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Noble Metals in Cretaceous/Tertiary Sediments from El Kef

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Abstract

Sediments from El Kef, Tunisia, were analysed by RNAA for Au, Ir and Os. All three elements show a 10 – 20 fold enrichment at the Cretaceous/Tertiary boundary. This enrichment must be the result of the addition of material with a high concentration of noble metals. It is plausible that this exotic material has an extraterrestrial origin.

Introduction

Siderophil elements (e.g. Ir, Pt, Ni) are normally very much depleated in the earth crust because of the formation of the earth core. The enrichment of noble metals in sediments from the Cretaceous/Tertiary boundary was first reported by ALVAREZ *et al.* [1] a few years ago. These authors propose, that the pronounced enrichment of Ir in sediments deposited 65 million years ago must be the result of the addition of extraterrestrial material with cosmic composition. Since the publication of these results many laboratories investigated sediments from various locations and of variable age for noble metals [2 – 4]. A very complete section of sediments containing the Cretaceous/Tertiary boundary was found in El Kef, Tunisia. This material was described by PERCH-NIELSEN [5]. Following macroscopic studies of the nanofossils, aliquots of this material were provided for chemical analyses for Os, Ir and Au.

Experimental

Sample description

The chemical composition of the analysed sediments changes considerably from below to above the Cretaceous/Tertiary boundary [5]. The $CaCO_3$ content decreases sharply at the boundary from 37% to about 5% and reaches 0% in 3 samples of the boundary clay. It increases slowly above these samples but does not again reach Cretaceous values in the measured samples. The weight percent distribution of clay minerals is as follows: more than 50% kaolin, 25 – 30% montmorillonite and 5 – 10% illite. Neither mineralogy proportions change significantly across the boundary.

Procedure

The dried material was sealed in suprasil vials and irradiated together with element standards for two days in the swimming pool reactor SAPHIR.

The irradiated samples were fused in crucibles of zirconium with NaOH and Na_2O_2 in presence of carriers of the interesting elements. After the decomposition of the melt, sulfides were precipitated and separated by centrifugation. The precipitate was transfered into a still head and acidified by 20 ml conc. HNO_3. During the destillation H_2O_2 was added continuously. OsO_4 was collected in 6 *M* NaOH. The residue of the destillation was transformed into the chlorides by multiple addition of conc. HCl and loaded onto an anion exchange column (Dowex 1 × 10, 100 – 200 mesh, diameter 1 cm, length 7 cm). The columns were then washed with 50 ml of 6 M HCl. A reduction with 50 ml of 0.1 *M* H_2SO_3 was performed and the Ir was eluted with 50 ml of 6 *M* HCl. Metallic Au on the column was dissolved with 10 ml of aqua regia 1 : 1 followed by washing with 20 ml H_2O. Finally, Au was eluted with 50 ml of a 10% solution of thiourea. An outline of the chemical separation is presented in Fig. 1. This is a modification of the procedure of KEAYS *et al.* [6]. The necessary radiochemical purification for the 3 elements was obtained by the following treatment:

- Gold with the shortest half live (2.7 d) was purified first and prepared for activity measurements. The Au solution was made alcaline with NH_3. Decomposition of thiourea produced Au_2S_3, which was dissolved in aqua regia, transformed to chlorides and reprecipitated as Au_2S_3. The chemical yield was 65 – 85%.
- Os was further purified by a second OsO_4 destillation and recovered as a complex of thiourea. The final precipitate was $Os(NH_2CSNH_2)_6Cr(SCN)_6$. The chemical yields were 50 to 70%.
- The solution containing Ir was evaporated on a water bath and dissolved in 0.03 *M* HCl. This solution was passed through a cation exchange column (Dowex 50 W × 8, 50 – 100 mesh) and Ir was collected in small glass tubes and measured on a well type detector. The chemical yield was determined by atomic absorption (50 – 60%).

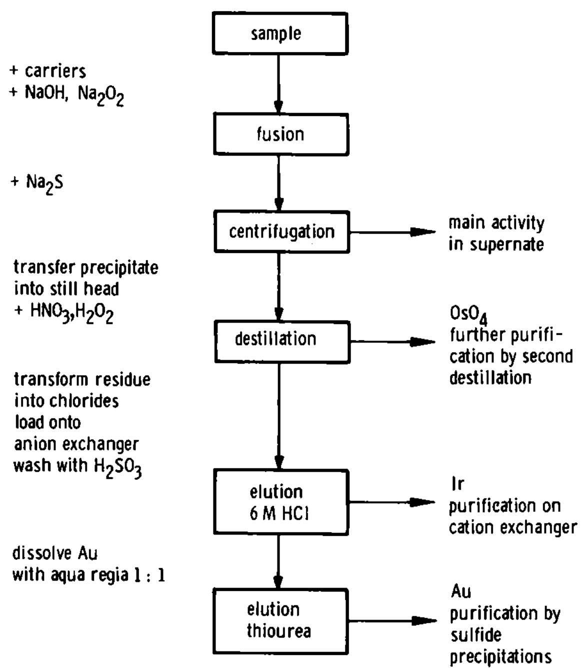

Fig. 1. Scheme of main separation and purification steps.

Results and discussion

The measured concentrations of Ir, Au and Os in the samples are summarized in Table 1 together with their distances above and below the Cretaceous/Tertiary boundary. The highest concentrations are observed at the boundary itself. The averages of the values of sample LM 31, LM 22 and LMC 16 are considered as the natural background content of these elements in the sediments at El Kef. At the boundary layer we observed a 16, 19 and 9 fold enrichment for Au, Ir and Os, respectively. This pronounced enrichment can be explained by small additions of material with extremely high concentrations of these elements. Material with these properties for the 3 geochemically different elements is found in meteorites.

However, at present there is no type of meteorite known with the observed ratios of the 3 elements. The original ratio may have been altered by fractionations e.g. by volatilization during the impact or by weathering during the prolonged contact with water. In addition, the effect of the observed bioturbation and gardening of a discrete layer upon the element ratios is not known. Under the assumption of a density of the sediments of 2 g cm^{-3}, a thickness of the analysed layers of 1 cm and a linear gradient of the concentrations for the trace elements between measured values, an integral enrichment of 66 ng Ir cm^{-2} is calculated. This corresponds to an addition of 125 mg cm^{-2} of material with a cosmic composition (e.g. C-1 meteorites [7]). RAMPINO and REYNOLDS [8] as well as others [e.g. 9, 10] dispute an extraterrestrial origin of the admixed material to the Cretaceous/Tertiary boundary clay at El Kef on the basis of the lack of ejecta from the impact site. They believe together with others [11] that at least 10 times more target material than projectile material should be found at the boundary. But their detection limit is only about 5% of admixed material with a different composition. It is also difficult to estimate the amount of ejecta which would be produced in case the impact had occured in the ocean. RAMPINO and REYNOLDS prefer vulcanic eruptions as cause for the anomalies. However, with this explanation it is very difficult to account for the distinct enrichment of the very refractory noble metals. On the other hand, SMIT and KLAVER [12] found sanidine spherules in the boundary clay at Caravaca, Spain, which were undoubtly produced by an impact.

The second, less pronounced enrichment found in our sample about 25 cm above the C/T boundary is not easy to explain. GLASS *et al.* [13] report two layers of mikrotektites about 10 cm apart in a North American sediment which are accompagned by enhanced Ir concentrations. These authors interpret the double layer as being produced from a single impact event by subsequent settling in a high water column (e. g. the ocean) at different sedimentation rates due to different densities of the particles. If similar processes operated after the Cretaceous/Tertiary event two horizons could only be detected in an area with extremely high sedimentation rates. This can be assumed for El Kef. However, this explanation needs further proof.

Table 1. Au, Ir *and* Os *concentrations* (ppb) *in sediment samples from El Kef.* Errors 1 σ. Distance from boundary: + denotes above, − beneath the boundary. The osmium in sample LMC 9 was lost

Distance from boundary in cm	Sample code	Au	Ir	Os
+ 670	LM 31	0.50±0.05	0.50±0.15	0.30±0.05
+ 650	LM 22	0.20±0.01	0.30±0.01	0.20±0.02
+ 32	LMC 1	1.55±0.10	2.30±0.10	1.10±0.10
+ 22	LMC 5	0.35±0.02	0.40±0.02	0.80±0.05
+ 16	LMC 5	0.40±0.05	1.05±0.05	0.50±0.05
+ 10	LMC 9	0.50±0.02	0.80±0.05	–
+ 6	LMC11	4.05±0.05	1.60±0.10	2.05±0.15
+ 3	LMC12	1.60±0.10	2.00±0.10	1.70±0.10
0	KPN 12/13	5.1 ±0.9	6.5 ±0.4	2.70±0.15
− 3	LMC13	0.25±0.01	0.85±0.05	0.65±0.05
− 10	LMC16	0.25±0.01	0.22±0.01	0.35±0.05

Conclusions

- Sediments at the Cretaceous/Tertiary boundary at El Kef, Tunisia, show an enrichment of noble metals (Au, Ir, Os) of up to a factor 20 compared to average concentrations at the same location.
- Two peaks can be distinguished in the concentrations of Au, Ir, and Os in the investigated sediment section from Tunisia. This result needs further investigation.
- An extraterrestrial origin of the exotic admixed material is plausible.
- At this time it is not possible to deduce the composition of the impacting body since fractionation may have altered the original concentrations of the measured elements.

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