boundary has shown that the sedimentation rates in the central Khatanga paleobasin dropped quickly from early to late Late-Volgian, then increased since the Berriasian. The sedimentation rate during formation of a 6-cm interlayer of phosphate limestone was, at least, an order as low as in the early Late-Volgian or in the middle Berriasian (see Fig. 2).

In the transitional time between the Jurassic and Cretaceous periods large restructurings in marine biota are noticed nowhere in the world and, in particular, neither in North-Siberian paleogeographical province, nor in the circumpolar region as a whole. In general, this boundary is one of the most "quiet" in the Phanerozoic in evolution of main groups of marine biota: ammonites, belemnites, bivalves, foraminifers, dinoflagellates (see Fig. 2).

The facts given make us to revise the hypothesis adopted by geologists and, partly, paleontologists that everywhere where mass extinctions are established and AHC's of platinum metals, in particular, cosmogenic Ir are found, the cause of these extinctions is the Earth's collision with one or more large cosmic bodies.

In many cases, the main destabilizing factors were drastic temperature variations and typically related high-dynamic glacioeustatics of the ocean.

The area-restricted AHC's of platinoids is more logically explained by a specific nature of sedimentation processes on the particular sites taking into account paleogeographic features of the territory.

CONCLUSIONS

1. At the Jurassic–Cretaceous boundary in the Berriasian bottom in an interlayer of phosphate limestones, we have established AHC's of iridium and other noble metals, whose trends normalized after *C1* chondrite are similar to iron meteorites and cosmic dust.

2. Mineral aggregates, Ir carriers, are established, which occur as micronodules and globules of pyrite composition and contain 230 and 1200 ppb Ir, correspondingly; they are related with diagenetically sulfidized iron particles of cosmic dust.

3. Based on general geological situation, geochemical trends of noble metal distribution and composition of Ir-bearing sulfide mineral aggregates, the nature of the geochemical anomaly of noble metals is explained by a drastic retardation of sedimentation rates at the Jurassic–Cretaceous boundary under conditions of supply of cosmic dust.

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