Positive Eu anomaly development during diagenesis of the K/T boundary ejecta layer in the Agost section (SE Spain): implications for trace-element remobilization

F. Martinez-Ruiz[1]*, M. Ortega-Huertas[2] and I. Palomo[2]

[1]*Instituto Andaluz de Ciencias de la Tierra,* [2]*Departamento de Mineralogía y Petrología, Facultad de Ciencias, Universidad de Granada, 18002 Granada, Spain*

ABSTRACT

K/T boundary geochemical anomalies have been used previously to support the impact event at the end of the Cretaceous. However, impact models and assessment of the extraterrestrial contribution to the boundary sediments should also consider the diagenetic alteration of the impact signatures. Mineralogical and geochemical studies centring on redox proxies reveal differences in trace-element concentrations at Agost and Caravaca (SE Spain), two of the most complete K/T boundary sections. These differences probably derive from variations in the diagenetic evolution of the ejecta layer. Several redox proxies, such as extensive pyrite formation, high authigenic uranium concentration and positive Eu anomalies, indicate very strong reducing conditions at Agost. Positive Eu anomalies are extremely unusual in sediments, and in this case are interpreted to indicate a highly reducing environment. In such conditions, certain trace elements such as Ir, may have been remobilized, thereby masking the original signature of the impact.

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Introduction

The nature and composition of the Cretaceous–Tertiary (K/T) boundary layer, as well as the data indicating the Chicxulub structure as the crater (e.g. Sigurdsson *et al.*, 1991; Koeberl and Sigurdsson, 1992; Smit *et al.*, 1992; Alvarez *et al.*, 1995), are indicative of a major extraterrestrial impact at the end of the Cretaceous. This impact was first indicated by an anomalously high concentration of Ir (Alvarez *et al.*, 1980), although the origin of Ir and other geochemical anomalies at the K/T boundary have been debated widely in the 'impact vs. volcanism' controversy. In the last decade, advances in knowledge of K/T boundary geochemical anomalies, such as Os and Cr isotope compositions (e.g. Meisel *et al.*, 1995; Koeberl and Shirey, 1997; Shukolyukov and Lugmair, 1998), further support the evidence for a bolide impact. However, interpretation of the geochemical record of the K/T impact also requires understanding of the preservation of the record and the diagenetic processes that may have altered the original trace-element concentrations. The mass extinction at the end of the Cretaceous and the deposition of the fireball layer led to unusual depositional conditions. Organic-matter and trace-element (terrestrial and extraterrestrial) fluxes would have been much higher during the ejecta deposition. As a consequence, such anomalous fluxes may have led to unusual oxygen consumption and, therefore, extreme reducing conditions. The ejecta sediments were later oxidized, and such reducing/oxidizing cycles can obscure the original signatures and concentrations.

In order to determine the diagenetic conditions in K/T boundary sediments, we analysed the K/T boundary interval focusing especially on redox-sensitive elements. One of the selected elements was Eu, since positive Eu anomalies are not common in sedimentary environments but, when present, provide significant constraints on the diagenetic evolution. In natural materials, all the REE are trivalent, with the exception of Ce, which is stable as Ce^{4+} in oxidizing conditions, and Eu, which is stable as Eu^{2+} under reducing conditions. During weathering REE can be mobilized and removed into solution (e.g. Nesbitt, 1979), and during diagenetic processes, in addition to remobilization, substantial changes in redox conditions may occur. Although, for most diagenetic conditions the aqueous chemistry of Eu is dominated by the trivalent state, Eu may be reduced in highly reducing environment (Sverjensky, 1984), providing interesting information about Eh conditions.

Samples and methods

Samples from the K/T boundary layer and sediments above and below were analysed at two of the most complete K/T boundary sections (Agost and Caravaca) located in SE Spain (Fig. 1a) in the Betic Cordillera, which is part of the peri-Mediterranean Alpine orogenic belt. The K/T boundary is marked by a 2–3 mm-thick clay layer (Fig. 1b,c) consisting mainly of smectite at both sections, abundant spherules of potassium feldspar and Fe-oxides at Agost and K-feldspar at Caravaca (e.g. Smit and Klaver, 1981; Smit, 1990; Martinez-Ruiz *et al.*, 1997). This layer is typically rust-coloured at Caravaca and mainly dark-green with rusty patches at Agost. It is underlain by a sharp contact of Cretaceous light-green marly limestones and is overlain by marly clays with early Danian microfossils. Bioturbation does not seem to have modified the original ejecta lamina significantly.

The K/T ejecta layer was sampled laterally at both sections for chemical analyses. The K/T boundary spherules were separated by sieving and hand-picking and their morphology and composition were studied using a Scanning Electron Microscope (Zeiss DSM 950). Bulk sediments and potassium feldspar spherules were homogenized and ground in an agate mortar for chemical analyses using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). ICP-MS analyses were performed following acid-clean digestion with HNO_3 + HF on 0.100 g of sample powder in a Teflon-lined vessel at high temperature and pressure, evaporation

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*Correspondence: Tel.: +34/958246228; Fax: +34/958243384; E-mail: fmruiz@goliat.ugr.es

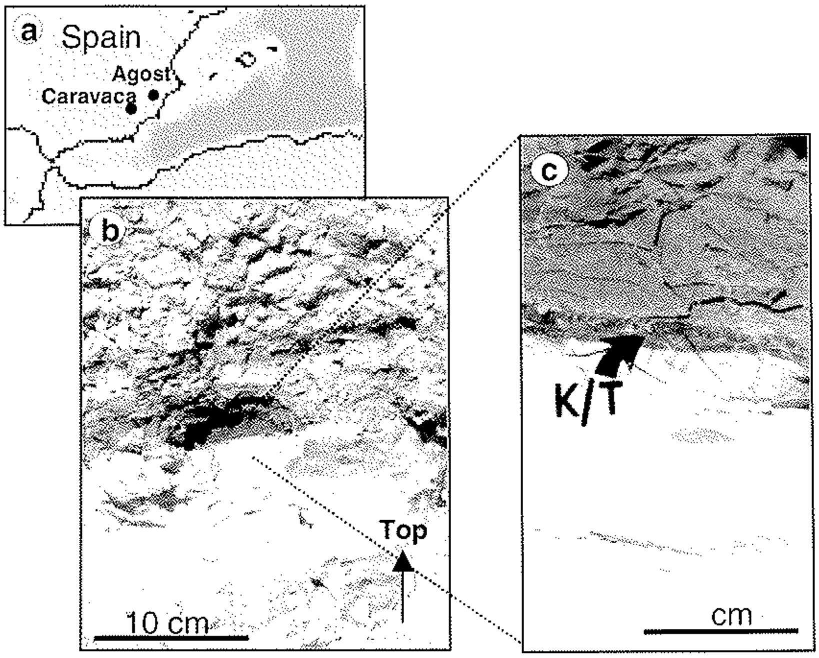

Fig. 1 (a) Location of the Agost and Caravaca sections in the SE of Spain. (b) Field photograph showing the K/T boundary interval at the Agost section. (c) Detail of the ejecta layer.

to dryness and subsequent dissolution in 100 mL of 4% (v/v) HNO_3. Instrument measurements were carried out in triplicate using a Perkin Elmer Sciex Elan-5000 spectrometer with Rh as internal standard. The quality of the analyses was monitored with laboratory and international standards. Precision was better than ± 2% and ± 5% rel. for analyte concentrations of 50 and 5 ppm, respectively.

This work is mainly focused on Eu and Ba concentrations, and therefore special attention has been paid to possible interferences. Isobaric interference on $^{151}Eu^+$ is caused by $^{135}Ba^{16}O^+$ and $^{133}Cs^{18}O^+$. Only the interference caused by $^{135}Ba^{16}O^+$ produces significant effects. In order to correct it, we analysed in each run a solution containing no Eu and 1000 ppb Ba, and calculated the mass ratio as 151/138. This factor was then applied to correct the Eu signal in the following way: ^{151}Eu corrected = ^{151}Eu uncorrected − (factor = 151/138) × ^{138}Ba. Isobaric interference on ^{160}Gd is caused by ^{160}Dy, $^{144}Sm^{16}O$, $^{144}Nd^{16}O$, $^{142}Nd^{18}O$ and $^{142}Ce^{8}O$. They were corrected in the same way as before, using pure solutions of Nd and Sm in each run to calculate the percentages of oxide formation: ^{160}Gd corrected = ^{160}Gd uncorrected − 0.0930 × ^{163}Dy − factor 1 × ^{149}Sm − factor 2 × ^{146}Nd, where factor 1 = mass ratio 160/149 for a Gd-free Sm solution, and factor 2 = mass ratio 160/146 for a Gd-free Nd solution.

Results

Previous works on the Agost and Caravaca sections have reported the mineralogical composition of the K/T boundary interval at these sections (e.g. Martinez-Ruiz *et al.*, 1992, 1997; Ortega Huertas *et al.*, 1995; Ortega-Huertas *et al.* (1998). The boundary layer comprises mostly smectite and abundant potassium feldspar spherules at both sections, with Fe-oxide spherules also abundant at Agost. At both sections, oxidized pyrite framboids have been observed also. A detailed study focusing on the diagenetic alteration of the boundary layer and spherules has shown that barite is prominent in the boundary layer (Fig. 2a) and also fills some iron oxide and potassium feldspar spherules (Fig. 2b,c,d). Optical and SEM analyses of iron oxide spherules have also demonstrated that most of these spherules resulted from the oxidation of pyrite spherules, and some pyrite relicts are still observable in oxidized spherules and framboids (Fig. 2e).

The trace-element concentrations for bulk sediments and K-feldspar spherules from Agost are presented in Table 1. Results from different samples taken in the boundary layer at Caravaca are similar; only one representative sample is included in Table 1 that reveals geochemical anomalies. However, the concentrations of Ba and Eu vary significantly from sample to sample at Agost; higher Eu concentrations are correlated with higher barite contents. Other than the K/T boundary sample where Ir was measured, two other representative samples (one Ba-poor and one Ba-rich) are included in Table 1. Plots representing some of the geochemical anomalies at both sections are presented in Fig. 3. Al data from Martinez-Ruiz *et al.* (1992) and Martinez-Ruiz (1994) have been used to correct for variations in the aluminosilicate fraction. All of the elements presented in Fig. 3 show positive anomalies at the boundary layer. Eu data from K/T boundary sediments, K-feldspar spherules and representative Cretaceous and Tertiary samples are presented in Table 1. Chondrite-and NASC-normalized patterns for REEs from Agost samples are shown in Fig. 4, where a positive Eu anomaly in barite-enriched samples can be observed.

Discussion

The geochemical composition of the ejecta layer at Agost and Caravaca supports the impact scenario at the end of the Cretaceous. Typical extraterrestrial elements such as Ir, Ni, Co, Cr and Fe are enriched in the boundary sediments. However, trace-element concentrations may have been severely modified and therefore may not reflect the original extraterrestrial contamination accurately.

Evidence for reducing conditions

Different geochemical and mineralogical proxies indicate that depositional conditions were unusually reducing during deposition/early diagenetic processes:

1 *Elevated U concentration.* Typical terrestrial crustal elements can be used to evaluate diagenetic concentrations in reducing conditions. The U/Th ratio is a potential redox indicator as Th is relatively immobile in the sedimentary environment and it is concentrated in

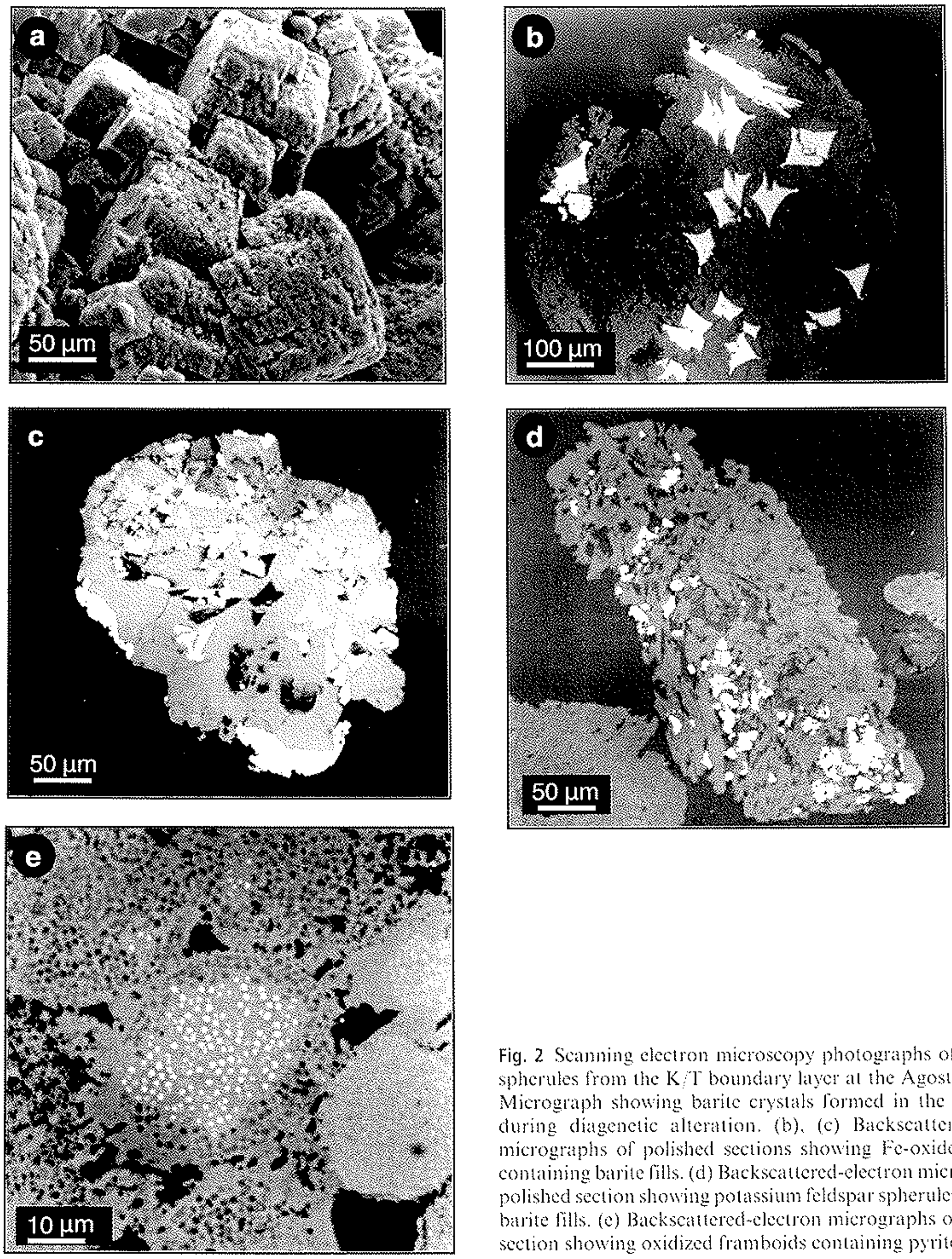

Fig. 2 Scanning electron microscopy photographs of barite and spherules from the K/T boundary layer at the Agost section. (a) Micrograph showing barite crystals formed in the ejecta layer during diagenetic alteration. (b), (c) Backscattered-electron micrographs of polished sections showing Fe-oxides spherules containing barite fills. (d) Backscattered-electron micrograph of a polished section showing potassium feldspar spherules containing barite fills. (e) Backscattered-electron micrographs of a polished section showing oxidized framboids containing pyrite relicts.

the detrital fraction. U^{6+} is soluble, but U^{4+} precipitates in a reducing environment raising the U/Th ratio. Wignall and Myers (1988) proposed the authigenic uranium (U_a) content as an index of bottom-water oxygenation calculated as: U_a = (total U)−Th/3, which can be a reliable redox proxy (Jones and Manning, 1994). The U_a content for the K/T boundary layer is extremely high at Agost (Table 1) compared to sediments above and below the boundary, and suggests extremely reducing conditions during deposition and early diagenesis. Although lower than in the Agost section, U_a is very high at the Caravaca K/T boundary layer compared to sediments above and below, also indicating reducing conditions (Table 1). This fact suggests that at Agost more extreme reducing conditions developed, probably related to palaeoceanographic conditions, and the expansion of the oxygen minimum zones (Smit, 1999).

2 *The extensive formation of pyrite during early diagenetic processes.* This also

Table 1 Geochemistry of the K/T boundary interval from the Agost (A) and Caravaca (CA) sections. Concentration values are expressed in ppm for trace elements and % for Al and Fe. Samples AK/T, AK/T1 and AK/T2 correspond to a lateral sampling at Agost K/T boundary layer. The position of samples is referred to 0 cm for the boundary layer.

Sample	Pos. (cm)	Al2O3	Fe2O3	Th	U	Ua	Ba	Eu	Cr	Co	Ni	Cu	Zn	As	Sb	Ir
A10	+23	5.46	2.34	3.6	1.9	0.70	75	0.33	57	3	31	6.5	47	2	0.3	–
A9c	+17	6.99	2.34	5.0	2.0	0.33	64	–	65	4	35	10.7	75	2	0.2	–
A9b	+13	5.28	1.84	3.0	1.6	0.60	143	–	47	3	27	8.4	55	2	0.2	–
A9	+11	10.90	3.26	6.8	3.3	1.03	119	–	110	23	58	11.0	69	3	0.4	0.5
A8b	+7	9.16	3.02	5.0	2.5	0.83	76	–	82	10	47	12.8	77	5	0.3	–
A8a	+5	15.10	4.85	8.0	3.1	0.43	123	–	130	12	775	21.8	138	10	0.4	–
A8	+4	15.10	4.67	9.0	3.8	0.80	91	–	138	10	82	25.0	110	10	0.6	–
A7a	+2	14.50	4.54	9.0	3.3	0.30	133	–	140	12	90	34.9	150	8	0.5	–
A7	+2	14.80	4.50	8.6	3.7	0.83	99	–	143	14	99	47.0	120	10	0.7	–
A6	+0	15.90	5.08	8.8	5.2	2.27	129	–	243	34	140	50.0	130	16	1.1	16.5
AK/T	0	13.60	11.18	8.2	23.4	20.67	1630	–	540	160	556	218.0	568	380	8.1	24.4
AK/T1	0	–	–	7.39	31.6	29.14	2940	0.38	762	211	791	377.3	936	–	–	–
AK/T2	0	–	–	3.69	15.5	14.27	62	0.15	496	103	362	227.3	411	–	–	–
Kfs sph.	0	–	–	33.11	71.8	60.76	32120	2.84	899	195	890	508.3	699	–	–	–
A5	−1	7.42	1.97	3.5	2.5	1.33	76		52	8	49	13.0	53	4	0.5	1.1
A4	−23	5.24	1.66	3.1	1.7	0.67	148	0.53	45	4	31	8.0	37	2	0.5	<0.1
CA12	−18	5.96	1.99	4.1	1.5	0.13	93	–	55	6	39	16.0	58	2	0.2	0.65
CA11	−14	7.03	2.40	4.2	1.0	−0.40	78	–	70	11	56	14.9	67	2	0.2	–
CA10	−12	6.72	2.40	3.9	1.0	−0.30	65	0.62	65	10	53	19.0	56	2	0.3	–
CA9	−9	7.71	2.63	4.1	1.1	−0.27	58	–	68	13	27	12.6	27	2	0.3	–
CA8	−6	6.92	2.46	3.6	0.8	−0.40	44	–	58	12	62	15.6	62	2	0.2	0.68
CA7	−4	13.00	4.42	7.1	1.4	−0.97	39	–	101	44	137	32.5	111	3	0.8	–
CA6	−2	13.60	4.64	7.4	1.7	−0.77	88	–	103	50	159	31.5	126	5	0.9	7.99
CA5	−1	14.60	4.61	7.2	1.7	−0.70	79	–	180	40	167	44.4	137	20	1.1	21.9
CAK/T	0	14.90	13.00	8.3	13.6	10.83	23	0.08	851	390	1350	257.0	986	720	15.0	35.2
CA4	−1	7.39	2.19	3.5	1.0	−0.17	119	–	57	14	62	14.7	52	3	0.3	1.23
CA3	−3	5.46	1.76	2.9	1.1	0.13	101	–	43	10	58	13.5	53	2	0.3	–
CA2	−8	5.25	1.73	2.8	0.9	−0.03	123	–	42	10	52	12.9	55	2	0.2	0.41
CA1	−13	5.61	1.76	2.9	0.6	−0.37	116	0.57	44	9	47	11.6	59	2	0.2	0.19

suggests that large amounts of organic matter deposited on the ocean floors after the extinction. In these conditions, pyrite replaced the original spherule material at Agost. In fact, some pyrite relicts are even observed in Fe-oxide spherules and oxidized framboids (Fig. 2c). Euhedral pyrite crystals also cover the surface of some spherules (Martinez-Ruiz *et al.*, 1997). At the Caravaca section, only pyrite framboids are observed; if pyrite also replaced spherules, they may have been completely altered. During oxidation, trace elements could have been remobilized also, lost into solution or concentrated in alteration phases.

3 *The development of positive Eu anomalies.* Eu anomalies attributable to diagenesis are not common, since Eu is trivalent under 'normal marine conditions'. Only a few cases have been reported where Eu has been reduced (and sometimes removed into solution) in sedimentary environments, always under strongly reducing conditions (Sverjensky, 1984; MacRae *et al.*, 1992). However, Eu is enriched relative to 'normal shales' in the conditions reported by MacRae *et al.*, (1992) while enrichment is absent when C1 normalised-patterns are considered. In contrast, Eu anomalies reported here in the K/T boundary layer at Agost indicate an enrichment of both the NASC- and the C1-normalized patterns (Fig. 4). The Eu^{3+}/Eu^{2+} equilibrium in aqueous solution illustrated in Eh-pH diagrams (Sverjensky, 1984; Brookins, 1988, 1989) indicate that Eu is only reduced under very low Eh. Therefore, this enrichment provides further support for the significant mobilization of Eu under very strong reducing conditions, and confirms that the rapid accumulation of organic matter after the mass extinction, and high metal concentrations led to an unusual oxygen consumption, responsible for Eu reduction and mobilization. At the Agost section, barite originated during pyrite weathering and is also the carrier phase for Eu and responsible for positive Eu anomalies, because Eu would have been coprecipitated with Ba. Thus, Eu anomalies are promoted by reducing/oxidizing reactions when reduced species were oxidized and barite precipitated. The removal of Eu and Ba into solution and precipitation of barite would have been controlled by circulation of fluids. An irregular distribution of secondary phases could have led to significant lateral variations in elemental abundance as reported for Eu and Ba (Table 1). Chondrite-normalized positive anomalies are displayed by barites formed in reducing sedimentary and metamorphic environments (Guichard *et al.*, 1979). This is consistent with the reduced divalent Eu cations substituting Ba by virtue of their similarity in size and charge.

Other data in the literature also support reducing conditions at the K/T

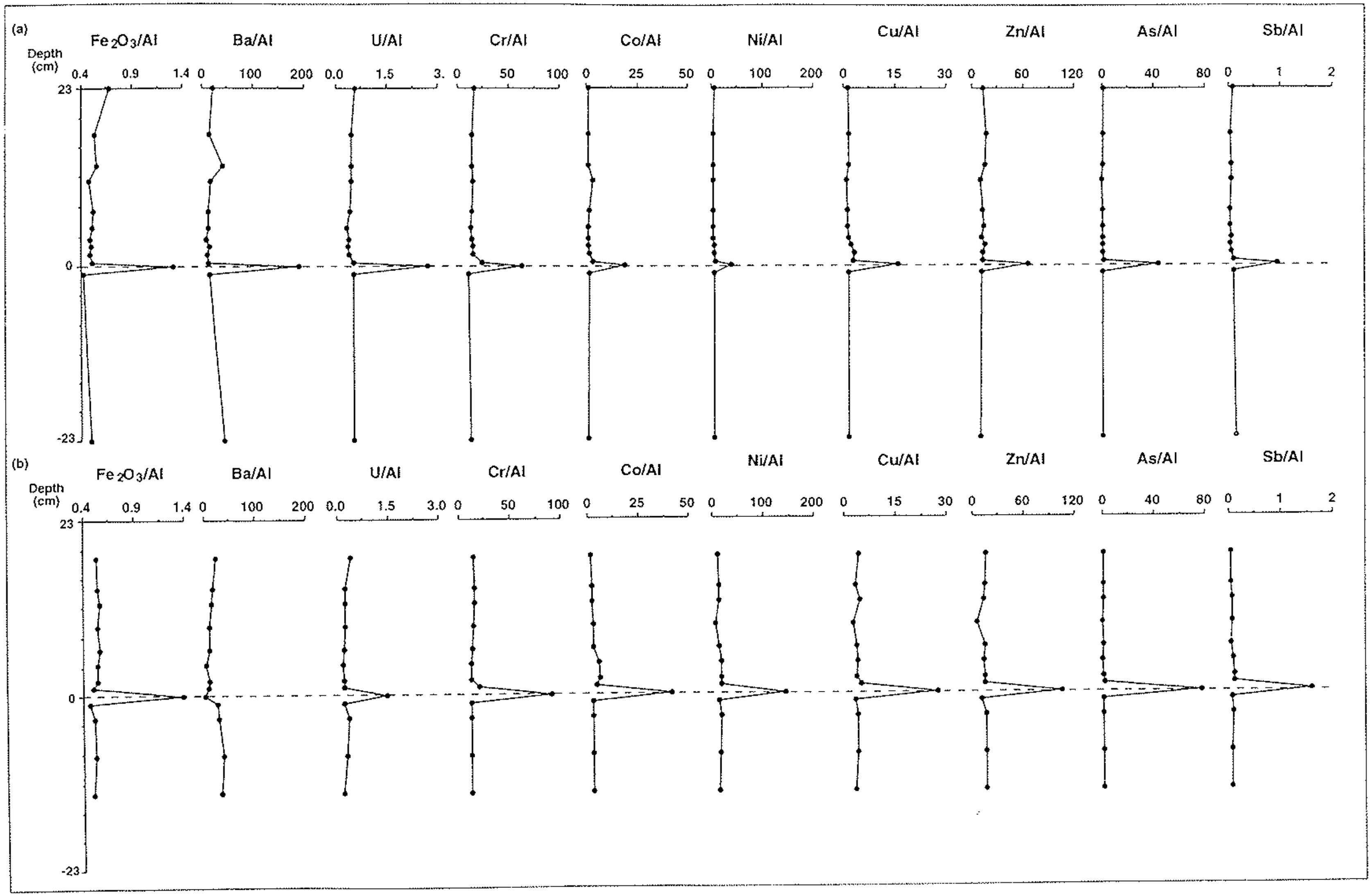

Fig. 3 Ba/Al weight ratio (x 10^4) vs. depth profiles for the K/T boundary interval at Agost (a) and Caravaca (b) showing the trace-element anomalies at these sections. The horizontal lines indicate the K/T boundary and depths are referred to 0 cm for the boundary.

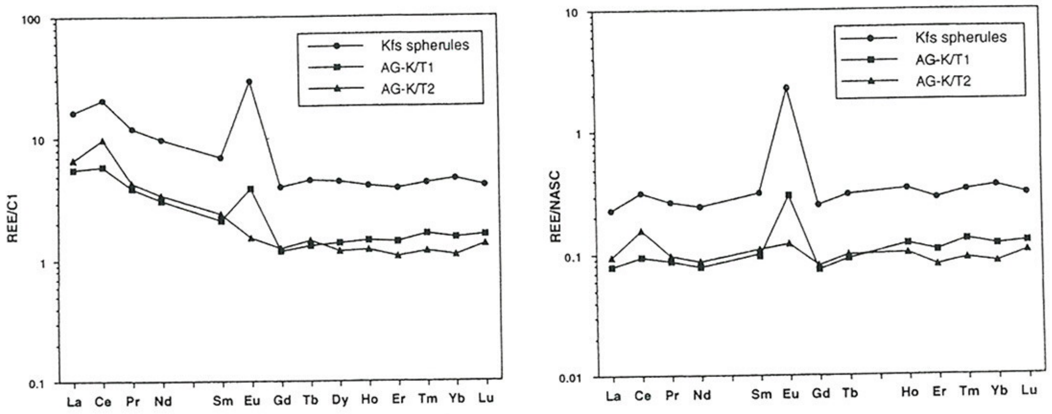

Fig. 4 Plots showing the Eu anomaly and REE abundances (normalized to C1 chondrite values of Anders and Ebihara, 1982; NASC values of Haskin *et al.*, 1968) from one Ba-enriched and one Ba-poor sample, and from potassium feldspar spherules from Agost (AG-K/T1, AG-K/T2 and KFS, respectively).

boundary; for example, reduction and leaching of iron in the White Beds below the K/T boundary in the Gubbio section (Italy), suggest that the K/T boundary clay in Italy was deposited under anomalously reducing conditions (Lowrie *et al.*, 1990). Montanari (1991) also detailed early diagenetic processes in the K/T boundary clay from Italy, demonstrating that the K/T boundary facies are consistent with reducing environments. Benthic fauna evidence (Coccioni and Galeotti, 1994), foraminiferal indices and S isotopes (Kaiho *et al.*, 1999) also indicate reducing conditions at the K/T boundary in the Caravaca section (Spain).

Implications for trace-element remobilization

At Agost and Caravaca, Ir reaches 24.5 and 35.2 ppb, respectively (Martinez-Ruiz *et al.*, 1992, 1994). As the source material in both sections should be quite similar, these differences can be explained in terms of a different diagenetic evolution of the boundary layer material. The mechanism of PGE behaviour and transport in low-temperature solutions is still poorly known, although Ir remobilization has been reported in relation to microbial activity (Dyer *et al.*, 1989) and in suboxic conditions (De Lange *et al.*, 1991). In other K/T boundary sections, Ir concentrations vary widely from place to place (e.g. Evans *et al.*, 1995). This probably results from different rates of extraterrestrial/terrestrial contribution at each location and from the diagenetic evolution of the boundary sediments. There is still some uncertainty regarding the original Ir concentrations in the K/T boundary sediments, and the first step towards determining original concentrations is to address the diagenetic alteration of the ejecta layer, since no evaluation of extraterrestrial fluxes can be based on the altered concentration. This consideration also applies for other trace elements. In this regard, positive Eu anomalies, higher U_a contents and a more extensive development of pyrite at Agost suggest a more reducing environment. Ir content is lower than at Caravaca, suggesting that Ir and possibly other trace elements may have been mobilized under stronger reducing conditions.

Conclusions

The high U_a content, the abundance of oxidized pyrite and the development of positive Eu anomalies all indicate strong reducing conditions during the deposition and early diagenesis of the ejecta layer at Agost. Positive Eu anomalies constrain the redox potential since this element can be mobilized only under very strong reducing conditions. In such conditions, Ir and other trace elements could also have been mobilized, thereby modifying the original geochemical record of the K/T impact. Alteration of the original concentration of extraterrestrial elements must therefore be considered for a correct evaluation of extraterrestrial fluxes to the boundary sediments, and modelling of the K/T impact.

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References

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

Alvarez, W., Claeys, P. and Kieffer, S., 1995. Emplacement of Cretaceous–Tertiary boundary shocked quartz from Chicxulub crater. *Science*, **269**, 930–935.

Anders, E. and Ebihara, M., 1982. Solar-system abundances of the elements. *Geochim. Cosmochim. Acta*, **46**, 2363–2380.

Brookins, D.G., 1988. *Eh–Ph Diagrams for Geochemistry*. Springer, Berlin.

Brookins, D.G., 1989. Aqueous geochemistry of rare-earth elements. In: *Geochemistry and Mineralogy of Rare Earth Elements* (B.R. Lipin and G.A. Mckay, eds), pp. 201–225. Mineralogical Society of America, Washington, DC.

Coccioni, R. and Galeotti, S., 1994. K–T boundary extinction: Geologically instantaneous or gradual event?. Evidence from deep-sea benthic foraminifera. *Geology*, **22**, 779–782.

De Lange, G.J., Van Der Sloot, H.A. and Wijkstra, J., 1991. Implications of the diagenetic mobility of Ir for the interpretation of the Ir anomaly at the K/T boundary. *Terra Abstract*, **3**, 306.

Dyer, B.D., Lyalikova, N.N., Murray, D. *et al.*, 1989. Role of microorganisms in the formation of iridium anomalies. *Geology*, **17**, 1036–1039.

Evans, N.J., Ahrens, T.J. and Gregoire, D.C., 1995. Fractionation of ruthenium from iridium at the Cretaceous-Tertiary

boundary. *Earth Planet. Sci. Letters*, **134**, 141–153.

Guichard, F., Church, T.M., Treuil, M. and Jaffrezic, H., 1979. Rare earths in barites: distribution and effects on aqueous partitioning. *Geochim. Cosmochim. Acta*, **43**, 983–997.

Haskin, L.A., Haskin, M.A., Frey, F.A. and Wildeman, T.R., 1968. Relative and absolute terrestrial abundance of the rare earths. In: *Origin and Distribution of the Elements* (L.H. Ahrens, ed.), pp. 889–912. Pergamon Press, Oxford.

Jones, B. and Manning, D.C.A., 1994. Comparison of geochemical indices used for the interpretation of paleoredox conditions in ancient mudstones. *Chem. Geol.*, **111**, 111–129.

Kaiho, K., Kajiwara, Y., Tazaki, K. *et al.*, 1999. Oceanic primary productivity and dissolved oxygen levels at the Cretaceous/Tertiary boundary: Their decrease, subsequent warming, and recovery. *Paleoceanography*, **14**, 511–524.

Koeberl, C. and Sigurdsson, H., 1992. Geochemistry of impact glasses from the K/T boundary in Haiti: Relation to smectites and a new type of glass. *Geochim. Cosmochim. Acta*, **56**, 2113–2129.

Koeberl, C. and Shirey, S.B., 1997. Re-Os isotope systematics as a diagnostic tool for the study of impact craters and distal ejecta. *Paleogeogr. Paleoclim., Palaeoecol.*, **132**, 25–46.

Lowrie, W., Alvarez, W. and Asaro, F., 1990. The origin of the White Beds below the Cretaceous–Tertiary boundary in the Gubbio section, Italy. *Earth Planet. Sci. Lett.*, **98**, 303–312.

MacRae, N.D., Nesbitt, H.W. and Kronberg, B.I., 1992. Development of a positive Eu anomaly during diagenesis. *Earth Planet. Sci. Lett.*, **109**, 585–591.

Martinez-Ruiz, F., 1994. *Geoquímica y Mineralogía del tránsito Cretácico-Terciario en las Cordilleras Béticas y en la Cuenca Vasco-Cantábrica*. PhD Thesis, University of Granada.

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

Martinez-Ruiz, F., Ortega-Huertas, M. and Palomo, I., 1994. The Cretaceous–Tertiary boundary in the Betic Cordilleras and Basque-Cantabrian basin: a comparative study of the platinum-group element anomalies. *Min. Mag.*, **58**, 563–564.

Martinez-Ruiz, F., Ortega Huertas, M., Palomo, I. and Acquafredda, P., 1997. Quench textures in altered spherules from the Cretaceous–Tertiary boundary layer at Agost and Caravaca, SE Spain. *Sediment. Geol.*, **113**, 137–147.

Meisel, T., Krähenbühl, U. and Nazarov, M.A., 1995. Combined osmium and strontium isotopic study of the Cretaceous–Tertiary boundary at Sumbar, Turkmenistan: a test for an impact vs. a volcanic hypothesis. *Geology*, **23**, 313–316.

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. Sedim. Petrol.*, **61**, 315–339.

Nesbitt, H.W., 1979. Mobility and fractionation of rare earth elements during weathering of a granodiorite. *Nature*, **279**, 206–210.

Ortega Huertas, M., Martínez-Ruiz, F., Palomo, I. and 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.

Ortega-Huertas, M., Palomo, I., Martinez-Ruiz, F. and González, I., 1998. Geological factors controlling clay mineral patterns across the Cretaceous–Tertiary boundary in Mediterranean and Atlantic sections. *Clay Minerals*, **33**, 483–500.

Shukolyukov, A. and Lugmair, G.W., 1998. Isotopic Evidence for the Cretaceous-Tertiary impactor and its type. *Science*, **282**, 927–929.

Sigurdsson, H., D'Hondt, S., Arthur, M.A. *et al.*, 1991. Glass from the Cretaceous–Tertiary boundary in Haiti. *Nature*, **349**, 482–487.

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

Smit, J., 1999. The global stratigraphy of the Cretaceous–tertiary boundary impact ejecta. *Ann. Rev. Earth Planet. Sci.*, **27**, 75–113.

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

Smit, J., Montanari, A., Swinburne, N.H.S. *et al.*, 1992. Tektite-bearing, deep-water clastic unit at the Cretaceous–Tertiary boundary in northeastern Mexico. *Geology*, **20**, 99–103.

Sverjensky, D.A., 1984. Europium redox equilibria in aqueous solution. *Earth Planet. Sci. Lett.* **67**, 70–78.

Wignall, P.B. and Myers, K.J., 1988. Interpreting the benthic oxygen levels in mudrocks: a new approach. *Geology*, **16**, 452–455.

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