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The geochemistry and mineralogy of the Cretaceous–Tertiary boundary at Agost (southeast Spain)

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ABSTRACT

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This paper gives the mineralogical and geochemical results of research made on the K/T boundary in the Agost stratigraphic sequence belonging to the Intermediate Units of the Betic Cordilleras (Spain). In this sequence the *Abathomphalus mayaroensis*, *Globigerina cretacea* and *Parvularugoglobigerina eugubina* Zones are present and the K/T level (2 mm) is very well defined. The K/T boundary is characterized by a decrease in carbonate content, an increase in the proportion of smectites and the presence of spherules of Fe-oxides and K-feldspar. We have detected a considerable enrichment in platinum-group elements (Ir = 24.4 ppb), As, Sb, Zn, Fe, Ti, Cr, Ni, V, Co, Sr among other elements, and an depletion in Ca and rare-earth elements. The Fe-oxide spherules are enriched in most of these trace elements. We suggest that these spherules were formed as a product of the alteration of pyrite originating in an oxygen-depleted marine environment, in which abundant sulphides and organic complexes would have formed and scavenged the metals. ⁸⁷Sr/⁸⁶Sr ratio for the K/T boundary is similar to the values reported for oceanic waters of the same age. The PGE values normalized to CI chondrites are very different to those corresponding to meteoritic composition. Post-depositional processes could have brought about a differential enrichment of these elements. Although meteorite impact cannot be discounted, we suggest that volcanic phenomena and early diagenetic processes were related to the chemical anomalies of the K/T boundary.

1. Introduction

The Cretaceous–Tertiary boundary (K/T) event is at present one of the most controversial subjects in the area of the Earth sciences, both by reason of the great faunal crisis marking the end of the Cretaceous, and also because of the geochemical anomalies associated with the sediments of this age. The discussion arose out of the discovery of Ir anomalies in the sediments marking the boundary at Stevns Klint, Denmark, at Gubbio, Italy, by Alvarez et al. (1980) and at Caravaca, Spain, by Smit and Hertogen (1980).

Given that Ir and other platinum-group elements (PGE) are rare in the Earth's crust in comparison with their cosmic abundances, a

high concentration of them in sedimentary materials could indicate extraterrestrial contamination. This possibility led Alvarez et al. (1980) to propose the impact of a large meteorite as the cause of the great faunistic extinction at the end of the Cretaceous. Such an impact would have produced a gigantic cloud of pulverized and shock-melted vaporized material in the atmosphere which would have been responsible for drastic environmental changes. The deposition of this material would have given rise to the geochemical and mineralogical anomalies observed in these sediments. This hypothesis is highly controversial as some of the criteria employed in its defense are used by other authors (Officer and Drake, 1985; Courtillot et al., 1986, 1988; Hallam, 1987; Ja-

voy and Courtillot, 1989) to propose terrestrial phenomena as the causes of the massive extinctions and the geochemical anomalies. In particular, the intense volcanic activity at the end of the Cretaceous could, in these authors' opinion, have created adverse environmental conditions and therefore the same effects as those produced by a supposed meteorite impact.

However, there are for the moment no conclusive data which to discount one or other of these hypotheses. In fact, certain questions discussed in recent papers continue to present problems such as, with regard to the extraterrestrial hypothesis, the nature of the phenomenon (Davis et al., 1984; Rocchia et al., 1984; Hut et al., 1987), the number of impacts which took place (Smit, 1990) and their location (Gilmour and Anders, 1989; Pope et al., 1991; Sigurdsson et al., 1991; Smit, 1991); or, concerning the possible terrestrial origins, the nature, magnitude and duration of the volcanic episode (Courtillot et al., 1988; Javoy and Courtillot, 1989).

This scientific discussion has given rise to the exhaustive search for complete stratigraphical sequences of this age which allow further research, at present, a great number of these have been recognized in both marine and continental environments. Some of the best marine sequences are found in Spain. This is the case with the traditionally well-known sequence at Caravaca (Murcia), which has been the subject of much research and about which a great number of papers have been published (Smit and Hertogen, 1980; Smit and ten Kate, 1982; Kyte et al., 1985). Nearby, at Agost (Alicante), another sequence similar to that at Caravaca appears, which likewise has no stratigraphical gap but which presents the additional advantages of being less affected by tectonic processes, being better exposed and having a lesser degree of alteration in the level which marks the K/T boundary. Previous work was carried out by Groot et al. (1989), who undertook a magnetostratigraphic and biostratigraphic study, and Smit (1990) on general geological aspects.

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2. Geological setting

The materials examined, which were of basically marly lithology, belong to the Intermediate Units of the Betic Cordilleras. The Betic Cordilleras, SE Spain, are part of the peri-Mediterranean Alpine orogenic belt (Fig. 1). Structurally it can be divided into two domains, the Internal and the External Zones (Fig. 1B), each of which are very different as regards their palaeogeographical significance and their tectono-metamorphic evolution. The Internal Zones consist mainly of overthrust units of Triassic and Palaeozoic materials. The External Zones, composed of Mesozoic and Cenozoic rocks deposited on a continental margin along the southern border of the Meseta (Iberian Massif), can be subdivided into the Prebetic Zone, closer to the Meseta, consisting to a great extent of carbonate and detrital platform sediments, and the Subbetic Zone, further to the south, where from the Middle Liassic onwards a system of troughs and swells developed (García Hernández et al., 1976) with largely pelagic sedimentation associated with basic volcanic and subvolcanic rocks. Between the Prebetic and Subbetic Zones a palaeogeographical realm, known as the "Intermediate Units" became individualized during the Mesozoic and Tertiary, taking the form of a subsiding trough, in which a sequence was deposited whose characteristics are "intermediate" between those of the Prebetic and Subbetic.

The sequence studied by us is situated 2 km north of Agost (Alicante) and west of the Agost-Castalla road (Fig. 1C). Both the datings by Canudo et al. (1991) and the papers by Groot et al. (1989) and Smit (1990) show that this is a complete sequence across the K/T boundary in which the *Abathomphalus mayaroensis*, *Guembelitra cretacea* and *Parvula-*

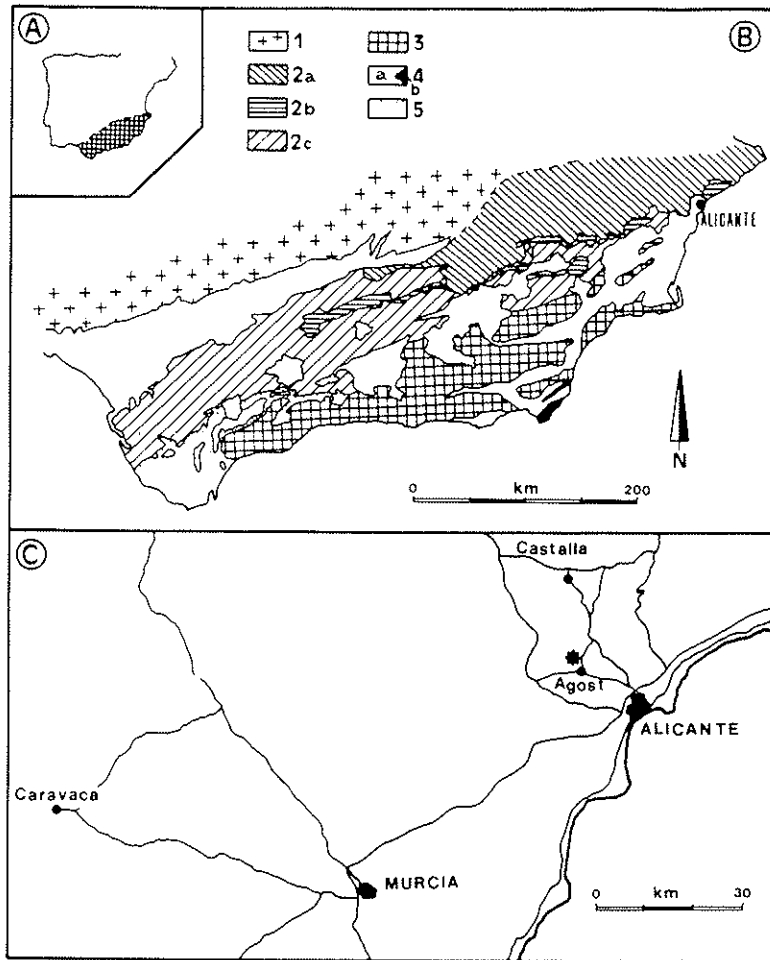


Fig. 1. Geological setting. A. Location of the Betic Cordilleras. B. Geological complexes in the Betic Cordilleras (modified from Foucault, 1974). [1 = Iberian Massif and Tabular Cover; 2 = External Zones (2a = Prebetic Zone, 2b = Intermediate Units, 2c = Subbetic Zone); 3 = Internal Zones; 4a = Neogene and Recent deposits; 4b = volcanic rocks; 5 = Campo de Gibraltar Units]. C. Location of the Agost section.

rugoglobigerina eugubina Zones are present. The Cretaceous materials are light-green marly limestones, which are lithologically very uniform, although they present some levels with abundant bioturbations. A very dark clayey layer 2 mm thick appears in clear contact on top of these materials. This layer, which marks the K/T boundary, is partially altered, thus causing its usual appearance in shades of red. On top of the K/T boundary dark-green marly clays are deposited in thicknesses of 8–10 cm, whose carbonate content gradually increases,

giving way to marls and marly limestones of lighter colour. Benthic foraminifera indicate deposition occurred in an upper bathyal to outer neritic environment and at somewhat shallower depth than at Caravaca (Keller, 1990).

Sampling was made of the Cretaceous materials from the K/T limit down to 1.50 m below. The sampling of the Tertiary materials was very detailed up to 40 cm above the K/T boundary and discontinuous up to 18 m above this level.

3. Methodology

The techniques used for the mineralogical and geochemical studies were the following.

3.1. X-ray diffraction (XRD)

After drying of the samples at room temperature, they were ground down to <2 mm in size. A homogeneous and representative part, ground and sieved to <270 mesh ASTM (0.053 mm), was used for the mineralogical study of the bulk sample, while another was used for the extraction of the clay fraction. The equipment used was a Philips® PW 1710 diffractometer with automatic slit. The reflecting factors, calculated for this equipment and its instrumental conditions, were: powder diffractograms (phyllosilicates, 0.09; quartz, 1.43; calcite, 1.05; feldspars, 1.03), oriented aggregate diffractograms (illite, 0.36; smectites, 0.93; chlorite; kaolinite, 0.98). The percentage of illite layers present in the smectite was calculated according to the Reynolds and Hower (1970) method.

3.2. Electron microscopy

The morphological study of the minerals, with special attention to the spherules, was carried out using scanning electron microscopy (SEM). The equipment used was a Zeiss® DSM 950 (Technical Services of the University of Granada, Spain) and a JEOL® Cambridge S 360 equipped with a Link® microanalysis (University of Bari, Italy). The quantitative microanalyses of the clays were obtained by means of transmission electron microscopy (TEM) using a JEOL® JEM 2000 FX fitted with Link® AN 10000 microanalysis (University Complutense of Madrid). This equipment enabled us to analyze particles of <1 µm and even discover the chemical composition of areas of between 200 and 300 Å. The spatial and genetic relations between illite and smectite were studied by means of

high-resolution transmission electron microscopy (HRTEM) (Zeiss® EM 10C). The samples were prepared according to the Eberhart and Trickett (1972) method. The observations were made with an acceleration voltage of 100 kV, a spherical aberration coefficient of 2.2 mm and 40-µm objective aperture.

3.3. Electron microprobe

The chemical composition of the spherules was determined by means of electron microprobe (Caméca-Camébox® SX 50, Technical Services of the University of Granada). The spherules were isolated from the >63-µm fraction and then separated by hand-picking using a stereoscopic microscope.

3.4. X-ray fluorescence (XRF)

The chemical analyses of the major elements were carried out by XRF using a Philips® PW 1600 spectrometer.

3.5. Inductively coupled plasma (ICP) and neutron activation (NA)

The analysis of trace elements and rare-earth elements (REE) was carried out using these techniques. In particular, the Fire Assay Nickel Sulphide Collection ICP-MS Finish method was used for the determination of the PGE, with a detection limit of 1 ppb for all of these except Ir and Os, where the limit was 0.1 and 3 ppb, respectively. XRF, ICP and NA chemical analyses were carried out at the X-Ray Assay Laboratories in Ontario (Canada).

3.6. Isotopic analyses

The isotopic composition of C was determined at the Geochemical Laboratory of the Estación Experimental Zaidín (CSIC, Granada). The $\delta^{13}\text{C}$ data are referred to the PDB standard. Strontium isotopic values were normalized to $^{86}\text{Sr}/^{88}\text{Sr}=0.1194$; measurements

of Sr-isotopic standard NBS 987 yield $^{87}\text{Sr}/^{86}\text{Sr}=0.71024 \pm 0.00002$. The Sr-isotopic values were obtained at Geochemical Laboratory at the University of Rome (Italy).

4. Results

4.1. Mineralogy

The mineralogy of the sequence, with the exception of the fine layer of sediment which marks the boundary, consists mainly of calcite, phyllosilicates and quartz. The Cretaceous samples show great uniformity; the proportions of the various minerals vary between 67% and 77% for calcite, and 20% and 28% for phyllosilicates with quantities of <5% for quartz (Table 1).

The layer marking the K/T boundary is characterized by a sharp (49%) decrease in carbonate content, a 37% increase in the proportion of phyllosilicates, the appearance of

celestite and barite, and, most particularly, the presence of spherules whose size varies between 50 and 500 μm . These spherules are made up of either potassium feldspar (Kfs) or iron oxides. The former present variable contents of SiO_2 (58.97–60.53%) and K_2O (6.24–8.06%). The iron oxide spherules are the most abundant and present variable contents of FeO (63.80–73.88%), NiO (0.16–1.45%), TiO_2 (0.16–1.07%), ZnO (0.14–0.49%), CoO (0.06–0.40%), V_2O_5 (0.03–0.14%), As (0.40–0.46%), S (0.11–0.13%) and lesser quantities of Cr, Mn and Pb. They may also be responsible for the alteration to the red colours which usually characterize the appearance of the K/T boundary layer in the field. Some of these spherules appear as aggregates of other smaller ones grouped together in a matrix made up of <2- μm particles which is very rich in Ti (Fig. 2). They show very different morphologies: spherical, oval, drop-shaped (Fig. 3A and B) and also, at times, disk-shaped, although this may be partly due to post-depositional deformation. Those composed of oxides show smooth surfaces and have either a glassy appearance or seem to be covered with tiny crystals (20–40 μm) which, in general, present idiomorphic octahedric forms typical of pyrite (Fig. 3C).

Concerning the clay minerals, with the exception of the layer marking the K/T boundary which has a greater content in smectites (82%), the remainder of the samples present

TABLE 1

Mineralogy of the sequence of Agost

Sample	Distance to K/T (cm)	Bulk mineralogy				Clay minerals			
		C	CM	Qtz	other	S	I	K	other
A-15	1,080+	62	35	<5	-	65	20	14	P
A-14	810+	73	25	<5	-	55	25	24	P
A-13	480+	75	22	<5	-	50	20	29	P
A-12	320+	82	17	<5	-	55	18	26	P
A-11	35–40+	87	12	<5	-	45	15	39	P
A-10	22–24+	73	14	<5	t	43	14	45	P
A-9	10–12+	52	43	5	t	16	41	42	Chl, P
A-8	3–4+	31	59	8	t	30	29	40	Chl, P
A-7	1–2+	29	58	9	t	35	34	30	Chl, P
A-6	0–1+	22	55	15	t	40	32	27	Chl, P
A-K/T	0	18	65	<5	t	82	7	9	Chl, P
A-5	0–2–	67	28	<5	-	42	28	30	-
A-4	20–25–	75	22	<5	-	42	23	35	-
A-3	50–55–	77	20	<5	-	22	37	41	-
A-2	80–85–	74	22	<5	-	42	16	42	-
A-1	120–	70	25	<5	-	41	23	36	-

Bulk mineralogy: C=calcite (%); CM=clay minerals (%); Qtz=quartz (%); t=minor minerals (K-feldspar, barite, celestite, goethite, rutile and Cr-oxides). *Clay minerals:* S=smectite (%); I=illite (%); K=kaolinite (%); with minor minerals: P=palygorskite and Chl=chlorite.

TABLE 2

PGE and Au content (in ppb) in K/T and adjacent levels

Sample	Au	Ru	Rh	Pd	Re	Os	Ir	Pt
A-12	<1	<1	<1	3	<1	<3	<0.1	<1
A-11	1	1	1	3	1	<3	0.2	<1
A-9	1	1	1	7	1	<3	0.5	3
A-6	10	10	4	18	1	4	16.5	14
A-K/T	23	43	12	27	5	5	24.4	26
A-5	5	1	1	5	1	<3	1.1	3
A-4	<1	<1	<1	5	<1	<3	<0.1	3
A-2	3	<1	<1	4	<1	<3	<0.1	<1

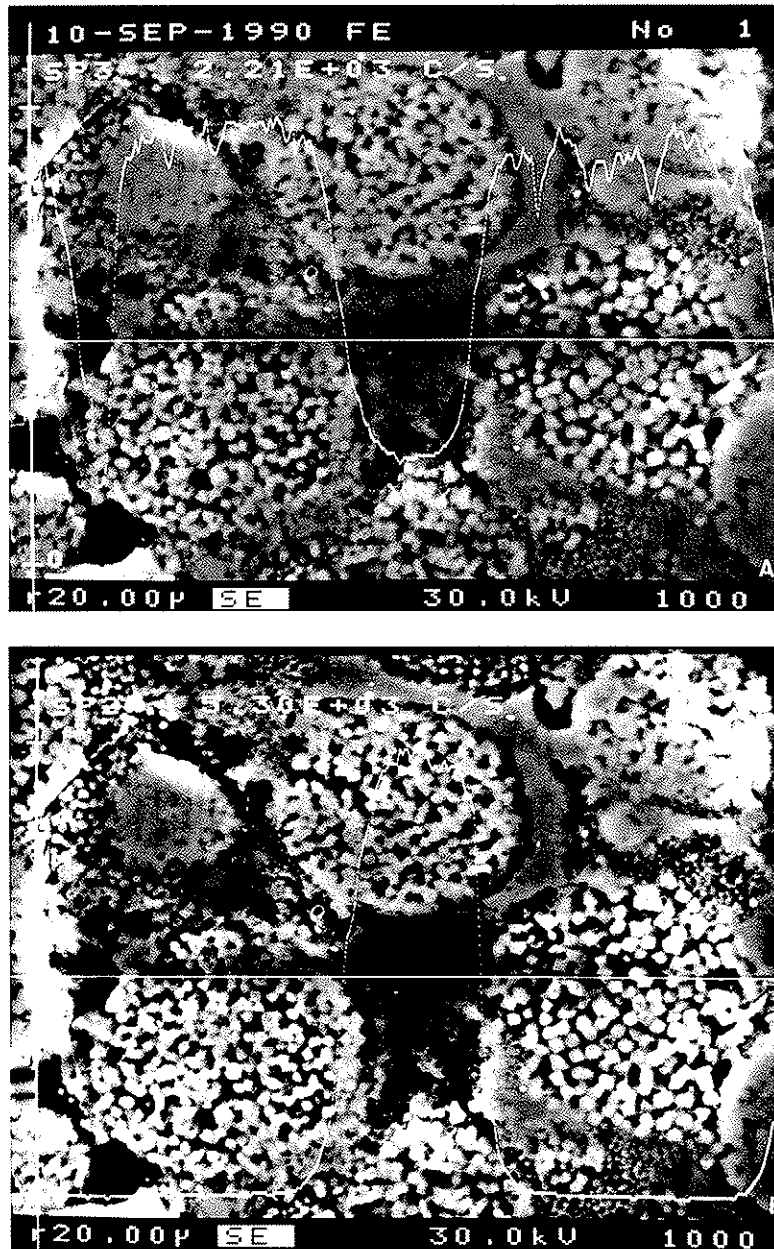
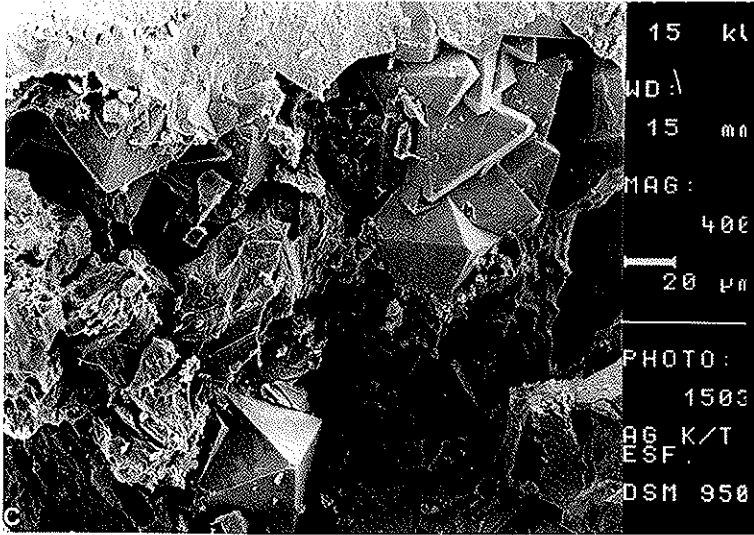
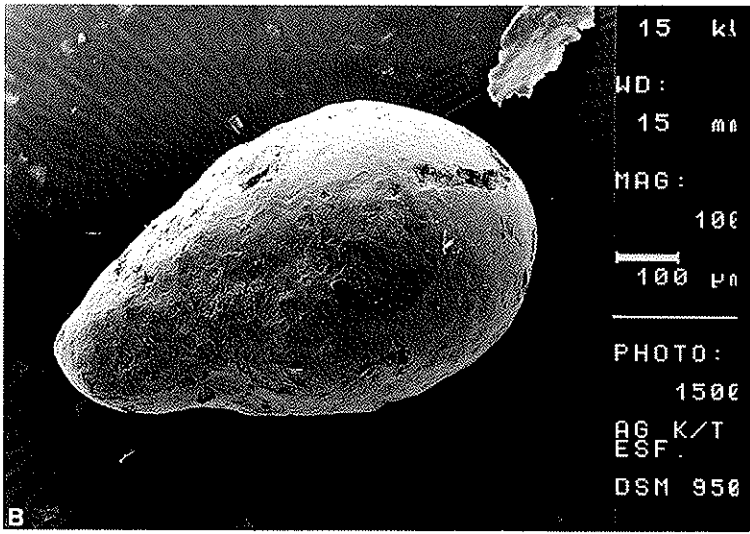
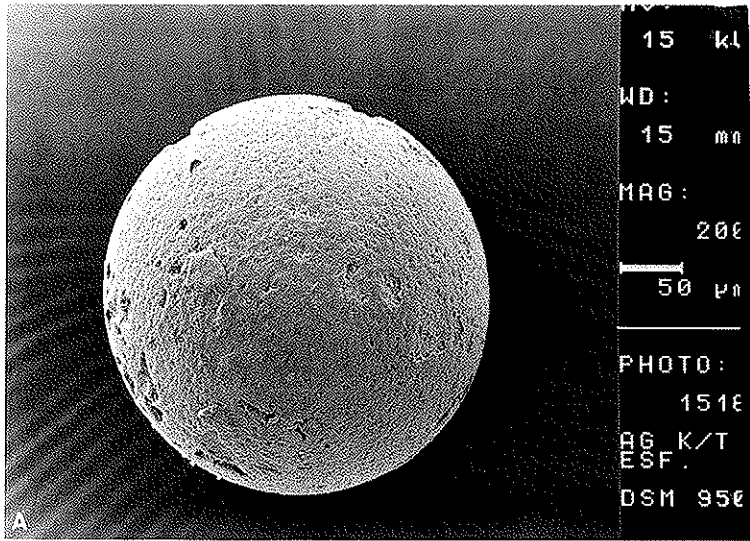


Fig. 2. Variation in the Fe (A) and Ti (B) content in a microaggregate of Fe-oxide spherules. Note the increase of Ti in the matrix of aggregate.

similar mineralogical characteristic consisting essentially of smectites, illite and kaolinite, while chlorite and palygorskite also appear as

minor phases in the Tertiary samples. The quantitative variations are shown in Table 1. In samples A-7 to A-9 a small increase is ob-

Fig. 3. SEM micrographs showing the morphology of the Fe-oxide spherules: (A) spherical; (B) drop-shaped; and (C) crystals of pseudomorphosed pyrite covering the surface of a spherule.



served in the illite and kaolinite content, together with a decrease in the proportions of smectites. This can clearly be correlated to an increase in detritism as indicated by the Ce/Ce^* parameter [Ce^* corresponds to the concentration obtained by extrapolation between La and Nd, as described by Courtois and Hofert (1977) whose values vary between 0.90 and 0.99].

The TEM microanalyses indicate the frequent presence in the Tertiary samples of grains of rutile, Cr-oxide and goethite.

The smectites are dioctahedral with percentages of Al_2O_3 (22.64–34.62), Fe_2O_3 (4.09–15.60) and MgO (3.15–11.49). The analytical data for the illites are variable throughout the sequence. The Cretaceous samples (e.g., A-5) present average compositions with percentages of $K_2O=6.71$, $FeO=0.96$ and $MgO=0.60$. However, in the A-K/T sample FeO (4.20–12.59%) and MgO (3.46–4.01%) increase, while the K_2O content remains within the previous range (6.52–8.01%). Similar average compositions are also found in samples A-6 and A-9 ($K_2O=7.30\%$; $FeO=5.34\%$; $MgO=3.33\%$). These differences, together

with their laminar morphology in the Cretaceous sediments and tabular morphology in the Tertiary samples, suggest the existence of neoformed micas and other inherited ones.

The HRTEM studies reveal that the smectites appears as anastomosing packets varying in size between 10 and 60 Å (according to c). The illite usually appears in packets of 270 to 300 Å (according to c) in crystals developed inside a smectitic matrix. A certain degree of deformation is often present due to compaction phenomena, which gives rise to interlayer slip. These data agree with the percentages of illite layers in the smectites obtained by the Reynolds and Hower (1970) method and which do not exceed 30%. In general, the Cretaceous samples give higher values of illite layers, possibly due to dehydration caused by diagenetic effects.

The chlorite crystals analyzed correspond to chamosite, although with very appreciable differences in the quantity of Fe. We have considered 10% of the Fe total to be Fe_2O_3 following Whittle (1986). The average composition of the A-6 sample is $FeO=22\%$; $Fe_2O_3=2.71\%$ and $MgO=14.03\%$. However, in samples lo-

TABLE 3

Chemical analyses (in wt.%) of the sequence of Agost (bulk sample)

Sample	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	P_2O_5
A-15	20.5	6.62	34.9	1.90	0.35	0.60	2.52	0.30	0.36
A-14	14.2	5.36	40.7	1.22	0.14	0.42	1.87	0.22	0.25
A-13	13.3	4.93	41.9	1.19	0.10	0.38	1.80	0.22	0.22
A-12	9.0	3.35	46.2	1.02	0.06	0.19	1.39	0.15	0.22
A-11	7.1	2.53	48.5	0.72	0.01	0.16	1.09	0.11	0.15
A-10	14.8	5.46	40.9	1.02	0.07	0.56	1.87	0.22	0.23
A-9	25.3	10.90	29.0	1.31	0.09	1.06	3.26	0.43	0.31
A-8	35.8	15.10	17.3	2.26	0.14	1.60	4.67	0.62	0.28
A-7	37.6	14.80	16.2	2.50	0.16	1.96	4.50	0.63	0.23
A-6	40.6	15.90	12.2	2.72	0.14	2.28	5.08	0.70	0.18
A-K/T	35.9	12.60	10.5	2.37	0.20	2.92	11.80	1.92	0.09
A-5	18.2	7.42	37.7	0.99	0.06	0.75	1.97	0.25	0.13
A-4	13.4	5.26	42.2	0.79	0.10	0.48	1.66	0.21	0.13
A-3	12.9	4.89	42.9	0.79	0.06	0.53	1.62	0.20	0.12
A-2	13.8	5.56	41.8	0.78	0.06	0.53	1.74	0.21	0.13
A-1	16.5	6.30	39.0	0.88	0.10	0.78	2.10	2.25	0.14

TABLE 4

Chemical analyses (in ppm) of the sequence of Agost (bulk sample)

Sample	V	Co	Ni	Cr	Cu	Zn	As	Sb	B	Rb	U	Sr	Ba
A-15	74	19	67	100	46	90	5	1.1	7	30	1.9	601	848
A-14	56	5	30	77	8.5	56	<2	0.5	50	20	1.2	766	104
A-13	54	6	32	70	6.0	44	<2	0.4	50	20	2.5	799	183
A-12	42	3	23	58	5.5	36	<2	0.3	30	20	2.0	721	109
A-11	26	3	25	30	18	30	<2	0.2	10	<20	1.7	572	72
A-10	54	3	31	57	6.5	47	<2	0.3	40	20	1.9	588	75
A-9	96	23	58	110	11	69	3	0.4	70	30	2.8	776	119
A-8	150	10	82	138	25	110	10	0.6	120	63	3.8	874	91
A-7	130	14	99	143	47	120	10	0.7	110	83	3.7	807	99
A-6	170	34	140	243	50	130	16	1.1	190	67	5.2	905	129
A-K/T	271	160	556	540	218	568	380	8.1	277	65	23.4	2,540	16,300
A-5	90	8	49	52	13	53	4	0.5	60	30	2.5	930	76
A-4	40	4	31	45	8	37	2	0.5	40	28	1.7	915	148
A-3	44	4	28	45	16	43	4	0.6	30	24	1.3	865	159
A-2	48	4	25	48	9	41	<2	0.4	40	22	0.9	861	103
A-1	50	4	24	52	7.5	40	<2	0.4	40	30	0.9	845	193

TABLE 5

REE content in the Agost sequence (La/Yb ratio in *C1* chondrites is 1.48, in Henderson, 1984)

Sample	Σ REE (ppm)	La/Yb	Ce/Ce*
A-15	99.32	12.73	0.77
A-14	71.92	14.13	0.75
A-13	67.93	14.07	0.71
A-12	53.18	13.92	0.65
A-11	34.75	10.06	0.80
A-10	58.59	13.00	0.84
A-9	112.64	17.25	0.99
A-8	114.76	17.52	0.97
A-7	105.76	16.82	0.90
A-6	91.17	25.82	0.71
A-K/T	44.65	16.57	1.00
A-5	57.16	15.18	0.81
A-4	54.45	18.11	0.82
A-3	49.35	15.78	0.86
A-2	53.54	17.22	0.83
A-1	64.06	16.82	0.86

cated further away from the K/T boundary (A-9) the Fe content decreases (FeO=6.05%; Fe₂O₃=0.78%; MgO=4.60%).

Crystals of palygorskite (sample A-9), with the following average composition SiO₂=

65.89%; Al₂O₃= 2.69% and MgO=31.40%, have also been analyzed.

4.2. Geochemistry

The Cretaceous-Tertiary boundary at Agost is marked by a large increase in the content of several chemical elements. Given that the K/T is characterized by a sharp decrease in the carbonate content and an increase in the proportion of phyllosilicates, the data obtained by chemical analysis of the bulk sample have been recalculated on a carbonate-free basis, in order to obtain the content of these elements independently of the percentage of carbonates, and thus obtain a clear idea of which elements really enrich the sediments which marking the K/T boundary. These calculations were not made for those elements which may substitute the Ca in the calcite, such as Sr and Mg.

Of all the elements analyzed from the Agost sequence, those which present anomalously high contents in the K/T boundary (sample A K/T) are the PGE (Table 2) (Ortega Huertas et al., 1991), Fe, Ti, Cr, K, Mg, Ni, V, Co, Cu, Zn, As, Sb, B, Hf, U, Sr and Ba (Tables 3 and

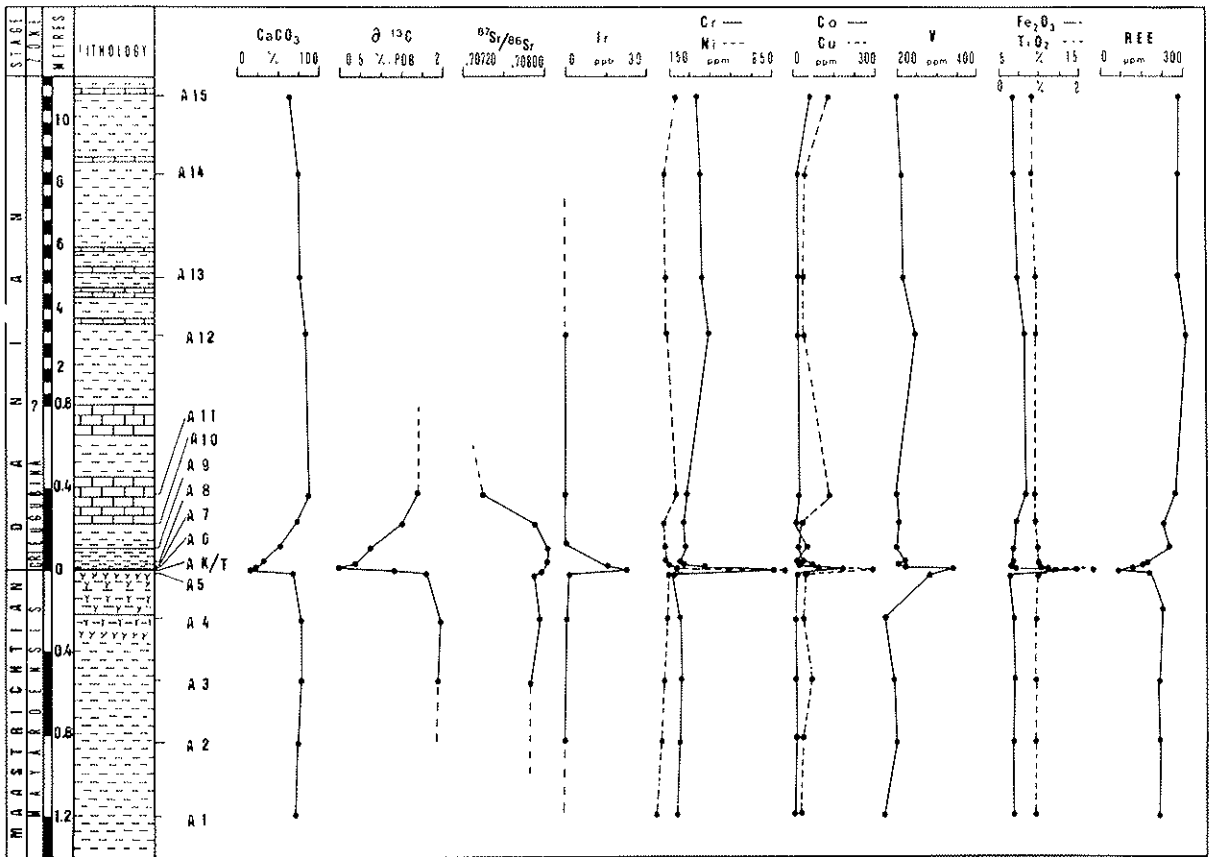


Fig. 4. Geochemical results (Cr, Ni, Co, Cu, V, Fe_2O_3 , TiO_2 and REE results have been recalculated on a carbonate-free basis).

TABLE 6

$\delta^{13}\text{C}$ (in ‰ vs. PDB) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the Agost sequence

Sample	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$
A-11	+1.38	0.70735
A-10	+0.95	0.70790
A-9	+0.26	0.70799
A-8	+0.24	0.70797
A-6	-0.59	0.70794
A-K/T	+0.83	0.70792
A-5	+1.58	0.70786
A-4	+1.93	0.70790
A-3	+1.79	0.70779

4). Moreover, the boundary is characterized by a decrease in the content of Ca, REE, Rb and P.

The REE content (Table 5), which is small-

est in the sample from the boundary, increases gradually in the first centimeters of the Tertiary, and maintains similar values in the rest of the sequence, these being slightly higher in the Tertiary than in the Cretaceous samples.

Isotopic analyses of C were also carried out on the samples closest to the K/T limit (Fig. 4; Table 6). The values obtained vary between -0.59 and +1.93‰ PDB, giving a negative signal which coincides with the A-6 sample situated 0.5 cm above the K/T boundary.

The study of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic data (Fig. 4; Table 6) reveals a pattern which is normal for both the Cretaceous samples and those of the K/T boundary and immediately above this boundary (up to sample A-9). This has been deduced by bibliographical comparison with the isotopic data of seawater for the

same ages provided by Koepnick and Burke (1985). The values which appear in samples A-10 and A-11 are anomalous. They are related to the low Sr contents in the soluble fraction (697 and 630 ppm, respectively), which also reveals the existence of diagenetic phenomena which could have modified the isotopic ratio, as suggested by DePaolo et al. (1983) for samples from the Caravaca section (Spain).

5. Discussion

The mineralogical and geochemical anomalies of the Agost sequence are similar to those described by other authors in other K/T boundary sequences. It is clear that the boundary marks a sharp break in the sequence analyzed here.

One of the most outstanding characteristics of this level in the Agost sequence is the abundant presence of spherules. Their morphologies are similar to spherules reported in other sequences, whose origin has been widely discussed. Smit and Klaver (1981) recognized crystalline spherules consisting of K-feldspar at the K/T boundary at Caravaca. These authors suggested that the spherules derived from a projectile rich in chalcophile and moderately rich in volatile elements such as K, As, Sb and Zn.

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. The spherules were interpreted differently by Hansen et al. (1986), who considered that they are the result of diagenetic infill of prasinophyte algae and are unrelated to bolide impact.

The Kfs spherules found by us at Agost do not present any internal structure that might suggest they were primary phases so they could be connected to diagenetic processes.

The Fe-oxide spherules are also very altered. In our opinion, they are products of weathering derived from diagenetic pyrite clumps (Fig.

3A and B) and are responsible for the high contents of chalcophile As, Cu and Zn, among other elements. Similarly spherules with high As content have been described by Brooks et al. (1984) at Woodside Creek (New Zealand). They could correspond to pyrite spherules formed in connection with the decomposition of organic material later altered to goethite and hematite. Some pyritic relics are found in these spherules (Fig. 3C) and the internal structure of some of them is even similar to the framboid texture of sedimentary pyrites (Fig. 2). Their formation is coherent with reductive bottom conditions as a consequence of an unusual influx of organic material in the bottom waters following a sudden mass extinction in the surface layers. Therefore, at least the spherules we have found are not related to the cause of the extinction, but are a consequence of this extinction.

We have not as yet found spinel crystals with dendritic textures in K/T boundary sediments, as reported by Kyte and Smit (1986), who interpret their origin as being an accretion of cometary or asteroidal material.

The Ce/Ce* ratio is normally taken to be indicative of the degree of detritism (Courtois and Hoffert, 1977). In the Agost sequence this parameter reaches its highest value (1) (Table 5), and so the greatest degree of detritism, in the K/T limit, and generally decreases from that position towards the top of the sequence. These data clearly indicate the existence of intense weathering which would have provided a large quantity of materials for the sedimentary basin and which would to a large extent explain the important anomalies of Sr (2,540 ppm) and Ba (16,300 ppm) (Table 4) detected in the K/T level at Agost.

However, the increase in detritism does not constitute a clear argument in favour of either a terrestrial or extraterrestrial hypothesis, since identical situations are reached as a result of volcanism or a hypothetical impact. Both hypotheses imply the existence of conditions of

acidity in the atmosphere caused by the emission of large quantities of H_2SO_4 or HCl, in the case of the volcanic hypothesis (Officer and Drake, 1985), or by the formation of large quantities of NO_x by impact, which would produce an extremely acid rain lasting a certain length of time (Prinn and Fegley, 1987).

The K/T boundary at Agost is characterized by the abundance of smectites in relation to the rest of the sequence (Table 1). The TEM microanalyses reveal that the Fe/Al ratio reaches values of ~ 0.4 and that the order of abundance of the octahedral cations is $Al > Fe > Mg$. Similar analytical data were interpreted by Kastner (1976) as being characteristic of smectites genetically related to the alteration of volcanic rocks (mainly basalts). These data differ clearly from those reported by Kastner et al. (1984), who found a Mg-smectite in the Fish Clay at Stevns Klint, which was interpreted as a direct isochemical alteration of impact ejecta.

On the other hand, the clay minerals above and below the K/T boundary in the Agost sequence are similar, with predominance of illite and kaolinite (Table 1), which indicates that the genesis of the K/T layer took place in different physico-chemical environmental conditions. The same interpretation should be made of the significant and progressive increase of the proportions of kaolinite from the K/T boundary to sample A-11 (35–40+ cm), the high Ce/Ce* ratio, and the constant presence of chlorite (chamosite) and palygorskite which cause a significant increase of Fe and Mg in the levels situated above the K/T boundary (up to the A-9 level, Table 3). In our opinion, the illite-kaolinite-chlorite (chamosite)-palygorskite mineral association must be considered as detrital and, therefore, indicative of the existence of weathering and input of materials during a certain length of time from the K/T deposition. In fact, the TEM microanalyses reveal that the smectite, illite and kaolinite deposited above the K/T boundary (A-6 to A-9) contain Ti, Cr and Zn as against the character-

istics of these minerals in the Cretaceous sediments of the Agost sequence. This fact, together with the presence in the same levels of Fe-, Ti- and Cr-oxides, could indicate that the environmental conditions in which the boundary layer was deposited continued for some time. In addition, the Ce/Ce* ratio reaches high values (Table 5) also indicative of the existence of material input and a high degree of detritism.

The association of palygorskite with chlorite, its constant presence in the levels with a greater quantity of kaolinite, and the absence in the Agost sequence of zeolites and opal-CT, are data concordant with a detrital origin for palygorskite, although a genesis related to diagenetic transformation of dioctahedral smectites cannot be discounted.

Other mineral phases detected by TEM, such as celestite and barite, must have been formed in the early diagenetic stage, coinciding with the oxidation processes of the sediments.

Other geochemical anomalies found in the Agost sequence refer to the enrichment of the PGE (Table 2). The following concentrations of Ir were detected: 24.4 ppb in the K/T boundary, 16.5 ppb in the sample located 1 cm above the boundary, and 1.1 ppb in the Cretaceous sediment immediately underlying (0–2 cm) the K/T. These positive anomalies have normally been used to support an extraterrestrial hypothesis (e.g., Alvarez et al., 1980) given the scarcity of this element in terrestrial rocks. However, Olmez et al. (1986) suggest that a deep source volcano could release sufficient Ir to account for most of that found in the K/T boundary. Similarly, Koeberl (1989) detected anomalies of Ir and other elements such as As, Sb, Cr or Se in deposits of volcanic ash intercalated in blocks of Antarctic ice. In these authors' opinion, this enrichment would have come about as a consequence of the condensation of the vapour phase after intensive volcanic eruptions, which shows that the source of Ir does not necessarily have to be of extraterrestrial origin. As an alternative to the im-

pact of extraterrestrial material, Crocket et al. (1988) and Graup et al. (1989) prefer the hypothesis of intense volcanic activity. At Gubbio (Italy) and Lattengebirge (Germany) these authors found multiple Ir anomalies in addition to the major Ir enrichment in the K/T boundary layer.

In the sequence studied by us, there is a certain similarity with these sequences, as the enrichment in Ir is not restricted to the boundary layer, but continues to show high values up to 1 cm above (16.5 ppb) and below (1.1 ppb) the K/T. We must not discount an important process of enrichment in these elements which could have occurred during the diagenesis of the sediments as a result of the activity of organisms. This has been shown for some sequences, Stevns Klint and Caravaca, where the Ir partially appears in association with kerogen, which suggests the possibility of the reduction and fixing of the noble metals during decomposition of organic material (Schmitz et al., 1988). We also consider the views of Dyer et al. (1989) to be of interest, according to whom the participation of microbial activity should be taken into account in many sedimentary Ir anomalies.

In the case of the sequence studied by us, the concentrations of PGE are too high to be explained simply by processes of enrichment from seawater. The added influence of a terrestrial or extraterrestrial source supplying the noble metals is required. We have looked into this question by comparing our analytical data for the PGE, normalized to *C1* chondrites, with those corresponding to a meteoritic pattern and also those from other stratigraphic sequences. In the case of the Agost sequence, the data available at present provide broken lines very different from the straight line (slope 1) corresponding to meteorites, and even from the patterns of the Stevns Klint and Caravaca sequences, in which a meteoritic origin has been suggested for the anomalies in noble metals (Kyte et al., 1985) (Fig. 5). On the other hand, the pattern found by us at Agost is similar to

that found in different samples of K/T boundary clays from the northern hemisphere (Fig. 5) by Tredoux et al. (1989), who proposed the existence of an extended period of later Cretaceous volcanism as an explanation for the features of the K/T geochemical anomalies. However, it must be pointed out that the normalized values of the Tertiary samples from the Agost sequence are higher than the normalized values corresponding to Iherzolite rock (Fig. 5).

Post-depositional processes could have brought about a differential enrichment of these elements, which would cause the difference between the Agost sequence and a meteoritic pattern and also that presented by the K/T layers at Stevns Klint and Caravaca. Nevertheless, according to the available mineralogical data, the diagenesis undergone by the sediments analyzed was slight, causing only partial transformation of smectite to illite, as revealed by HRTEM. Therefore, the differences in the patterns of these elements cannot only be explained by secondary alteration of a layer that was originally chemically homogeneous, especially for elements of dubious crustal mobility, such as Os and Ir.

Other geochemical parameters normally in use also provide some additional information in this sense. Thus, the Pt/Ir ratio is 1.06 in the Agost sequence as against the 1.75 corresponding to chondrites. Similarly the Au/Ir ratio is high in Agost (0.94) in comparison to that of chondrites (0.30). On the other hand, the Ni/Ir ratio in the Agost sequence (22.79) is practically identical to that found in meteorites (23.25) (Anders and Ebihara, 1982). However, the La/Yb ratio found in Agost is 16.57, which is much higher than that corresponding to meteorites and falls clearly within the range of crustal rocks (Henderson, 1984).

It is also of interest to point out the positive anomalies found in the Agost sequence of chemical elements of clearly terrestrial origin, such as As, Sb, Zn, Sr, Ba, K, and U (Table 4), which are not abundant in meteorites (Anders

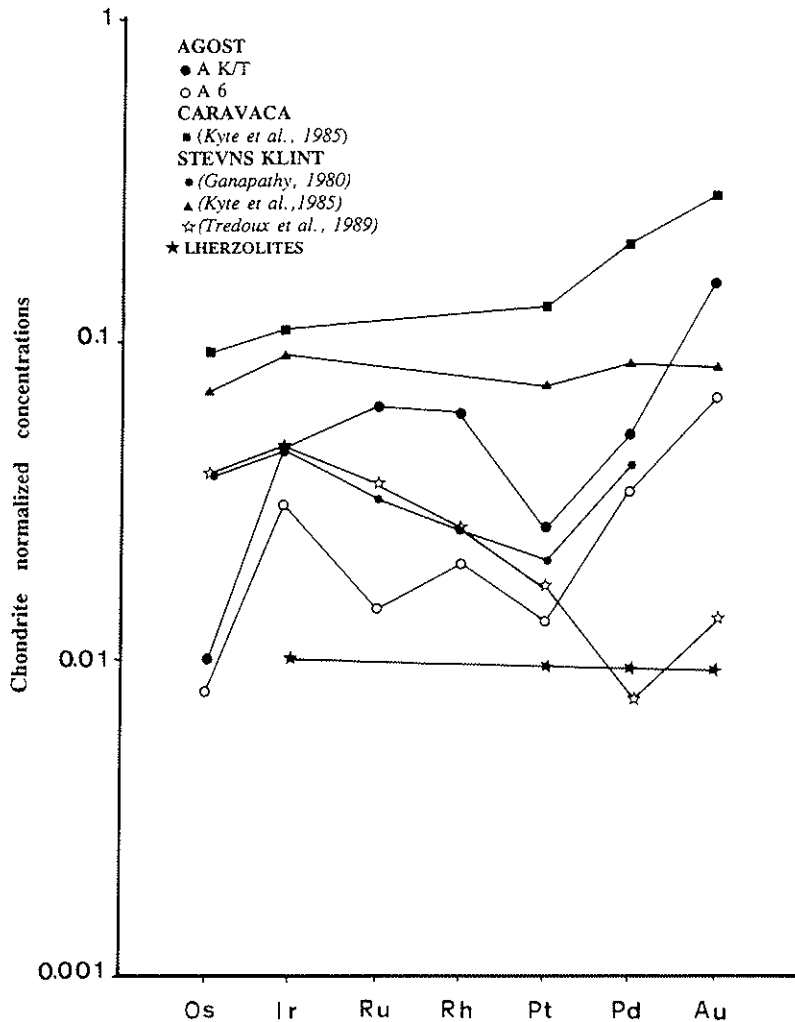


Fig. 5. Chondrite-normalized PGE and Au contents of samples of Agost. As a reference data from Caravaca and Stevns Klint (Kyte et al., 1985), Stevns Klint fishclay samples (Ganapathy, 1980; Tredoux et al., 1989) and lherzolites (Stockman, 1982) have been also represented.

and Ebihara, 1982). Some of these (As, Sb, Zn) are found here in much greater concentrations than in any sedimentary rock. Given that this enrichment is found in the majority of sequences studied, the defenders of the impact theory suggest the target zone as source of these elements (Gilmour and Anders, 1989). This hypothesis poses the problem of the much greater abundance of these elements in comparison to any other type of rock.

Additional factors must taken into account

to explain this enrichment. As proposed by Schmitz (1985) and Schmitz et al. (1988), the redox processes during diagenesis could have controlled the enrichment of these elements, precipitating many of them during the reduction of the sulphates and the formation of sulphides. This hypothesis seems in our opinion to be a basically feasible mechanism by which really high concentrations could be reached with no need for the existence of other anomalously enriched sources of As, Zn or Sb.

6. Summary

The K/T boundary of the Agost sequence, like all the other worldwide K/T layers is characterized mineralogically, by a sharp decrease in the carbonate content and an increase in the proportions of clay minerals, especially dioctahedral smectites. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the K/T boundary is similar to the values reported for oceanic water of the same age. Kfs and Fe-oxide spherules are frequent, with spherical, oval and drop-shaped morphologies. Some of the Fe-oxide spherules are covered with octahedrons or cubic crystals of pseudomorphized pyrite.

An enrichment was detected in PGE (Ir=24.4 ppb), As, Sb and Zn, among others. The Ce/Ce* ratio reaches its maximum value (1) in the K/T level, indicating the influence of relevant input of materials to the sedimentary basin.

We have detected an abundance of dioctahedral smectites and their diagenetic transformation into illite. The values of the Pt/Ir and Au/Ir ratios and the PGE values normalized to CI chondrites in the samples from Agost are very different from those corresponding to meteorites. Post-depositional processes could have brought about a differential enrichment of these elements and the original pattern would then have been modified.

Some of the results of our research could be consisted with meteoritic impact, but the majority indicate intense volcanic activity. Considering the importance of the volcanic activity at the end of the Cretaceous on a global scale, we do not think it necessary to have recourse to the idea of meteoritic impact in order to explain the geochemical anomalies of the K/T boundary.

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