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PLATINUM-GROUP ELEMENTS IN THE CORES OF POTASSIUM FELDSPAR SPHERULES FROM THE CRETACEOUS-TERTIARY BOUNDARY AT CARAVACA (SPAIN)

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ABSTRACT

The abundant spherules present in the Cretaceous-Tertiary boundary layer at Caravaca are diagenetically transformed to potassium feldspar. Before our study no possible relicts of the precursor material had been reported, but in this paper we describe the presence of cores in these spherules that could represent a relict of the «unknown precursor». These cores are made up of C mixed with Si, Mg, Al, Cr, Ca among other elements. Laser Ablation System analysis also reveals an enrichment in PGE could suggest an extraterrestrial origin for this material. Pt, Pd and Ir do not show a chondritic ratio; however, a severe modification of their concentration could be expected during the early diagenetic processes.

Key words: *PGE, cores, potassium feldspar, spherules, Cretaceous-Tertiary boundary.*

RESUMEN

Las esférulas existentes en la lámina de sedimento del tránsito Cretácico-Terciario de la sección de Caravaca han sido transformadas diagenéticamente a feldespato potásico. En este trabajo se describe la existencia de núcleos encontrados en el interior de las esférulas, los cuales pueden representar relictos del material precursor. Dichos núcleos están constituidos por C, Si, Mg, Al, Cr y Ca entre otros elementos. Se pone de relieve, por vez primera, su notable enriquecimiento en elementos del grupo del platino, cuyas relaciones no condríticas pueden ser debidas a la existencia de importantes modificaciones en su concentración inicial causadas por los procesos diagenéticos y por la existencia de materia orgánica.

Palabras clave: *Elementos del grupo del Pt, feldespato potásico, esférulas, límite Cretácico-Terciario.*

Introduction

One of the most outstanding characteristics of the Cretaceous-Tertiary (K/T) boundary layer at Caravaca (Betic Cordilleras, SE Spain) is the presence of K-feldspar spherules. Smit & Klaver (1981) were the first to describe these spherules, suggesting that the potassium feldspar formed at high temperature as a consequence of an impact event. The quench-crystal textures presented and the morphology similar to microtektites led these authors to link the origin of the spherules to an extraterrestrial bolide. Subsequent research has shown that the feldspar is of diagenetic origin and formed at low temperature (e. g. Montanari *et al.*, 1983; DePaolo *et al.*, 1983; Ortega Huertas *et al.*, 1992; Smit *et al.*, 1992; Martínez Ruiz, 1994).

The textures and morphology of the spherules really support an extraterrestrial origin although their characteristics differ from those of microtektites. Applying the new term proposed by Glass & Burns (1987) and used later by Smit *et al.* (1992), the diagenetically altered spherules from the K/T boundary should be considered as microkrystites. Among ot-

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her differences, the microkrystites show evidence of a crystalline phase, whereas the microtektites are of glassy nature, and microkrystites are associated with iridium anomalies.

As in Caravaca, in most of the known K/T sections the spherules are diagenetically altered, with total replacement of the original material. In this case the K-feldspar replaced the precursor and no relicts have been reported before now.

In this paper we describe the presence of a possible relict of the «unknown precursor». The discovery of cores in the K-feldspar spherules, whose composition differs from that of the K-feldspar, suggests the existence of such relicts. In addition, the high content of platinum group elements (PGE) in the cores also supports the possible extraterrestrial origin of this material.

Table 1.—**Microprobe data (wt %) of the Kfs spherules**

	K-feldspar		Core
	Mean n = 10		Mean n = 10
SiO_2	64.90	SiO_2	27.35
TiO_2	0.04	TiO_2	0.49
Al_2O_3	18.29	Al_2O_3	4.67
FeO	0.08	FeO	5.45
MnO	0.004	MnO	0.02
MgO	0.01	MgO	3.76
CaO	0.08	CaO	1.47
Na_2O	0.08	Na_2O	0.74
K_2O	15.55	K_2O	0.63
BaO	0.001	BaO	0.002
		SrO	0.04
Total	99.04	Total	44.62

Methods

The spherules were isolated from > 63 μm fraction and then separated by hand-picking using a stereoscopic microscope. For the study of the K-feldspar spherules and their cores, the following techniques were used: X-ray diffraction using a Philips diffractometer with automatic slit (Department of Mineralogy and Petrology of the University of Granada); Scanning Electron Microscopy (SEM) (DSM 950 equipped with Link microanalysis QX 2000) and Electron Microprobe (Cameca Camebax SX 50) (Centro de Instrumentación Científica of the University of Granada); SEM (Cambridge S360 coupled with a Link AN10000 ED detector, University of Bari). In particular, the C in the core of 35 % of the spherules was detected and quantified using the Link detector in windowless position with acceleration voltage set at 9 kV. Trace-element microanalyses on some cores were carried out using a Perkin Elmer 302 Laser Ablation System coupled to a PE Scier ICP-MS Elan 5000 Spectrometer (Perkin Elmer, Uberlingen, Germany). Calibration was done in two ways: externally, with NBS-612 glass; internally, using SiO_2 (previously determined by microprobe in the same sections) as standard. The detection limits is 0.1-0.15 ppm.

Potassium feldspar spherules and composition of the cores

The bulk mineralogy of the K/T boundary layer at Caravaca is essentially characterized by 80 % of smectites $(Si_{3.63}\ Al^{IV}_{0.37})\ O_{10}\ (Al^{VI}_{1.30}\ Mg_{0.34}\ Fe_{0.46}\ Ti_{0.04})\ K_{0.23}\ (OH)_2$, 10 % of calcite and 5 % of quartz, as well as small amounts of kaolinite, illite, palygorskite, chamosite (Fe = 2.21 a.f.u. and Mg = 0.98 a.f.u), celestite, barite, gypsum, rutile and zircon. Transmission Electron Microscopy has been used to study both smectites and minor minerals. The total carbon content (TOC) in the K/T boundary layer is 0.27 % and 0.23 % at the beginning of the Danian (1 cm above K/T), with much lower values in later Tertiary levels (0.08 %, sample at 10 cm above K/T).

K-feldspar spherules are very abundant at Caravaca. Their size usually ranges from 100 μm to 500 μm, with sizes outside this range less frequent. Morphologies are globulous, either spherical or drop-shaped. They present a porous structure in which the crystals of K-feldspar are distributed in fibroradial and dentritic textures (Martínez Ruiz *et al.*, 1992; Martínez Ruiz, 1994). The EPMA analyses of the K-feldspar reveal a composition (Table 1) close to the $KAlSi_3O_8$ end member. Its structural characterisation corresponds to a monoclinic Kfs ($\Delta = 0$) with a moderately ordered Si:Al distribution (T_1o and $T_1m = 0.41$, $2T_2 = 0.19$) similar to that of orthoclase or adularia. However, one of the most interesting results obtained during our study was the discovery of cores made up of C and a mixture of Si, Ti, Al, Mn, Mg and Na (Table 1) whose sizes usually range from 10 to 20 μm (fig. 1a). The SEM backscattered image of the spherule cores reveals a composition with an average atomic number clearly lower than that of K-feldspar (fig. 1a). This is due to the systematic presence of C, with most frequent percentages of around 50 %, although proportions of 90 % have been punctually detected by SEM. EPMA analyses reveal that there is scarcely any chemical variation in any one core, which indicates that the carbonaceous material is mixed with the other chemical elements on an extremely fine scale. The Ablation Laser System analyses also reveal strong enrichment in Ir (0.59 ppm), Pd (15.70 ppm), Pt (2.89 ppm), Ru (6.33 ppm), Rh (4.31 ppm) and Ni (3000 ppm).

Discussion

Cores found in the impact-related K-feldspar spherules from the Cretaceous/Tertiary boundary layer at Caravaca are possibly a relict of the precursor mate-

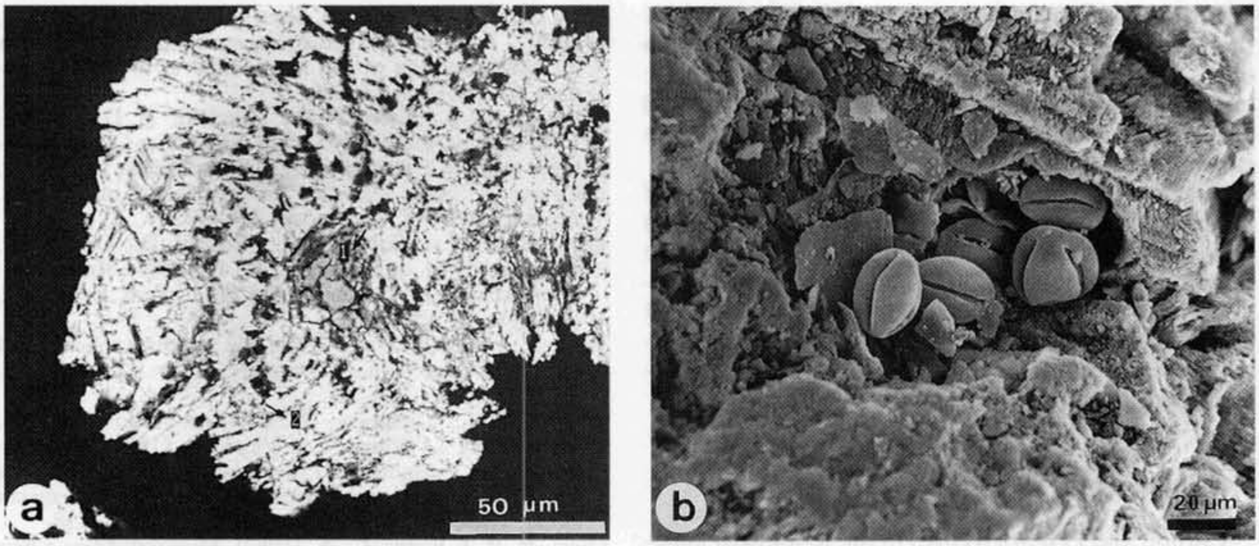

Fig. 1.—SEM micrographs of microkrystites from Caravaca. a: Backscattered image: 1, carbonaceous core; 2, authigenic Kfs. b: Pollen grains replaced by Kfs.

rial of the spherules, but it is difficult to affirm their exact nature. The cores could be similar to carbon rich veins described in ureilites by Tomeoka & Takeda (1990), whose origin is linked to carbonaceous chondrites. In Caravaca an organic association of Ir has been proposed; Schmitz (1988) considered that 50 % of the bulk sample Ir is associated with organic compounds. On the other hand, the presence of relict carbon (microdiamonds) has been reported in the Cretaceous/Tertiary boundary layer at Red Deer Valley (Alberta, Canada) by Carlisle & Braman (1991). Recently an extraterrestrial origin for these microdiamonds was confirmed by Carlisle (1992).

The values obtained for the PGE are highly significant and show a clear enrichment that could suggest an extraterrestrial source. However it is difficult to prove extraterrestrial derivation of the PGE-rich cores, which do not present chondritic ratios. In fact, the spherule cores present a ratio Σ(Ir, Pd, Pt)/Ni = 0.006, which is much higher than the chondritic ratio (0.002). Indeed, even the ratios between the different PGE show enrichment in Pd and Pt as regards Ir, and of Pd as regards Pt (Pd/Ir = 26.61, Pt/Ir = 4.90, Pd/Pt = 5.40).

To explain the high concentration of PGE in the spherule cores, it is necessary to take in account that PGE can be remobilized in most geological environments. Although the processes contributing to remobilization of PGE in sedimentary environments are not well understood, among other reasons because they are present in concentrations that are sometimes very difficult to detect, it is clear that remobilization is possible in this environment. Dyer *et al.* (1989) carried out different experiments to show that certain types of cyanobacteria can play an important role in Ir concentration. During processes of early diagenesis of the sediments, microbial activity could have therefore considerably modified the Ir concentration. The experiment by De Lange *et al.* (1991) showed that Ir anomalies may be explained by remobilization and redox controlled precipitation and Mountain & Wood (1988) also showed that mobility of PGE is possible at temperatures characteristic of sedimentary environments. Other authors as Bowles (1986), Wallace *et al.* (1990), Evans *et al.* (1993) or Sawlowicz (1993) have reported low temperature mobilization of PGE.

Isotopic composition of the boundary clay and K-feldspar spherules (DePaolo *et al.*, 1983) reveals that the K/T at Caravaca underwent severe modification during diagenetic processes, with important neoformation of mineral phases. There is evidence which proves that the Kfs is clearly of authigenic origin and formed at low temperature, such as the fact that its composition corresponds to an end-member of the alkaline series, and, moreover, is of high chemical purity (Table 1), both of which are characteristics of this type of genesis (Kastner & Siever, 1979); also the $\delta^{18}O$ value is 27 ‰ (Epstein, 1982). In addition, the presence of pollen grains replaced by Kfs (fig. 1b) is also significant. This indicates the Kfs could therefore have replaced the spherules and possibly other particles.

The PGE may have been remobilized during diagenetic alteration, and therefore chondritic ratios of these elements could not be expected. During the early diagenetic processes the presence of organic matter, complex-forming elements, and the pH and Eh conditions could have considerably affected the concentrations of the PGE.

Other impact signatures such as Ni-rich spinels of cosmic origin (e. g. Bohor, 1990; Robin *et al.*, 1992) and shocked minerals (e. g. Bohor, 1990) support the hypothesis that the Ir is due to an extraterrestrial origin. However, the high concentration in Ir, Pd or Pt could be the result of concentration by terrestrial processes rather than a consequence of exclusively extraterrestrial contamination.

Conclusions

Carbon and PGE-rich cores in the K-feldspar spherules from Caravaca are possibly a relict of the precursor material of the spherules. The high PGE content could suggest an extraterrestrial origin, although these elements do not show a chondritic ratio. Other impact signatures in the boundary layer may support an extraterrestrial origin of the PGE, but the considerable alteration that took place in the K/T layer during the early diagenetic processes could led to a severe modification of their original patterns. Therefore the enrichment is not only the consequence of extraterrestrial source but also the result of terrestrial processes, in particular diagenesis and carbon acting as a geochemical trap for the PGE.

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