The environmental disaster of Aznalcóllar (southern Spain) as an approach to the Cretaceous–Palaeogene mass extinction event

F. J. RODRÍGUEZ-TOVAR¹ AND F. J. MARTÍN-PEINADO²

¹Departamento de Estratigrafía y Paleontología, Universidad de Granada, Granada, Spain ²Departamento de Edafología, Universidad de Granada, Granada, Spain

ABSTRACT

Biotic recovery after the Cretaceous-Palaeogene (K-Pg) impact is one unsolved question concerning this mass extinction event. To evaluate the incidence of the K-Pg event on biota, and the subsequent recovery, a recent environmental disaster has been analysed. Areas affected by the contamination disaster of Aználcollar (province of Sevilla, southern Spain) in April 1998 were studied and compared with the K-Pg event. Several similarities (the sudden impact, the high levels of toxic components, especially in the upper thin lamina and the incidence on biota) and differences (the time of recovery and the geographical extension) are recognized. An in-depth geochemical analysis of the soils reveals their acidity (between 1.83 and 2.11) and the high concentration of pollutant elements, locally higher than in the K-Pg boundary layer: values up to 7.0 mg kg⁻¹ for Hg, 2030.7 mg kg⁻¹ for As, 8629.0 mg kg⁻¹ for Pb, 86.8 mg kg⁻¹ for Tl, 1040.7 mg kg⁻¹ for Sb and 93.3-492.7 p.p.b. for Ir. However, less than 10 years after the phenomenon, a rapid initial recovery in biota colonizing the contaminated, 'unfavourable', substrate is registered. Nesting of the ant Tapinoma nigerrima (Nylander) has taken place through the tailing layer, with arranged particles from inside the soils showing similar values in pollutant elements as the deep soils. This agrees with recent ichnological evidence of a rapid colonization of the K–Pg boundary layer, classically interpreted as an inhabitable substrate, by organisms with a high independence with respect to substrate features (i.e. Chondrites trace makers). The dramatic consequences of the K–Pg boundary impact and the generalized long-time recovery interpreted after the event (in the order of $10^4 - 10^5$ years) could have been overestimated due to the absence of a high-temporal resolution in the range of 10^2-10^3 years.

Received 24 April 2009; accepted 03 July 2009

Corresponding author: F. J. Rodríguez-Tovar. Tel.: +34 958 242724; fax: +34 958 248528; e-mail: fjrtovar@ugr.es

INTRODUCTION

A profusely studied environmental disaster from the fossil record is that corresponding to the Cretaceous–Palaeogene (K–Pg) boundary event, considered to be one of the most significant mass extinctions during the Phanerozoic. This boundary is characterized by relatively rapid and dramatic changes that affected marine and terrestrial communities (Kauffman & Hart, 1996). Most researchers agree that the catastrophic environmental changes were related to a large bolide impact (the Chicxulub impact event), although other hypotheses have also been proposed (Keller & Barrera, 1990; Smit, 1990). The K–Pg boundary layer (the ejecta layer, a usually mm-thick reddish lamina) contains the evidence of the extra-terrestrial impact, including spherules (altered microtecktites in Smit, 1990), as well as Ir and other platinum-group element anomalies in Ni, Co, Cr and Fe (for

an updated review, see Smit, 2005). These contaminated sediments were initially discovered in marine rocks (Alvarez et al., 1980) but more recently have also been registered in the K-Pg boundary layer from continental sediments deposited under freshwater conditions (Orth et al., 1981; Pillmore et al., 1984; Tschudy et al., 1984), including palaeosols spanning the K-Pg transition (Fastovsky, 1987; Fastovsky & McSweeney, 1987; Retallack et al., 1987; Fastovsky et al., 1989; Retallack, 1996, 2004). The dramatic environmental changes that occurred during the K-Pg event continued after impact, as is interpreted in view of the prolonged delay in the recovery of the biota, especially in marine ecosystems, in contrast to a faster recovery of the terrestrial counterparts (Beerling et al., 2001). However, recent ichnological analyses have revealed a relatively rapid colonization of the macrobenthic marine environment by trace makers (Rodríguez-Tovar & Uchman, 2004, 2006, 2008; Rodríguez-Tovar, 2005).

Interpretation of this recovery proves to be of special significance.

On 25 April 1998, the Doñana National Park (southern Spain), the largest wetland area in Europe, was affected by the failure of a tailing pond at the pyrite mine of Aznalcóllar (province of Sevilla). Approximately 4500 ha of the Agrio and Guadiamar rivers and adjacent land, as far as 45 km downstream, were affected by a spill of about 4 million cubic metres of acidic water and 1 million cubic metres of tailing with high concentrations of toxic elements (mainly As, Cd, Cu, Pb, Sb, Tl and Zn; Simón et al., 1999, 2002; Del Río et al., 2002). All affected soils were covered by a layer of tailings (7 cm average thickness) and the uppermost 10 cm of the soils were intensely polluted (Simón et al., 1999); however, infiltration of acidic waters and tailings also affected the soils at depth. After a few days, as a result of the drying and aeration of tailings, sulphides oxidized to sulphates, the pH acidified markedly and the toxicity of the soils strongly increased (Simón et al., 2002). This 'event' was considered to constitute one of the worst environmental disasters in western Europe over the last decades, affecting different ecosystems along the Guadiamar river and the Guadalquivir estuary. Laboratory and field analysis was performed on biotic communities (animals and plants) in order to evaluate the different stages of recovery, and to facilitate restoration. In most cases this recovery is 'artificial' supported by the addition of different substances (amendments rich in organic matter, calcium carbonate, clay and iron oxides). Overall, recovery is relatively rapid, with a variety of higher plant species being capable of colonizing the polluted environments (Del Río et al., 2002). The macroinvertebrate community showed a general impoverishment 2 years after the Aznalcóllar event, with only few species managing to live in the most polluted areas with very low pH and high metal concentrations (Solà et al., 2004). However, 5 years after this environmental disaster, the contaminated area shows the incipient recovery of ant communities, particularly the record of Tapinoma nigerrima (Nylander) (Luque et al., 2007). This species is abundant in the Doñana National Park (Carpintero et al., 2003; Luque et al., 2007), and active from February to October in olive groves in southern Spain (Redolfi et al., 2005). Tapinoma nigerrima is considered an opportunist species, forming large colonies, building mounds of soil that are used as nurseries (Pickles, 1943), and showing an aggressive behaviour featuring response to attacks in large numbers, leading them to be considered a dominant species (Carpintero et al., 2003 and references therein).

Whereas the origin of the two phenomena (K–Pg event and Aznalcóllar) is totally different, as is the geographical extension of the affected area, certain similarities of another nature can be discerned: the sudden impact, the high levels of toxic components registered in a thin lamina, and the important incidence on the biotic community. Significant is the different time recovery involved after the two phenomena, which is

comparatively short in the current example. Here, we study the incidence of the 'inhabitable' substrates on the colonizing biota, focusing on the geochemical analysis of the soils affected by the Aznalcóllar disaster and the behaviour of *T. nigerrima*. The comparison with the K–Pg boundary event was evoked in order to assess the unavailability of the environment after this mass extinction event.

MATERIALS AND METHODS

After the Aznalcóllar disaster, most of the tailing was physically removed, but some experimental areas (two plots; 10×15 m² each) were maintained without any treatment, preserving a thin layer of tailing over the soils (Figs 1 and 2). These plots are located in the area known as Vado del Quema, 25 km from the tailing pond, within the flooding plane of the Guadiamar river (Figs 1 and 2). The tailing in this area has a mean thickness of 2-5 cm (Fig. 2); and the soil was characterized by a low degree of differentiation, a sandy-loam texture (12% clay), low organic matter content (<2%), a mean calcium carbonate content of 13% and a pH close to 8. The continuous infiltration of acidic and toxic solutions coming from the pyrite tailing oxidation during 4 years (1998-2002) produced a strong degradation of many soil properties as well as important changes in the soil morphology (Martín et al., 2007). Most noteworthy among these were the intense acidification of the upper part of the soil (with pH values close to 2.0), the partial alteration of clay minerals, feldspars and organic matter content, and an increase in the electrical conductivity of the soil solution (10-fold greater than in unaffected soil). The most evident change in the morphology of the soil is the appearance of horizons with colorations strongly differing from those of the original soil (a discoloured layer with pale greyish tonalities in the first 2-3 cm, followed by a reddishbrown layer to a depth of around 40 cm; Fig. 2). At the same time, the carbonates weathered, disappearing completely from the upper 6 cm and partially to 20 cm in depth. The resulting products in this process give rise to an intense neoformation of gypsum and iron hydroxysulphates (mainly jarosite-group minerals, schwertmannite and ferrihydrite) which, together with the acidic conditions of the medium, determine the distribution of the main elements of the soil, both in their total and soluble forms.

Ant nests of the species *T. nigerrima* were studied in the experimental area during August 2005 and February 2007. Mounds show a subcircular plan, and a typical cone-shaped nest structures; particles from the excavations are carried from the nest and accumulated outside forming the conical mound (Fig. 3). Sediment constituting the mounds shows variations in colour coincident with those registered in the soil profile (Fig. 3). Thus, single colour (light grey, dark grey and red) and more than one-colour (light grey and red, or light grey and dark grey) conical mounds could be differentiated.



Fig. 1 Location of the experimental plots in the area known as Vado del Quema, 25 km from the tailing pond, close to the Doñana National Park (southern Spain), indicating the flooding plane of the Guadiamar river affected by the tailing spill.

Fig. 2 (A) General view of the uncovered experimental plot surrounded by vegetation. (B) Close-up view of the tailing layer covering the soils. (C) Tailing layer showing a mean thickness of 2–5 cm. Scale bar: 10 cm. (D) Soils at depth showing horizons with different colorations, pale greyish in the upper part and reddish-brown downward.

Soil samples from the mounds (external; E) and from the soil material at depth (internal; I) were collected from the dark grey tailing (ETG and IT), strongly altered greyish soil (EG and IG), moderately altered reddish soil (ER and IR), and unaltered brown soil (EB and IB) (Fig. 4). For iridium analysis a more detailed sampling was performed, especially in the

moderately altered reddish (IR to IR-5) and unaltered brown soils (IB-1 and IB-2). Soil samples were air dried and sieved to 2 mm to calculate the percentage of gravels; all the analyses were carried out with the fine earth fraction (<2 mm). In soil samples, pH was determined potentiometrically in a 1 : 2.5 soil : water suspension, in a Crison micropH 2002 instrument

536 F. J. RODRÍGUEZ-TOVAR AND F. J. MARTÍN-PEINADO



(Crison, Barcelona, Spain). Total content in major elements (Si_T, Al_T, Fe_T and S_T) was determined after preparation of soil pellets with lithium tetraborate (0.6 : 5.5) using X-ray fluorescence in a Philips PW-1404 instrument (Philips, Eindhoven, the Netherlands). Total concentrations of arsenic and heavy metals were determined in finely ground soil samples (<0.05 mm), after digestion in strong acids (HNO₃ + HF) using ICP-MS with a PE SCIEX ELAN-5000A spectrometer (Perkin-Elmer, Überlingen, Germany). The accuracy of the method was corroborated by analyses (six replicates) of Standard Reference Material: SRM 2711 (Simón *et al.*, 2002). All analyses were performed at the University of Granada.

RESULTS

A significant increase in the number of active nests of *T. nigerrima* during the second visit (from 3–4 August 2005 to around 15 February 2007). Nests show a random distribution, as is



usual in the first phases of colonization, when density and intra-specific competition is low (i.e. Redolfi *et al.*, 2005), being comparatively more abundant close to the edge of the experimental area. Apart from the nesting holes, several trails were registered between nests. Cone structures were similar in morphology, only with minor differences in size. Remobilization of the upper tailing layer revealed that ant's eggs were located directly in contact with this surface (Fig. 3).

An in-depth geochemical analysis of the sediment forming the mounds and of the soil reveals a similar composition between same-colour materials, corroborating that mounds consist of particles carried out from the deep soil.

The pH values and the main pollutant element concentrations are shown in Tables 1 and 2. The tailing deposited over the soil (IT) and the one remobilized by the ants (ETG) present highly acidic pH values (1.83–2.20), showing a very strong influence of the tailing oxidation and the infiltration



Fig. 4 Scheme showing different types of mound composition (EG, external grey; ER, external red; ETG, external tailing and grey), tailing layer (IT) and soils at depth (IG, internal grey; IR, internal red; IB, internal unaltered brown).

of the pollutant solution into the soil. Accordingly, both the soil sampled at depth and the soil remobilized by the ants have very acidic pH values; the strongly altered layer (pale grey) gives a pH between 2.08 and 2.13, and the moderately altered layer (reddish) has a pH between 2.11 and 2.46.

The main toxic elements concentrated in the soil by the oxidation of the tailings are Hg, As, Pb, Tl and Sb. Because of their low mobility, the highest concentration of these elements lies in the first 5–10 mm of the soil; with values up to 7.0 mg kg⁻¹ for Hg, 2030.7 mg kg⁻¹ for As, 8629.0 mg kg⁻¹ for Pb, 86.8 mg kg⁻¹ for Tl and 1040.7 mg kg⁻¹ for Sb. The concentration of these elements in the contaminated soil samples represents respective increases of 18-, 107-, 226-, 124- and 578-folds in comparison with the concentration of these elements in the uncontaminated soils of the area. A high concentration of Ir is also registered from 93.3 to 492.7 p.p.b. (Table 2).

INTERPRETATIONS AND DISCUSSION

Contaminated substrates resulting from the Aznalcóllar and K–Pg events

The presence of the layer of tailing and the contamination of the uppermost centimetres of the underlying soil in the experimental area signal a dramatic event in the normal functionality of the soil, even as registered nearly 10 years after the disaster of Aznalcóllar. The maximum concentration of the different elements in the soil samples greatly exceeds the toxic levels for agricultural soils (values in mg kg⁻¹, Hg, 2; As, 50; Pb, 500; Tl, 5; Sb, 10; Kabata-Pendias & Pendias, 1984; Aguilar *et al.*, 1999). Moreover, pH values indicate the noteworthy acidity in the experimental area with respect to normal soil.

Comparison with the K-Pg event reveals similarities and differences with respect to the recent disaster of Aznalcóllar. As occurs with the tailing layer, the K-Pg boundary layer (ejecta layer) shows the presence of strongly anomalous contents in some elements. Iridium abundance anomalies, together with those in other platinum-group elements, are one of the features characterizing the K-Pg boundary layer. Element concentrations at the K-Pg boundary layer in marine and continental sections are compiled in several papers, and compared with values in crust, mantle, ocean or chondrites (i.e. Gilmore et al., 1984; Strong et al., 1987; Gilmour & Anders, 1989; Schmitz, 1992; Martínez-Ruiz, 1994). Here, we compare the concentrations of some elements as registered in the tailing layer and soils at depth from the studied area with those from the K-Pg boundary layer in selected marine and continental sections, including palaeosols spanning the K-Pg transition (Table 2). Regardless of the particular depositional setting (marine or continental), the anomalous values in some of the analysed elements at the K-Pg boundary layer, including those considered as deriving from an extraterrestrial source (i.e. Os and Ir), are in the order of, or even lower than, those registered in the experimental area.

Especially interesting, due to its significance in the interpretation of the K–Pg impact event, are the high concentrations of Ir. In terrestrial sections, iridium concentrations registered at the K–Pg boundary are lower than in marine ones but in comparison with the average background are significantly enriched (Orth *et al.*, 1981; Nichols *et al.*, 1986; Lerbekmo *et al.*, 1987; Pillmore *et al.*, 1999; Hartman *et al.*, 2002), in some cases within the range of 21–56 p.p.b. (Alvarez *et al.*, 1984; Gilmore *et al.*, 1984; Pillmore *et al.*, 1984; Bohor *et al.*, 1987; Schmitz, 1992) and with the highest values of 71 p.p.b.

Table 1 Values of pH and of some elements in the experimental area, together with data in uncontaminated soils of the area

Sample	pН	Au	Be	Bi	Cd	Hg	In	Mn	Мо	Pb	Sc	Se	Sn	Tİ	V	Y
ER	2.46	0.306	0.847	3.285	0.342	7.237	0.254	237.618	2.057	275.380	7.390	3.388	4.280	1.674	74.227	10.836
EG	2.13	0.181	1.463	4.805	1.630	3.550	0.276	501.941	1.027	356.418	8.943	2.075	5.163	2.323	69.250	18.492
ETG	2.20	0.515	0.704	45.651	1.276	5.587	0.550	186.746	4.948	5801.085	3.885	6.582	24.310	43.394	38.021	20.895
IT	1.83	0.932	0.337	66.509	1.773	6.982	0.134	103.571	11.787	8425.875	0.720	9.654	35.283	47.628	24.852	5.334
IG	2.08	0.887	0.666	93.494	2.129	4.065	1.771	163.786	3.010	8629.018	2.879	0.433	54.276	86.795	37.446	11.842
IR	2.11	0.107	1.118	4.197	0.873	1.767	0.139	260.392	0.633	111.594	6.247	3.486	2.949	0.941	72.026	11.848
UCS	7.9	0.088	1.91	0.49	0.33	0.4	0.063	678.0	0.53	38.2	12.5	<0.1	1.27	0.70	94.4	17.8

Sampling sites are mound sediments (ER, external red; EG, external grey; ETG, external tailing and grey), tailing layer (IT) and soils at depth (IG, internal grey; IR, internal red altered). Comparison with data from uncontaminated soils (UCS) of the area (Cabrera *et al.*, 1999). Geochemical values in p.p.m.

538 F. J. RODRÍGUEZ-TOVAR AND F. J. MARTÍN-PEINADO

Sample	As	Sb	Ba	Cr	Со	Ni	Cu	Zn	U	Th	lr
ER	954.630	26.240	244.328	52.695	4.817	13.838	110.168	191.577	1.018	6.781	
EG	233.543	28.269	263.205	54.801	14.981	21.184	329.304	513.413	1.832	8.555	
ETG	943.119	558.003	543.731	41.585	4.344	4.938	158.418	341.335	1.260	4.869	
IT	1008.290	1566.628	1248.014	67.185	25.529	5.560	142.823	460.669	1.646	4.346	93.3
IG	2030.705	1040.690	1112.190	55.616	4.106	6.896	409.489	552.051	1.595	5.089	492.7
IR	700.443	9.648	229.254	47.285	6.231	14.456	105.332	303.254	1.077	5.469	314.2
IR-2											249.0
IR-3											223.6
IR-4											173.6
IR-5											118.9
IB-1											106.1
IB-2											99
UCS	18.9	1.8	302	68.6	12.4	26.9	30.9	109.0	1.65	11.1	
K–Pg continental											
Moody Creek	635		445	140	816			51.7	2.62	6.17	70.2
Raton Basin	36	6.3		67	10						1.7
Sugarite				100	7	50					3.2
York Canyon				85	54			390			5.6
Montana-1											
1 : 1 Claystone			129.4			17.4	11.8	32.8			
2 : 1 Claystone			292			31.8	42.2	103.1			
Montana-2											
Sapakot clay			458	93	10	43	57	103			
Ottsko clay			790	91	13	39	45	106			
K–Pg Marine											
Agost	380	8.1	1630	540	160	556	218.0	568	23.4	8.2	24.4
Caravaca	720	15.0	23	851	390	1350	257.0	986	13.6	8.3	35.2
Gubbio	19	2.5		149	48	177		167			9.1
Stevens Klint	83	9.4		225	146	1370		810			47.4
El Kef	9.2	1.7		50	48	219		108			6.5/22.2

Table 2 Values of some elements registered in the experimental area, together with data of uncontaminated soils in the area and in the K–Pg boundary layer

Sampling sites as in Table 1, together with IR-2–IR-5 for different samples into internal red moderately altered; IB-1–IB-2 for different samples into internal brown unaltered. Comparison with data from uncontaminated soils (UCS) of the area (Cabrera *et al.*, 1999). K–Pg boundary sections: Moody Creek Mine (Vadja *et al.*, 2001); Raton Basin and York Canyon (Gilmour & Anders, 1989; Schmitz, 1992); Sugarite (Gilmore *et al.*, 1984); Montana-1, 1 : 1 and 2 : 1 Claystone (Fastovsky *et al.*, 1989); Montana-2, a horizon in palaeosols types Sapakot and Ottsko clay (Retallack, 1994); Agost and Caravaca (Martínez-Ruiz *et al.*, 1999); Gubbio (Alvarez *et al.*, 1980; Smit & ten Kate, 1982); Stevens Klint (Kyte *et al.*, 1985); El Kef (Kuslys & Krähenbühl, 1983; Meyer *et al.*, 1993; for the interval 0–1cm; Rocchia & Robin, 1998). Geochemical values in p.p.m., except Ir in p.p.b.

obtained from the K–Pg boundary layer at the Moody Creek Mine section (West Coast, New Zealand; Vadja *et al.*, 2001). Iridium anomalies in marine sections have been reported at numerous localities, with values locally in the range of hundreds of p.p.b. (for a general compilation, see Alvarez *et al.*, 1984). In the soils we analysed, the high concentrations of Ir (from 93.3 to 492.7 p.p.b.) are several times the values usually registered in the K–Pg boundary layer, including those from Ir-bearing coals (Fastovsky & Dott, 1986; Retallack *et al.*, 1987; Rigby *et al.*, 1987; Smit *et al.*, 1987; Retallack, 1994), evidencing a high level of contamination.

Palaeosols and K–Pg boundary sediments in eastern Montana reveal significant amounts of acid, interpreted as a likely consequence of catastrophic events postulated for the K–Pg boundary (nitric acid from atmospheric shock by bolide and the burning of trees, sulphuric acid from volcanic aerosols and from impact vaporization of evaporates, hydrochloric acid from volcanic aerosols and carbonic acid from carbon dioxide of volcanoes and fires), and selectively affecting the different components of the biota (Retallack *et al.*, 1987; Retallack, 1996, 2004). In any case, however, the lowest pH values are estimated between 4.0 and 5.5 for soil and groundwater in Montana, and between 7.6 and 8.2 for average ocean water; some past theoretical estimates of acidification at the K–Pg boundary of pH 2–4 are considered unreasonable (see table 2.1 in Retallack, 2004). These estimated pH values for the K–Pg boundary are considerably higher than those from the soils at depth in Aznalcóllar (between 1.83 and 2.11).

Recovery after the Aznalcóllar and K-Pg events

A significant difference is revealed between the two phenomena at hand: the comparatively rapid initial recovery of the highly altered substrate in the experimental area after the disaster of Aznalcóllar, in contrast to the interpreted prolonged recovery occurring after the K–Pg impact event. *Tapinoma nigerrima* rapidly colonized (less than 10 years after the disaster) a highly polluted substrate, producing nests in the tailing layer with particles arranged from inside the soils that show similar values in pollutant elements as those from the soils at depth.

Although the K-Pg event reveals selective extinctions between biota - i.e. the biotic effects of acid rain could have been more or less severe from place to place, and within the same ecosystem (Retallack, 1996, 2004) - in general, the marine ecosystem recovered more slowly than the terrestrial one (i.e. Beerling et al., 2001). Calibration of the initial recovery in the marine environment is in the range of hundreds to thousands of kiloyears, although differences in time recovery are registered between planktic and benthic populations. Initial recovery of the surface-to-deep water carbon isotope gradient is estimated at over 500 kyr, whereas full restoration may not have occurred for 1-3 Ma (D'Hondt et al., 1998; Arens & Jahren, 2000). Yet, some plankton populations recovered faster, with the record of initial recovery of planktonic foraminifera at about 230 kyr (Keller & Barrera, 1990), or early pioneer calcareous nannoflora at just about 25 kyr after the K-Pg boundary mass extinction event (Lamolda et al., 2005). Some hypotheses point to 10 kyr as the time required to restore food chains and repair ecosystems, after which the oceans were repopulated with planktonic species characterized by high turnover rates (Mukhopadhyay et al., 2001). Benthic foraminifera show no significant extinction at the end of the Cretaceous. A comparatively rapid recovery of the benthic foraminiferal ecosystem was interpreted by Coccioni & Galeotti (1994), with the reappearance of complex trophic structures at around 7 kyr after the K-Pg boundary, but with low oxygen tolerant epifauna reappearing between 600 and 1200 years after the event.

The terrestrial ecosystem recovers comparatively faster after the K-Pg event, especially the vegetation community. Although occasionally the recovery in diversity of early Palaeocene vegetation is interpreted on an evolutionary - not ecological - timescale (i.e. Wolfe & Upchurch, 1987), in many papers the calibration of time recovery is in the range of $10-10^2$ years, showing rapid recovery in the earliest Palaeogene. The continental ecosystem was also perturbed by the bolide impact at the K-Pg boundary, determining the photosynthesis crisis (Vadja & McLoughlin, 2004) and significant variations in climate (Beerling et al., 2001; Lomax et al., 2001; Wilf & Johnson, 2004; Twitchett, 2006), also registered from changes in palaeosol development across the K-Pg boundary (Fastovsky, 1987; Fastovsky & McSweeney, 1987; Retallack et al., 1987; Fastovsky et al., 1989; Retallack, 1994). Climatic effects have been estimated to have a duration in the range of months or years (Wolfe, 1991; Pope et al., 1997). Associated with the Chicxulub impact, the palynofloral signature is interpreted as revealing a massive vegetation disruption (Vadja et al., 2001, 2003; Vadja & Raine, 2003; Vadja & McLoughlin, 2004), and the instantaneous (days to months) destruction of diverse forest communities, exhibiting significant regional differences in floristic turnover (Vajda & McLoughlin, 2007). Insect feeding damage reveals the impact of the terminal Cretaceous event on plant-insect associations, showing a major extinction of insect hervibores, as well as depauperate levels of plant-insect associations in the early Palaeocene (Labandeira et al., 2002a,b; Wilf et al., 2006). The existence of regions considered as biodiversity refugia during the global environmental K-Pg boundary event could lead the effects to be comparatively less dramatic in the terrestrial ecosystem compared with the marine realm. For some authors, biodiversity refugees are intrinsically hypothetical (e.g. Wignall & Benton, 1999); however, in most cases, refugia are considered to be sanctuaries sheltering Lazarus taxa during an environmental crisis before they recolonize the altered areas, and reappear in the fossil record (Jablonski, 1986; Kauffman & Harries, 1996; Fara, 2001 and references therein). While areas of refugia during the end-Cretaceous mass extinction event are interpreted for the marine environment (e.g. Wooldridge, 2008), these are more frequently evoked for the terrestrial ecosystem, with relictual fossil and 'extant' organisms being registered in regions that can be considered a biodiversity refuge for surviving biota (Tschudy et al., 1984; Beerling et al., 2001; McLoughlin et al., 2008). Lower extinction rates in plants are related to a dormant phase in their life cycle, allowing for survival despite long-term environmental disruptions (Vajda & McLoughlin, 2007). These lower extinction rates are interpreted as the possible cause of the comparatively rapid carbon isotopic recovery in the terrestrial environment (in a maximum interval of 130 ± 5 kyr; Arens & Jahren, 2000), with respect to the marine counterpart. Model simulations predict a terrestrial primary productivity recovery within 10 years, and global terrestrial carbon storage in vegetation biomass recovery on a 60- to 80-year timescale (Lomax et al., 2001). In this range, Vajda & McLoughlin (2007) proposed the probable recovery of the herbaceous vegetation community within a few months to years of the Chicxulub impact. Palaeosol features, including plant remains, allow estimation of the time for the formation of palaeosols across the K-Pg boundary in eastern Montana in the order of some hundreds to a few thousand years (Retallack et al., 1987; Fastovsky et al., 1989; Retallack, 1994).

The comparatively rapid recovery of the contaminated soils after the disaster of Aználcollar by *T. nigerrima* may be related to several factors, such as the comparatively smaller geographical extension of the affected area and the opportunistic character of this species. In the case of the Aznalcóllar event, the different extents of extinction, of a geographically local range, could facilitate a rapid recolonization of the polluted areas. Adjacent populations of *T. nigerrima* inhabiting areas not contaminated by the environmental disaster have served as sources for repopulating the affected areas, determining a rapid recolonization. By contrast, the global nature of the K-Pg event, geographically vast, could condition the recovery of the affected zone. In the latter case, only biodiversity refuges adjacent to the affected areas could facilitate recolonization. Whereas on a local or regional scale, the refugium hypothesis is more widely accepted, it is more difficult to confirm for a global extension (Fara, 2001). The opportunistic character and aggressive behaviour of T. nigerrima, together with their independence from substrate features, allow for the colonization of an inhabitable, highly polluted, substrate. This would be consistent with recent ichnological data obtained from the K-Pg boundary layer, revealing the existence of a well-developed endobenthic multitiered assemblage established shortly after the K-Pg boundary event (Rodríguez-Tovar & Uchman, 2004). Moreover, the existence of spherules in the K-Pg boundary layer infilling Thalassinoides (Rodríguez-Tovar, 2005) and the lateral disturbation of this layer by Chondrites (Rodríguez-Tovar & Uchman, 2006, 2008) evidence the colonization of the ejecta layer, interpreted as an unfavourable substrate, due to the independence of Chondrites trace makers to substrate features, and their adaptation to lowered oxygenation and food content in sediments. This agrees with the record of faecal pellets from detritivorous soil invertebrates, such as earthworms, registered in Late Cretaceous and Early Palaeocene palaeosols, which would be less affected by the K-Pg boundary event (Retallack, 2004). Thus, although a simple comparison between the organisms involved - ants and Chondrites trace makers - is difficult, we could interpret that a contaminated laver, like those represented by the K-Pg boundary layer or by the Aznalcóllar tailing layer, does not impede colonization of those organisms with an opportunistic behaviour, and showing a high independence from the substrate.

In this context, the interpreted dramatic incidence of the K–Pg boundary impact on biota might be overestimated, as well as the generalized long-time recovery proposed after the impact due to the absence of a high-temporal resolution that would be detailed enough to characterize temporal intervals in the range of 10^2 – 10^3 years. Comparison with actual examples of environmental disasters proves useful to approach palaeo–environmental events (Kuhnt *et al.*, 2005).

CONCLUSIONS

The contamination disaster of Aználcollar (Sevilla province, southern Spain) in April 1998 reveals similitude (the sudden impact, the high levels of toxic components especially registered in an upper thin lamina and the incidence on the biotic community) and differences (the time recovery involved after the event and the geographical extension) with respect to the K–Pg boundary event. Comparison between the two phenomena provides for a valuable approach to interpret how

dramatic the K–Pg boundary impact and the recovery after the event actually were.

1 Soils at depth in the experimental area affected by the Aznalcóllar disaster show a high concentration in pollutant elements. Values up to 7.0 mg kg⁻¹ for Hg, 2030.7 mg kg⁻¹ for As, 8629.0 mg kg⁻¹ for Pb, 86.8 mg kg⁻¹ for Tl, 1040.7 mg kg⁻¹ for Sb and from 93.3 to 492.7 p.p.b. for Ir have been registered 10 years after the event.

2 The pH values (close to 2.0) indicate an intense acidification of the upper part of the soil.

3 The values obtained for the analysed elements are, in several cases (i.e. Ir), higher in the tailing from the experimental area than those registered in the ejecta layer from marine and terrestrial K–Pg boundary sections.

4 The ant *T. nigerrima* is recognized, less than 10 years after the disaster, performing nesting in the tailing layer, with particles arranged from inside the soils that show similar values in pollutant elements as those from the deep soils.

5 The rapid initial recovery seen could be related to the comparatively smaller geographical extension of the affected area, and the opportunistic behaviour of *T. nigerrima*, its aggressive character and its independence with regard to the features of the polluted substrate. This agrees with the comparatively short, nearly coetaneous, macrobenthic colonization after the K–Pg boundary event by organisms with a high independence from substrate features (i.e. *Chondrites* trace makers).

6 The interpreted dramatic consequences of the K–Pg impact event could be reconsidered, at least for the macrobenthic community, in the light of the possibility of colonization of 'inhabitable' highly contaminated substrates, by organisms with a high independence regarding substrate conditions.

7 The long-time recovery proposed after the K–Pg boundary impact (in the order of 10^4-10^5 years) may be overestimated due to the absence of a high-temporal resolution, that was precise enough to characterize temporal intervals in the range of the 10^2-10^3 years.

8 Comparison between actual and fossil phenomena can be proved informative particularly for researches, opening a new approach to advance in the knowledge of catastrophic events registered throughout the Earth's history.

ACKNOWLEDGEMENTS

We thank Dr A. Tinaut (Univ. Granada) for the identification and information of *T. nigerrima*. We thank L.A. Buatois (Univ. Saskatchewan), A. Uchman (Jagiellonian Univ.), two anonymous reviewers, the journal editor (K. Konhauser) and the subject editor (N. Butterfield) for valuable suggestions and comments on the manuscript. This research was supported by the projects CGL2005-01316/BTE, CGL2006/40233 and CGL2008-03007, and the RNM-178 and RNM-269 groups.

REFERENCES

Aguilar J, Dorronsoro C, Galán E, Gómez L (1999) Criterios y estándares para declarar un suelo como contaminado en Andalucía. Servicio de Publicaciones, Universidad de Sevilla.

Alvarez LW, Alvarez W, Asaro F, Michel HV (1980) Extraterrestrial cause for the Cretaceous–Tertiary extinction. *Science* 208, 1095– 1108.

Alvarez W, Alvarez LW, Asaro F, Michel HV (1984) The end of the Cretaceous: sharp boundary or gradual transition. *Science* 223, 1183–1186.

Arens NC, Jahren AH (2000) Carbon isotope excursion in atmospheric CO₂ at the Cretaceous–Tertiary boundary: evidence from terrestrial sediments. *Palaios* 15, 314–322.

Beerling DJ, Lomax BH, Upchurch GR, Jr, Nichols DJ, Pillmore CL, Handley LL, Scrimgeour CM (2001) Evidence for the recovery of terrestrial ecosystems ahead of marine primary production following a biotic crisis at the Cretaceous–Tertiary boundary. *Journal of the Geological Society, London* 158, 737–740.

Bohor BF, Triplehorn DM, Nichols DJ, Millard HT, Jr (1987) Dinosaurs, spherules, and the "magic" layer: a new K–T boundary clay site in Wyoming. *Geology* **15**, 896–899.

Cabrera F, Clemente L, Díaz-Barrientos R, López R, Murillo JM (1999) Heavy metal pollution of soils affected by the Guadiamar toxic flood. *Science of the Total Environment* **242**, 117–129.

Carpintero S, Reyes-López J, Arias de Reyna L (2003) Impact of human dwellings on the distribution of the exotic Argentine ant: a case study in the Doñana Nacional Park, Spain. *Biological Conservation* 115, 279–289.

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

D'Hondt S, Donaghay P, Zachos JC, Luttenberg D, Lindinger M (1998) Organic carbon fluxes and ecological recovery from the Cretaceous–Tertiary mass extinction. *Science* **282**, 276–279.

Del Río M, Font R, Almela C, Vélez D, Montoso R, De Haro Bailón A (2002) Heavy metals and arsenic uptake by wild vegetation in the Guadiamar river area alter the toxi spill of the Aznalcóllar mine. *Journal of Biotechnology* **98**, 125–137.

Fara E (2001) What are Lazarus taxa? *Geological Journal* **36**, 291–303.

Fastovsky DE (1987) Paleoenvironments of vertebrate-bearing strata during the Cretaceous–Paleogene transition, eastern Montana and western North Dakota. *Palaios* **2**, 282–295.

Fastovsky DE, Dott RH (1986) Sedimentology, stratigraphy, and extinctions during the Cretaceous–Paleogene transition at Bug Creek, Montana. *Geology* 14, 279–282.

Fastovsky DE, McSweeney K (1987) Paleosols spanning the Cretaceous–Paleogene transition eastern Montana and western North Dakota. *Geological Society of America Bulletin* 99, 66–77.

Fastovsky DE, McSweeney K, Norton LD (1989) Pedogenic development at the Cretaceous–Tertiary boundary, Garfield County, Montana. *Journal of Sedimentary Petrology* 59, 758–767.

Gilmore JS, Knight JD, Orth CJ, Pillmore CL, Tschudy RH (1984) Trace element patterns at a non-marine Cretaceous–Tertiary boundary. *Nature* **30**7, 224–228.

Gilmour I, Anders E (1989) Cretaceous–Tertiary boundary event: evidence for a short time scale. *Geochimica et Cosmochimica Acta* **53**, 503–511.

Hartman JH, Johnson KR, Nichols J (eds) (2002) The Hell Creek Formation and the Cretaceous–Tertiary boundary in the Northern Great Plains: An integrated continental record of the *end of the Cretaceous.* The Geological Society of America Special Paper 361, Boulder, CO.

Jablonski D (1986) Causes and consequences of mass extinctions: a comparative approach. In *Dynamics of Extinction* (ed Elliot DK). Wiley & Sons, New York, pp. 183–229.

- Kabata-Pendias A, Pendias H (1984) Trace Elements in Soils and Plants. CRC Press, Boca Raton, FL.
- Kauffman EG, Harries PJ (1996) The importance of crisis progenitors in recovery from mass extinction. In *Biotic Recovery from Mass Extinction Events* (ed. Hart MB). Geological Society Special Publication 102, pp. 15–39.

Kauffman EG, Hart MB (1996) Cretaceous bio-events. In Global Events and Event Stratigraphy (ed. Walliser OH). Springer, Berlin, pp. 289–312.

Keller G, Barrera E (1990) The Cretaceous/Tertiary boundary impact hypothesis and the paleontological record. In *Global Catastrophes* in Earth History: An Interdisciplinary Conference on Impacts, Volcanism, and Mass Mortality (eds Sharpton VL, Ward PD). Geological Society of America Special Paper 247, Boulder, CO, pp. 563–575.

Kuhnt W, Hess S, Holbourn A, Paulsen H, Salomon B (2005) The impact of the 1991 Mt. Pinatubo eruption on deep-sea foraminiferal communities: a model for the Cretaceous–Tertiary (K/T) boundary? *Palaeogeography, Palaeoclimatology, Palaeoecology* 224, 83–107.

Kuslys M, Krähenbühl U (1983) Noble metals in Cretaceous/Tertiary sediments from El Kef. *Radiochimica Acta* **34**, 139–141.

Kyte FT, Smit J, Wasson JT (1985) Siderophile interelement variations in the Cretaceous–Tertiary boundary sediments from Caravaca, Spain. *Earth and Planetary Science Letters* **73**, 183–195.

Labandeira CR, Johnson KR, Wilf P (2002a) Impact of the terminal Cretaceous event on plant–insect associations. *PNAS* **99**, 2061– 2066.

Labandeira CR, Johnson KR, Lang P (2002b) Preliminary assessment of insect herbivory across the Cretaceous–Tertiary boundary: major extinction and minimum rebound. In: *The Hell Creek Formation and the Cretaceous–Tertiary Boundary in the Northern Great Plains: An Integrated Continental Record of the End of the Cretaceous* (eds Hartman JH, Johnson KR, Nichols J). The Geological Society of America Special Paper 361, Boulder, CO, pp. 297–327.

Lamolda MA, Melinte MC, Kaiho K (2005) Nanofloral extinction and survivorship across the K/T boundary at Caravaca, southeastern Spain. *Palaeogeography, Palaeoclimatology, Palaeoecology* 224, 27–52.

Lerbekmo J, Sweet A, Louis RMS (1987) The relationship between the iridium anomaly and palynological floral events at three Cretaceous–Tertiary boundary localities in western Canada. *Geological Society of America*, *Bulletin* **99**, 325–330.

Lomax BH, Beerling D, Upchurch G, Jr, Otto-Bliesner BL (2001) Rapid (10-yr) recovery of terrestrial productivity in a simulation study of the terminal Cretaceous impact event. *Earth and Planetary Science Letters* 192, 137–144.

Luque GM, Reyes-López J, Fernández-Haeger J (2007) Recovery of ground ant (Hymenoptera: Formicidae) communities six years after a major environmental disaster. *Community and Ecosystem Ecology* 36, 337–347.

Martín F, Diez M, García I, Simón M, Dorronsoro C, Iriarte A, Aguilar J (2007) Weathering of primary minerals and mobility of major elements in soils affected by an accidental spill of pyrite mailing. *Science of the Total Environment* **378**, 49–52.

Martínez-Ruiz F (1994) Geoquímica y mineralogía del tránsito Cretácico-Terciario en las Cordilleras Béticas y en la Cuenca Vasco-Cantábrica. PhD Thesis, Universidad de Granada.

Martínez-Ruiz F, Ortega-Huertas M, Palomo I (1999) Positive Eu anomaly development during diagenesis of the K/T boundary ejecta layer in the Agost section (SE Spain): implications for traceelement remobilization. *Terra Nova* **11**, 290–296.

McLoughlin S, Carpenter RJ, Jordan GJ, Hill RS (2008) Seed ferns survived the end-Cretaceous mass extinction in Tasmania. *American Journal of Botany* 95, 465–471.

Meyer G, Piccot D, Rocchia R, Toutain JP (1993) Simultaneous determination of Ir and Se in K–T boundary clays and volcanic sublimates. *Journal of Radioanalytical and Nuclear Chemistry*, 168, 125–131.

Mukhopadhyay S, Farley KA, Montanari A (2001) A short duration of the Cretaceous–Tertiary boundary event: evidence from extraterrestrial Helium-3. *Science* **291**, 1952–1955.

Nichols DJ, Jarzen DM, Orth CJ, Oliver PQ (1986) Palynological and Iridium anomalies at Cretaceous–Tertiary boundary, South-Central Saskatchewan. *Science* 231, 714–717.

Orth ChJ, Gilmore JS, Knight JD, Pillmore ChL, Tschudy RH, Fassett JE (1981) An iridium abundance anomaly at the palynological Cretaceous–Tertiary boundary in Northern New Mexico. *Science* **214**, 1341–1343.

Pickles W (1943) Variations in the ground plan of a nest of the ant Tapinoma nigerrima. Journal of Animal Ecology 12, 109–114.

Pillmore CL, Tschudy RH, Orth CJ, Gilmore JS, Knight JD (1984) Geologic framework of nonmarine Cretaceous–Tertiary boundary sites, Raton Basin, New Mexico and Colorado. *Science* 223, 1180– 1183.

Pillmore CL, Nichols DJ, Fleming RF (1999) Field guide to the continental Cretaceous–Tertiary boundary in the Raton basin, Colorado and New Mexico. In *Colorado and Adjacent Areas 1* (eds Lageson DR, Lester AP, Trudgill BD). The Geological Society of America Field Guide 1, Boulder, CO, pp. 135–155.

Pope KO, Baines KH, Ocampo AC, Ivanov BA (1997) Energy, volatile production, and climate effects of the Chixulub Cretaceous/Tertiary impact. *Journal of Geophysical Research* 102, 21645–21664.

Redolfi I, Ruano F, Tinaut A, Pascual F, Campos M (2005) Distribución espacial y permanencia temporal de hormigueros en el agrosistema del olivo en Granada, España. *Ecología aplicada* **4**, 71–76.

Retallack GJ (1994) A pedotype approach to latest Cretaceous and earliest Tertiary paleosols in eastern Montana. *Geological Society of America Bulletin* **106**, 1377–1397.

Retallack GJ (1996) Acid trauma at the Cretaceous–Tertiary boundary in eastern Montana. *GSA Today* 6, 1–7.

Retallack GJ (2004) End-Cretaceous acid rain as a selective extinction mechanism between birds and dinosaurs. In *Feathered Dragons: Studies on the Transition from Dinosaurs to Birds* (eds Currie PJ, Koppelhus EB, Shugar MA, Wright JL). Indiana University Press, Bloomington, IN, pp. 35–64.

Retallack GJ, Leahy GD, Spoon MD (1987) Evidence from paleosols for ecosystem changes across the Cretaceous/Tertiary boundary in eastern Montana. *Geology* 15, 1090–1093.

Rigby JK, Jr, Newman KR, Smit J, van der Kaars S, Sloan RE, Rigby JK, Sr (1987) Dinosaurs from the Paleocene part of the Hell Creek Formation; McCone County, Montana. *Palaios* 2, 296–302.

Rocchia R, Robin E (1998) L'iridium à la limite Crétacé–Tertiaire du site d'El Kef, Tunisie. Bulletin de la Société Géologique de France 169, 515–526.

Rodríguez-Tovar FJ (2005) Fe-oxide spherules infilling *Thalassinoides* burrows at the Cretaceous–Paleogene (K–P) boundary: evidence of a near-contemporaneous macrobenthic colonization during the K–P event. *Geology* **33**, 585–588.

Rodríguez-Tovar FJ, Uchman A (2004) Trace fossils after the K–T boundary event from the Agost section, SE Spain. *Geological Magazine* 141, 429–440. Rodríguez-Tovar FJ, Uchman A (2006) Ichnological analysis of the Cretaceous–Palaeogene boundary interval at the Caravaca section, SE Spain. *Palaeogeography, Palaeoclimatology, Palaeoecology* 242, 313–325.

Rodríguez-Tovar FJ, Uchman A (2008) Bioturbational disturbance of the Cretaceous–Palaeogene (K–Pg) boundary layer: implications for the interpretation of the K–Pg boundary impact event. *Geobios* 41, 661–667.

Schmitz B (1992) Chalcophile elements and Ir in continental Cretaceous–Tertiary boundary clays from the western interior of USA. *Geochimica et Cosmochimica Acta* 56, 1695–1703.

Simón M, Ortiz I, García I, Fernández E, Fernández J, Dorronsoro C, Aguilar J (1999) Pollution of soils by the toxic spill of a pyrite mine (Aznalcóllar, Spain). *The Science of the Total Environment* 242, 105–115.

Simón M, Dorronsoro C, Ortiz I, Martín F, Aguilar J (2002) Pollution of carbonated soils in a Mediterranean climate due to a tailings spill. *European Journal of Soil Science* 53, 321–330.

Smit J (1990) Meteorite impact, extinctions and the Cretaceous– Tertiary boundary. *Geologie en Mijnbouw* 69, 187–204.

Smit J (2005) The section of the Barranco del Gredero (Caravaca, SE Spain): a crucial section for the Cretaceous/Tertiary boundary impact extinction hypothesis. *Journal of Iberian Geology* **31**, 179– 191.

Smit J, ten Kate WGHZ (1982) Trace-element patterns at the Cretaceous–Tertiary boundary – consequences of a large impact. *Cretaceous Research* **3**, 307–332.

Smit J, van der Kaars WA, Rigby JK, Jr (1987) Stratigraphic aspects of the Cretaceous–Tertiary boundary in the Bug Creek area of eastern Montana, U.S.A. Société Géologique de France Mémoire 150, 53– 73.

Solà C, Burgos M, Plazuelo A, Toja J, Plans M, Pratt N (2004) Heavy metal bioaccumulation and macroinvertebrate community changes in a Mediterranean stream affected by acid mine drainage and an accidental spill (Guadiamar River, SW Spain). Science of the Total Environment 333, 106–126.

Strong CP, Brooks RB, Wilson SM, Reeves RD, Orth ChJ, Mao X-Y, Quintana LR, Anders E (1987) A new Cretaceous–Tertiary boundary site at Flaxbourne River, New Zealand: biostratigraphy and geochemistry. *Geochimica et Cosmochimica Acta* 51, 2769– 2777.

Tschudy RH, Pillmore CL, Orth CJ, Gilmore JS, Knight JD (1984) Disruption of the terrestrial plant ecosystem at the Cretaceous– Tertiary boundary, Western Interior. *Science* **225**, 1030–1032.

Twitchett RJ (2006) The palaeoclimatology, palaeoecology and palaeoenvironmental analysis of mass extinction events. *Palaeogeography*, *Palaeoclimatology*, *Palaeoecology* 232, 190–213.

Vadja V, McLoughlin S (2004) Fungal proliferation at the Cretaceous–Tertiary boundary. *Science* 303, 1489.

Vadja V, Raine JI (2003) Pollen and spores in marine Cretaceous/Tertiary boundary sediments at mid-Waipara River, North Canterbury, New Zealand. New Zealand Journal of Geology and Geophysics 46, 255–273.

Vadja V, Raine JL, Hollis CJ (2001) Indication of global deforestation at the Cretaceous–Tertiary boundary by New Zealand fern spike. *Science* **294**, 1700–1702.

Vadja V, Raine JL, Hollis CJ, Strong CP (2003) Global effects of the Chicxulub asteroid impact on terrestrial vegetation – the palynological record from New Zealand K–T boundary. In *Impact Studies* (ed Clayes P). Springer-Verlag, Berlin, 57–74.

Vajda V, McLoughlin S (2007) Extinction and recovery patterns of the vegetation across the Cretaceous–Palaeogene boundary – a tool for unravelling the causes of the end-Permian mass-extinction. *Review of Palaeobotany and Palynology* 144, 99–112. Wignall PB, Benton MJ (1999) Lazarus taxa and fossil abundance at times of biotic crisis. *Journal of the Geological Society, London* 156, 453–456.

Wilf P, Johnson KR (2004) Land plant extinction at the end of the Cretaceous: a quantitative analysis of the North Dakota megafloral record. *Paleobiology* **30**, 347–368.

- Wilf P, Labandeira CC, Johnson KR, Ellis B (2006) Decoupled plant and insect diversity after the end-Cretaceous extinction. *Science* 313, 1112–1115.
- Wolfe JA (1991) Palaeobotanical evidence for a June "impact winter" at the Cretaceous/Tertiary boundary. *Nature* 352, 420– 423.
- Wolfe JA, Upchurch GR, Jr (1987) Leaf assemblages across the Cretaceous–Tertiary boundary in the Raton Basin, New Mexico and Colorado. *Proceedings of the National Academy of Sciences*, USA 84, 5096–5100.
- Wooldridge SA (2008) Mass extinctions past and present: a unifying hypothesis. *Biogeosciences Discuss* 5, 2401–2423.