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Quench textures in altered spherules from the Cretaceous–Tertiary boundary layer at Agost and Caravaca, SE Spain

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Abstract

Abundant spherules are observed in a well preserved Cretaceous–Tertiary boundary (KTB) layer at the Agost and Caravaca sections (Betic Cordilleras, SE Spain). These spherules have been diagenetically altered to goethite or K-feldspar. Different morphologies are observed ranging from perfect spheres to droplet shapes. This is the first time that dendritic and fibroradial textures are reported in goethite spherules with clearly splash-form morphology. This morphology suggests that they originated from melt in the hot vapour plume and not as condensate. As unaltered KTB spherules are composed of clinopyroxene, this could be the probable precursor of part of the altered spherules at Agost and Caravaca, which may have been derived from an expanding vapour plume with a significant contribution of extraterrestrial material. In addition C-rich cores have been detected in K-feldspar which are enriched in Ir, Pt, Pd and Ni. Although postdepositional processes and microbial activity could have led to severe modification of the original element concentrations, the high content of noble metals and Ni suggests extraterrestrial contamination.

Keywords: Cretaceous–Tertiary boundary; spherules; textures; diagenesis; C-cores

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1. Introduction

Since Alvarez et al. (1980) proposed the impact theory to explain the mass extinction at the end of the Cretaceous, several lines of evidence have been cited to support their model, including noble metal anomalies (e.g. Smit and Hertogen, 1980; Kyte et al., 1980, 1985), the discovery of shocked minerals (e.g. Bohor, 1990), Ni-rich spinels (e.g. Kyte and Smit, 1986; Bohor and Foord, 1987; Izett, 1987; Bohor, 1990; Robin et al., 1991), and the presence of spherules that may be impact-related (Smit and Klaver, 1981; Montanari et al., 1983; Montanari, 1991; Smit et al., 1992; Pollastro and Bohor, 1993).

The impact origin of the spherules has been questioned by a number of authors since they were first reported by Smit and Klaver (1981) at the KTB in Caravaca (Spain), but over the past decade evidence for a high-temperature origin has increased constantly. Examples are a more complete record of the KTB spherules and their differentiation in two strewn fields, one apparently restricted to North America and the Gulf of Mexico, and the other with

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worldwide distribution, their association with high-temperature phases that have survived diagenetic alteration and other impact signatures (e.g. Montanari, 1991; Smit et al., 1992; Pollastro and Bohor, 1993; Kyte and Bohor, 1995).

Spherules are restricted to the boundary layer. The nature of this layer differs according to the distance from the Chicxulub structure in Yucatan. In proximal sections, such as those reported in the Western Interior of North America, and the Caribbean (e.g. Beloc in Haiti), the KTB is marked by a two-layered clay unit. The lower claystone layer represents melted siliciclastic target rocks, whereas the uppermost layer mainly consists of altered vitric dust and contains shocked material and magnesioferrite crystals. Its composition and a high Ir content suggest that this layer originated from a cloud of vaporized bolide and target material (Bohor, 1990; Pollastro and Bohor, 1993). The KTB layer in distal sections is equivalent to the uppermost layer of the clay unit in proximal sections. Two types of spherules have also been reported at the KTB occurring in two different strewn fields (Bohor and Betterton, 1990; Smit et al., 1992; Bohor and Glass, 1995). One type is interpreted as originally composed of target rock melt glass, with a radial distribution around the impact crater in the Caribbean area. These are smectitic spherules with minor amounts of glass in Haiti and Mexico and are confined to the lower layer of the clay unit. The other type, confined to the upper layer of the clay unit in proximal sections and to the single-layered boundary in distal sections, are the globally distributed spherules referred to as microkrystites by Smit et al. (1992) and interpreted by some authors as formed from condensed material from the impact vapour cloud (e.g. Pollastro and Bohor, 1993). Most of these globally distributed spherules are composed of authigenic phases that have replaced the original material and it is therefore difficult to know the exact nature of such material.

We have studied the spherules from the Agost and Caravaca sections. Some previous papers (e.g. Smit and Hertogen, 1980; Kyte et al., 1985; Groot et al., 1989; Smit, 1990; MacLeod and Keller, 1991; Martínez Ruíz et al., 1992) showed these sections to be among the most complete marine sections, in which the KTB layer provides an excellent record of the KTB event. At Agost and Caravaca spherules are microkrystites composed of K-feldspar and Fe-oxides. K-feldspar spherules at the Caravaca section were first identified as high-sanidine by Smit and Klaver (1981), who suggested that these spherules solidified from a melt probably derived from the impacting body. Further studies by Epstein (1982), Shaw and Wasserburg (1982) and DePaolo et al. (1983) supported an authigenic origin for the K-feldspar. Montanari et al. (1983) interpreted these spherules as diagenetically altered spherules of basaltic composition produced by the impact of a large asteroid in an oceanic basin. Alternatively, Bohor (1984) suggested that they may be droplets of the meteoritic projectile itself and not of the target material.

As we are dealing with diagenetically altered phases, we have focused this study on the morphology, texture and any possible relict of the original material, in search of clues to the spherule origin.

2. Location of samples

The Agost section is located 2 km north of the village of Agost in the province of Alicante. The Caravaca section is located in the 'Barranco del Gredero' 4 km from the village of Caravaca in the province of Murcia (Fig. 1). Both sections belong to the Betic Cordilleras (SE Spain) which are part of the peri-Mediterranean Alpine orogenic belt.

At both sections marl is the predominant lithology. Light-green marly limestones correspond to the Cretaceous and a clayey layer 2–3 mm thick appears in clear contact on top of this material. This layer marking the KTB is completely altered, causing its usual appearance in shades of red. On the top of the KTB greenish marly clays are deposited, whose carbonate content gradually increases, giving way to marls and marly limestones of lighter colour. The spherules are confined to the boundary layer. Our data confirm the abundance of 200–400 spherules/cm^3 cited by Smit (1990) at Caravaca in both sections.

Concerning the mineralogy of these sections, both of them are composed mainly of calcite, quartz and clay minerals (smectite, illite and kaolinite). The KTB is characterized by a sharp decrease in carbonate content and by an important increase in clay minerals. In both sections the smectite content

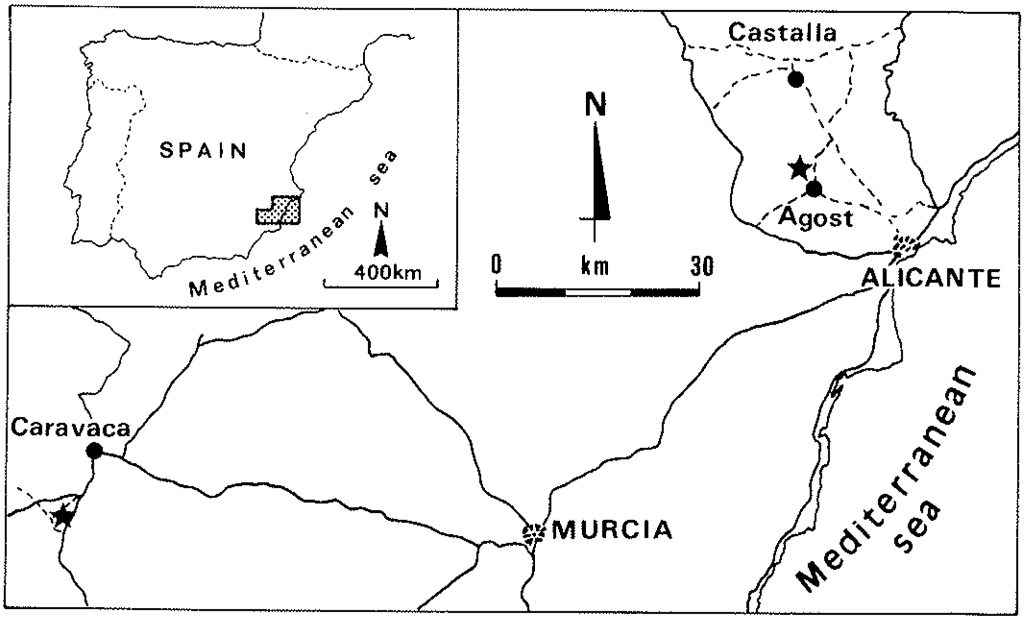

Fig. 1. Location of the Agost and Caravaca sections.

increases significantly at the boundary layer, where the spherules and smectites are the main components together with minor proportions of illite and kaolinite (Ortega Huertas et al., 1995).

3. Methods

X-ray diffraction (XRD), scanning electron microscopy (SEM), electron microprobe analysis (EMPA) and inductively coupled plasma–mass spectrometry (ICP–MS) were used for the mineralogical and geochemical study of the sections.

The spherules were studied by sieving representative amounts of samples from each boundary layer. They were recovered from the >53 μm fraction by hand-picking using a stereoscopic microscope and cleaned ultrasonically with distilled water. For the XRD characterization a Philips PW 1710 instrument at the Department of Mineralogy and Petrology of the University of Granada was used. Structural determination of the K-feldspar was carried out following the recommendations of Post and Bish (1989).

The morphological study of these spherules was carried out using a Zeiss DSM 950 scanning electron microscope equipped with a Link QX 2000 microanalysis system at the 'Centro de Instrumentación Científica' (CIC) of the University of Granada. Some spherules were glued on a glass support using epofix resin and polished thin sections were prepared. Several sections were sputtered with carbon to analyze the K-feldspar by EMPA, Cameca Camebax SX 50 at CIC; all the elements were analyzed in wavelength dispersive spectroscopy. The electron beam was focused to about 1 μm diameter. The following compounds were used as standards: albite, orthoclase, periclase, wollastonite, galena, sphalerite, synthetic oxides (Al_2O_3, Fe_2O_3, $MnTiO_3$, Cr_2O_3, NiO) and metallic Co. Some cores present in the K-feldspar spherules were evidenced by a lower back-scattered electron (BSE) signal and then analyzed by SEM–EDS using a Cambridge S360 (University of Bari, Italy). The very small dimension of these cores (5–40 μm) and their light matrix suggested the choice of an ED microanalyser and a Link AN 10000 ED detector, that require a narrow and less intense beam, instead of a WD microanalyser that requires a higher probe current. Several minerals and pure compounds manufactured by Micro-Analysis Consultants Ltd. were used for standardization (i.e. wollastonite for Si, titanite for Ti, synthetic corundum for Al, [pyrope] garnet for Fe, synthetic periclase for Mg, wollastonite for Ca, jadeite for Na, orthoclase for K, pure metal for Cr, pure metal for Zn, barytes for S, galene for Pb). Some of these specimens were also sputtered with Al in order to determine the carbon content of some of the cores. Carbon was quantified by EMPA and by SEM–EDS using the detector in windowless position and the acceleration electron voltage set at 9 kV. A pure carbon stub sputtered with Al was used as reference standard. Replicate analyses in these cores showed a precision better than 10% for C content.

Additional trace element microanalyses were carried out on the largest cores using a Perkin Elmer 302 Laser ablation system coupled to a PE Scier ICP–MS Elan Spectrometer (Überlingen, Germany). Calibration was done in two ways: external, with NBS-612 glass, and internal, using silicon (previously determined by microprobe on the same section) as standards. The detection limit for Platinum Group Elements (PGE) was approximately 0.1–0.15 ppm.

4. Results

Two different types of spherules were observed at the Agost and Caravaca sections: K-feldspar spherules and Fe-oxide spherules.

4.1. K-feldspar spherules

K-feldspar spherules are very abundant at the Agost and Caravaca sections, with a density distribution of 100–200/cm^3. The size range is usually 100–500 μm. They mostly occur as spheres (Fig. 2a), other morphologies similar to dumbbells have been observed but they seem to be smaller spherules fused to larger ones. They have a porous structure in which K-feldspar crystals are arranged with fibroradial and dendritic textures (Fig. 2c,d) similar to quench-crystal textures. The spherules consist mostly of pure K-feldspar (Table 1). The XRD results are consistent with orthoclase. Some Fe-oxides usually coat the K-feldspar crystals. These spherules contain cores (Fig. 2e,f) with a composition different from K-feldspar (Ortega Huertas et al., 1992, 1994). The size of these cores usually ranges from 5 to 30 μm and, less frequently, they are larger than 30 μm. They represent a very unusual phase made up of variable percentages of carbon mixed with other elements (Table 2) on an extremely fine scale. Laser ablation system analyses on these cores revealed enrichment in Ir (0.59 ppm), Pt (2. 89 ppm), Pd (15.70 ppm) and Ni (3000 ppm).

4.2. Goethite spherules

The Fe-oxide spherules at Agost are more abundant than K-feldspar spherules, with a density distribution of 100–300/cm^3, but are rare at Caravaca. From a morphological point of view two types can be distinguished: (1) individual spheres to droplets, with shapes similar to small tektites (Fig. 3a,b,i–k); (2) aggregates of spherules with framboidal textures (Fig. 3c,d). Euhedral pyrite crystals replaced by Fe-oxides are also observed in the spherule aggregates and covering the surface of spherules (Fig. 3e).

Both types of spherules were diagenetically replaced by goethite. XRD analyses reveal easily recognizable goethite peaks, although these sometimes correspond to a mixture of Fe-oxides and hydroxides, with Fe as the main component of these spherules (Table 3). We shall refer to them in general as 'goethite spherules'.

Most of these spherules do not show internal textures (e.g. Smit et al., 1992). However we found fibroradial and dendritic textures in the type (1) spherules (Fig. 3i–k).

5. Discussion

In the studied section the spherules have been diagenetically altered. The chemical and mineralogical characteristics of K-feldspar as well as the isotopic composition (Epstein, 1982; DePaolo et al., 1983) support its diagenetic origin. Goethite is also a clearly secondary alteration product.

As regards the goethite spherule aggregates, type 2, they were observed at both sections, with sizes ranging from 100 to 1000 μm, and are more abundant at Agost and scarcer at Caravaca. Although pseudomorphically replaced by Fe-oxides and hydroxides (Table 3) their textures in fact correspond to pyrite framboids and they cannot be considered as impact related. The death of most of the marine plankton led to the accumulation of organic matter which resulted in reducing conditions. Under anoxic conditions, pyrite formation could have developed

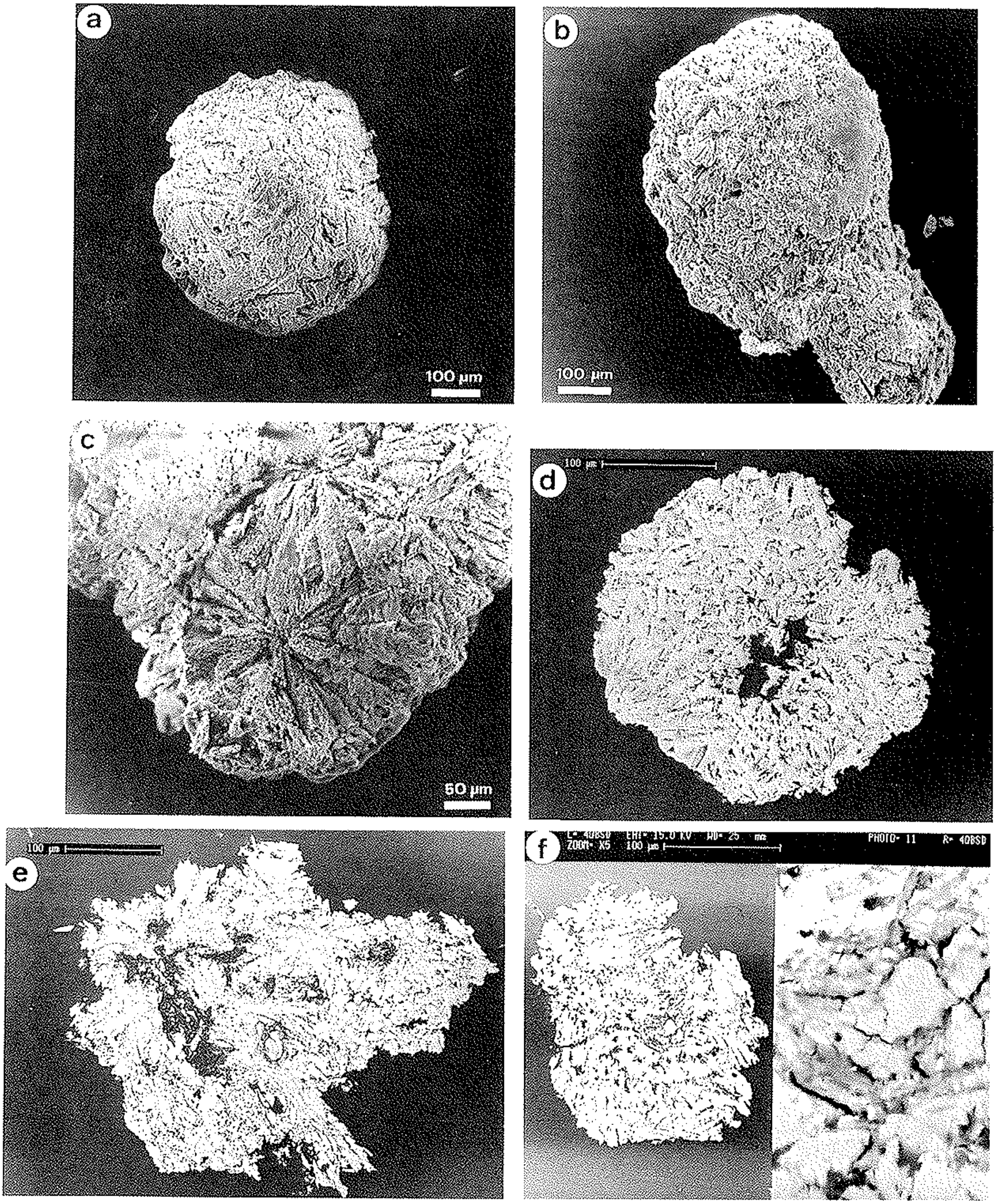

Fig. 2. SEM images of the K-feldspar spherules. (a, b) Different morphologies. (c) Detail of the fibroradial texture. (d) Porous structure of the spherules and dendritic textures. (e, f) BSE images showing C-rich cores.

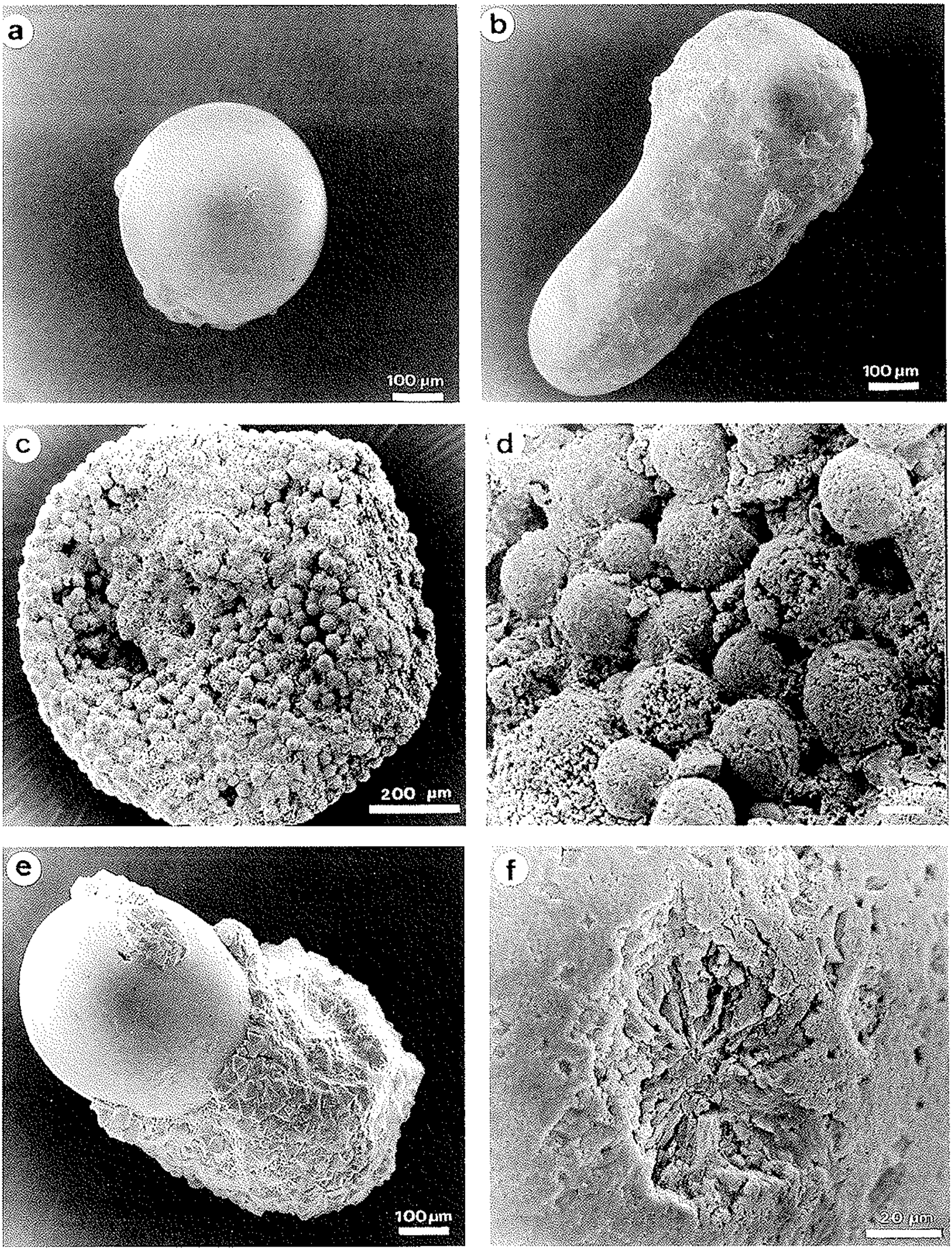

Fig. 3. SEM images of the Fe-oxide spherules. (a, b) Different morphologies. (c) Spherule aggregates. (d) Detail of the spherule aggregates showing framboidal texture. (e) Euhedral pyrite crystal replaced by Fe-oxides covering a spherule. (f, g, h) Fibroradial texture. (i, j, k) Splash-form morphologies.

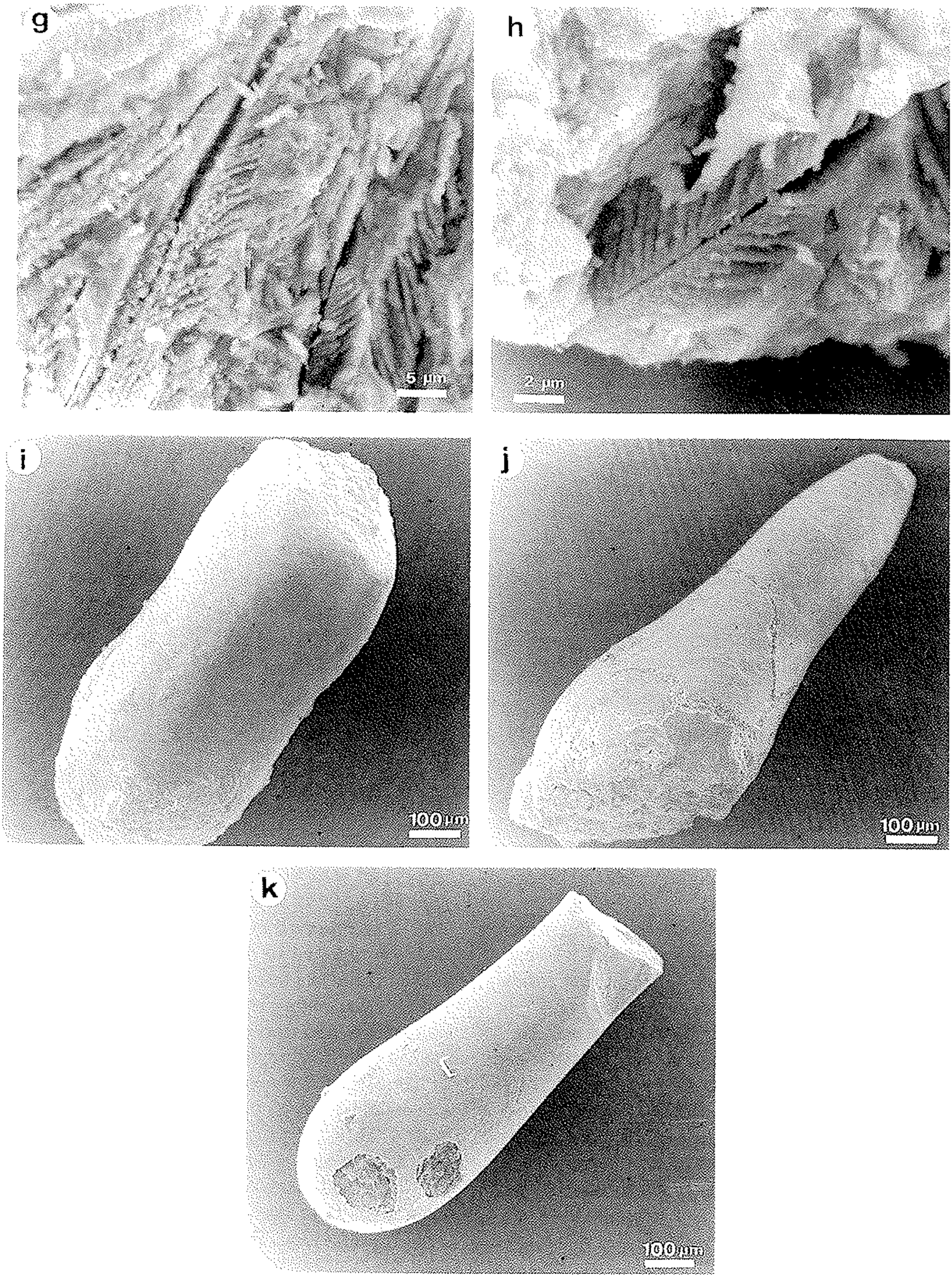

Fig. 3 (continued).

Table 1
Representative EMPA analyses of K-feldspar spherules from the KTB at Agost (A) and Caravaca (CA)

	A	A	A	A	A	CA	CA	CA	CA	CA
SiO_2	65.57	65.78	65.99	64.42	64.70	65.45	65.17	65.07	65.16	65.10
TiO_2	0.08	0.12	0.10	0.32	0.35	0.04	0.03	0.45	0.10	0.02
Al_2O_3	18.44	18.34	18.68	17.94	18.36	18.32	18.75	18.03	18.27	18.21
FeO	0.16	0.08	–	0.05	0.17	0.07	0.15	0.06	0.14	0.06
CaO	0.05	0.04	0.10	0.33	0.06	0.07	0.04	0.05	0.07	0.05
Na_2O	0.15	0.06	0.18	0.10	0.04	0.15	0.08	0.09	0.07	0.10
K_2O	14.75	14.96	14.55	15.20	15.34	15.00	15.58	15.28	15.81	15.90
Total	99.20	99.38	99.61	99.34	99.01	99.10	99.80	99.62	99.62	99.43

Table 2
SEM–EDS/EMPA microanalytical data from different cores observed in K-feldspar spherules from KTB at Caravaca

	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	28.64	40.77	34.78	9.90	46.48	29.63	42.22	32.90	28.41	31.40	34.27	14.93
TiO_2	0.47	0.95	2.77	0.27	1.77	0.62	1.65	0.37	0.27	0.43	1.08	0.32
Al_2O_3	3.38	7.05	5.71	3.83	7.93	4.14	10.58	4.72	3.99	4.93	4.78	2.39
FeO	7.12	6.36	9.25	6.91	5.73	7.26	7.06	7.66	6.46	7.26	8.75	1.27
MgO	3.25	2.60	4.21	3.32	2.60	3.69	3.08	4.48	3.38	4.19	3.61	0.71
CaO	1.41	1.04	1.51	1.27	1.11	1.62	1.67	1.55	1.40	1.58	1.52	0.89
Na_2O	1.25	1.17	1.69	1.33	1.44	1.54	1.33	2.16	1.29	1.56	1.51	0.69
K_2O	0.27	3.81	0.43	0.20	3.19	0.27	2.06	0.94	0.22	0.37	0.90	1.27
Cr_2O_3	1.64	1.17	1.89	1.73	1.32	1.89	1.35	2.31	1.83	1.51	2.59	0.13
ZnO	1.82	1.15	2.04	1.54	0.98	1.82	1.43	1.84	1.12	1.93	2.26	0.10
SO_3	2.69	1.85	1.73	2.42	1.92	2.79	2.22	3.14	2.52	2.72	2.52	0.85
PbO	2.14	1.54	2.33	1.94	1.54	2.16	1.90	2.85	2.40	2.44	2.23	0.13
Total	54.04	69.49	68.36	54.66	76.03	57.40	76.55	65.02	53.28	60.32	66.05	23.65
C	44	30	31	44	23	41	23	33	45	38	33	72

considerably during early diagenesis. The presence of framboids and euhedral crystals of pyrite also indicates extensive bacterial activity in the boundary sediments responsible for important element remobilization (Martínez Ruíz, 1994).

However, the point to be addressed in this paper concerns the impact-related spherules and we shall therefore focus our discussion on them. Since they are pseudomorphically altered, morphology and texture may provide some clues to their origin. This study reports fibroradial textures and splash-form morphologies in impact-related goethite spherules for the first time. Smit et al. (1992) considered that an extreme alteration of goethite spherules at Stevns Klint (Denmark), El Kef (Tunisia), Woodside Creek (New Zealand) or Agost (Spain) led to the absence of crystalline textures. However these textures are well preserved at Agost. They are similar to the textures produced in rapid crystallization of pyroxene and olivine (e.g. Bryan, 1972) and are also similar to those of the clinopyroxene in glass spherules associated with North American microtektites (John and Glass, 1974). In addition, dendrites of magnetite have been observed in extraterrestrial spherules such as those reported by Koeberl and Hagen (1989) in glacial sediments from the Transantarctic Mountains. Another interesting point is that these textures also correspond with those of unaltered KTB clinopyroxene spherules reported by Smit et al. (1992) at DSDP Site 577, which suggests that the clinopyroxene could have been the original spherule material.

It is difficult to know the exact nature of the precursor material since the composition of the spherules and therefore the original element concentrations have been severely modified during diagenetic alteration. However, the presence of cores

Table 3
Representative EMPA analyses of the Fe-oxides spherules (total Fe is expressed as Fe_2O_3)

	1	2B	2I	2N	3	4B	4I
SiO_2	3.61	3.49	3.33	3.44	8.15	3.18	3.23
TiO_2	0.02	0.01	0.02	–	1.43	0.15	0.01
Al_2O_3	0.16	0.11	0.09	0.06	0.62	0.09	0.06
Fe_2O_3	92.82	93.11	93.15	94.19	83.88	90.72	90.12
MgO	0.75	0.76	0.66	0.68	0.53	0.66	0.76
CaO	0.35	0.34	0.35	0.34	0.75	0.27	0.30
ZnO	0.20	0.21	0.24	0.15	0.40	0.11	0.21
NiO	0.42	0.24	0.24	0.30	0.15	–	0.49
CoO	0.10	0.10	0.14	0.06	0.11	0.09	0.09
Total	98.44	98.36	98.23	99.31	97.03	95.78	95.29

H_2O^+ not determined. B, spherule shell; I, intermediate point; N, core spherules.

in the K-feldspar that could represent a relict of the original material is an important clue to infer the spherule origin.

No cosmic influence is suggested by the element concentrations observed in K-feldspar or goethite spherules, which are secondary phases that do not reflect the original chemical composition. However, the C cores found in K-feldspar spherules present a high content of noble metals that could indicate cosmic contamination. It is difficult to determine the exact nature of such cores or consider them as simply derived from the supposed extraterrestrial body. They also contain Cr, Zn, or Pb (Table 2), which are less common in extraterrestrial material. These elements have probably a secondary origin since this material was also altered during diagenetic processes undergoing an important compositional modification. However, the enrichment in Ir, Pt, Pd or Ni suggests a cosmic source for these elements. The fact that they do not present chondritic ratios could also indicate diagenetic remobilization. Although the processes contributing to remobilization of PGE in sedimentary environments are not well understood, different authors have reported that PGE remobilization is possible at low temperature (e.g. Dyer et al., 1989; Evans et al., 1993). Even taking into account the possible remobilization processes, an exclusively terrestrial source cannot satisfactorily explain the high PGE values detected, which, on the contrary suggest an extraterrestrial source and therefore an impact-related origin for the KTB spherules.

The composition of these cores (Table 2) can also suggest that the precursor material may be a mixture of sulphide and silicate phases. As regards the silicate phase, the whole chemistry and, in particular, the relative abundance of Na and Ca (Table 2), which are absent from the other phases detected in the KTB, suggest that the silicate precursor in these cores could be a pyroxene.

Considering that pyroxene was the precursor, the scenario proposed by Melosh and Vickery (1991) could explain the characteristics of the studied spherules. These authors presented a theory for estimating the sizes of droplets formed as a consequence of impacts. Material shocked to high pressure breaks up into an expanding spray of liquid droplets. Sizes calculated according to impactor size and velocity are consistent with observations of microtektites and microkrystites at the KTB. These authors showed that at common asteroidal impact velocities, the projectile material is ejected first and attains the highest speed whereas the target material is ejected later and is slower. This model agrees with the dual nature of the KTB layer in proximal sections and sizes of the studied spherules. On the basis of their morphologies, the presumably mafic precursor material and the quench crystal textures in splash-form goethite spherules, we propose that at least part of the microkrystites was originated from melt and not as condensate. These spherules derive from the more energetic part of the impact cloud, where composition would be more mafic and the contribution of extraterrestrial material considerable.

6. Conclusions

At the Agost and Caravaca sections, abundant KTB spherules have been diagenetically altered and replaced by K-feldspar and Fe-oxides (goethite), but they still show evidence of the original spheroid material. For the first time fibroradial and dendritic textures, similar to quench-crystal textures have been reported in goethite spherules with splash form. As this type of textures has also been observed in unaltered KTB spherules of clinopyroxene, this can be considered a likely precursor. Additional evidence of a mafic precursor is provided by the C cores observed in the K-feldspar spherules. The composition of these cores with a significant enrichment in PGE suggests extraterrestrial contamination. Although these cores represent an unusual phase that may also have been altered during diagenetic processes, they indicate the presence of a mixture of C with sulphide and silicate phases. The presence of these cores, together with the spherule morphologies and textures, suggest that at least part of the microkrystites were entrained as melt blebs in the hot vapour plume and they originated from melt and not as condensate.

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References

Alvarez, L.W., Alvarez, W., Asaro, F., Michel, H.V., 1980. Extraterrestrial cause for the Cretaceous/Tertiary extinction. Science 208, 1095–1108.

Bohor, B.F., 1984. Comment and Reply on 'Spheroids at the Cretaceous–Tertiary boundary are altered impact droplets of basaltic composition'. Geology 12, 695–696.

Bohor, B.F., 1990. Shock-induced microdeformation in quartz and other mineralogical indications of an impact event at the Cretaceous/Tertiary boundary. Tectonophysics 171, 359–372.

Bohor, B.F., Betterton, W.J., 1990. K/T boundary spherules: Clarifying the concept (abstr.). Lunar Planet. Sci. Conf. 21, 108–109.

Bohor, B.F., Foord, E.E., 1987. Magnesioferrite from a nonmarine K–T boundary clay in Wyoming. Lunar Planet. Sci. 18, 101–102.

Bohor, B.F., Glass, B.P., 1995. Origin and diagenesis of K/T impact spherules — from Haiti to Wyoming and beyond. Meteoritics 30, 182–198.

Bryan, W.B., 1972. Morphology of quench crystals in submarine basalts. J. Geophys. Res. 77, 5812–5819.

DePaolo, D.J., Kyte, F.T., Marshall, B.D., O'Neil, J.R., Smit, J., 1983. Rb–Sr, Sm–Nd, K–Ca, O and H isotopic study of Cretaceous–Tertiary boundary sediments, Caravaca, Spain: evidence for an oceanic impact site. Earth Planet. Sci. Lett. 64, 356–373.

Dyer, B.D., Lyalikova, N.M., Murray, D., Doyle, M., Kolesov, G.M., Krumbein, W.E., 1989. Role of microorganisms in the formation of Ir anomalies. Geology 17, 1036–1039.

Epstein, S., 1982. The delta $\delta^{18}O$ of the sanidine spherules at the Cretaceous–Tertiary boundary. Lunar Planet. Sci. Conf. 13, 205–206.

Evans, N.J., Gregorie, D., Goodfellow, W.D., McInnes, B.I., Miles, N., Veizer, J., 1993. Ru/Ir ratios at the Cretaceous/Tertiary boundary: implications for PGE source and fractionation within the ejecta cloud. Geochim. Cosmochim. Acta 57, 3149–3158.

Groot, J.J., de Jonge, R.B.G., Langereis, G.H., ten Kate, W.G.H.Z., Smit, J., 1989. Magnetostratigraphy of the Cretaceous–Tertiary boundary at Agost (Spain). Earth Planet. Sci. Lett. 94, 385–397.

Izett, G.A., 1987. Authigenic 'spherules' in the K/T boundary sediments at Caravaca, Spain, and Raton Basin, Colorado and New Mexico, may not be to carbonaceous chondrites. Geol. Soc. Am. Bull. 99, 78–86.

John, C., Glass, B.P., 1974. Clinopyroxene-bearing glass spherules associated with North American microtektites. Geology 2, 599–602.

Koeberl, C., Hagen, E.H., 1989. Extraterrestrial spherules in glacial sediments from the Transantarctic Mountains, Antarctica: Structure, mineralogy, and chemical composition. Geochim. Cosmochim. Acta 53, 937–944.

Kyte, F.T., Bohor, P.F., 1995. Nickel-rich magnesiowüstite in Cretaceous/Tertiary boundary spherules crystallized from ultramafic, refractory silicate liquids. Geochim. Cosmochim. Acta 59, 4967–4974.

Kyte, F.T., Smit, J., 1986. Regional variation in spinel compositions: An important key to the Cretaceous–Tertiary event. Geology 14, 485–487.

Kyte, F.T., Zhou, Z., Wasson, J.T., 1980. Siderophile-enriched sediments from the Cretaceous–Tertiary boundary. Nature 288, 651–656.

Kyte, F.T., Smit, J., Wasson, J.T., 1985. Siderophile interelement variations in the Cretaceous–Tertiary boundary sediments from Caravaca, Spain. Earth Planet. Sci. Lett. 73, 183–195.

MacLeod, N., Keller, G., 1991. How complete are Cretaceous — Tertiary sections? A chronostratigraphic estimate based on graphic correlation. Geol. Soc. Am. Bull. 103, 1439–1457.

Martínez Ruíz, F., 1994. Geoquímica y mineralogía del tránsito Cretácico–Terciario en las Cordilleras Béticas y en la Cuenca Vasco-Cantábrica. Ph. Thesis, Univ. Granada, 280 pp.

Martínez Ruíz, F., Ortega Huertas, M., Palomo, I., Barbieri, M., 1992. The geochemistry and mineralogy of the Cretaceous–Tertiary boundary at Agost (southeast Spain). Chem. Geol. 95, 265–281.

Melosh, H.J., Vickery, A.M., 1991. Melt droplet formation in energetic impact events. Nature 350, 494–497.

Montanari, A., 1991. Authigenesis of impact spheroids in the K/T boundary clay from Italy: new constraints for high-resolution stratigraphy of terminal Cretaceous events. J. Sediment. Petrol. 671, 315–339.

Montanari, A., Hay, R.L., Alvarez, W., Asaro, F., Michel, H.V., Alvarez, L.W., Smit, J., 1983. Spheroids at the Cretaceous–

Tertiary boundary are altered impact droplets of basaltic composition. Geology 11, 668–671.

Ortega Huertas, M., Martínez Ruíz, F., Acquafredda, P., Palomo, I., 1992. Microanalytical data on K/T boundary potassium feldspar spherules. Electr. Microsc. 2, 579–580.

Ortega Huertas, M., Martínez Ruíz, F., Acquafredda, P., Palomo, I., 1994. Platinum-group elements in the cores of potassium feldspar spherules from the Cretaceous–Tertiary boundary at Caravaca (Spain). Estud. Geol. 50, 3–7.

Ortega Huertas, M., Martínez Ruíz, F., Palomo, I., Chamley, H., 1995. Comparative mineralogical and geochemical clay sedimentation in the Betic Cordilleras and Basque–Cantabrian Basin areas at the Cretaceous–Tertiary boundary. Sediment. Geol. 94, 209–227.

Pollastro, R.M., Bohor, B.F., 1993. Origin of the clay-mineral genesis of the Cretaceous/Tertiary boundary unit, Western Interior of North America. Clays Clay Miner. 41, 7–25.

Post, J.E., Bish, D.L., 1989. Rietveld refinement of crystal structures using powder X-ray diffraction data. In: Bish, D.L., Post, J.E. (Eds.), Modern Power Diffraction. Rev. Mineral. 20, 277–398.

Robin, E., Boclet, D., Bonté, Ph., Froget, L., Jéhanno, C., Rocchia, R., 1991. The stratigraphic distribution of Ni-rich spinels in Cretaceous–Tertiary boundary rocks at El Kef (Tunisia), Caravaca (Spain) and Hole 761 C (Leg 122). Earth Planet. Sci. Lett. 107, 715–721.

Shaw, H.P., Wasserburg, G.J., 1982. Age and provenance of the targets materials for tektites and possible impactites as inferred from Sm–Nd and Rb–Sr systematics. Earth Planet. Sci. Lett. 60, 155–177.

Smit, J., 1990. Meteorite impact, extinctions and the Cretaceous–Tertiary boundary. Geol. Mijnbouw 69, 187–204.

Smit, J., Hertogen, J., 1980. An extraterrestrial event at the Cretaceous–Tertiary boundary. Nature 285, 198–200.

Smit, J., Klaver, G., 1981. Sanidine spherules at the Cretaceous–Tertiary boundary indicate a large impact event. Nature 292, 47–49.

Smit, J., Alvarez, W., Montanari, A., Swinburne, N., Van Kempen, T.M., Klaver, G., Lustenhouwer, W.J., 1992. 'Tektites' and microtektites at the Cretaceous–Tertiary boundary: two strewn fields, one crater?. Proc. Lunar Planet. Sci. 22, 87–100.