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Trace element concentrations in the Mexico-Belize ejecta layer: A link between the Chicxulub impact and the global Cretaceous-Paleogene boundary

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Abstract–Four exposures of Chicxulub impact ejecta along the Mexico-Belize border have been sampled and analyzed for major and trace element abundances.

The ejecta deposits consist of a lower spheroid bed, containing clay and dolomite spheroids, and an upper diamictite bed with boulders and clasts of limestone and dolomite. The matrix of both beds is composed of clay and micritic dolomite. The rare earth element (REE) compositions in the matrix of both units show strong similarities in concentrations and pattern. Furthermore, the Zr/TiO_2 scatter plot shows a linear correlation indicating one source. These results indicate that the basal spheroid bed has the same source and was generated during the same event as the overlying diamictite bed, which lends support to a single-impact scenario for the Albion Formation ejecta deposits.

The elevated concentrations of non-meteoritic elements such as Sb, As, U, and Zn in the matrix of the lower spheroid bed are regarded to have been derived from the sedimentary target rocks at the Chicxulub impact site. The positive Eu and Ce anomalies in clay concretion and in the matrix of the lower part of the spheroid bed in Albion Island quarry is probably related to processes involved in the impact, such as high temperature and oxidizing conditions.

Analogous trace element anomalies have been reported from the distal Cretaceous-Paleogene (K/T) boundary clay layer at different sites. Thus, the trace element signals, reported herein, are regarded to support a genetic link between the Chicxulub impact, the ejecta deposits along the Mexico-Belize border, and the global K/T boundary layer.

INTRODUCTION

The Cretaceous-Paleogene (K/T) boundary is marked globally by a biotic turnover evidenced in the marine realm by, e.g., the demise of ammonites, marine reptiles and extensive extinction among planktic foraminifera and other micro-organisms (Smit 1999). In the terrestrial realm this is evidenced by the extinction of non-avian dinosaurs and major die-back of other terrestrial fauna (e.g., Sheehan and Fastovsky 1992; Buffetaut 2004; Labandeira et al. 2002). The magnitude of the event is further evidenced by a global turnover of the flora (Sweet et al. 1990; Vajda et al. 2001; Nichols and Johnson 2002; Vajda and McLoughlin 2004, 2005, 2007).

In the geological record, the K/T boundary is seen as a millimeter- to centimeter-thick layer (the fireball layer) containing shocked quartz, spherules (e.g., Bohor et al. 1987; Kring et al. 1994), and geochemical anomalies such as enrichment in iridium (e.g., Alvarez et al. 1980). Enrichment in Ni, Co, Cr, and in the non-meteoritic elements As, Sb, Se, and Zn also characterizes the global boundary layer (e.g., Smit and ten Kate 1982; Schmitz 1985, 1992; Schmitz et al. 1988; Gilmour and Anders 1989; Ebihara and Miura 1996; Strong et al. 1987; Martinez-Ruiz et al. 1999, 2006).

However, the exact relation of the Chicxulub impact to the 65 Myr old K/T boundary sediments is still debated. It has been suggested that the Chicxulub impact preceded the K/T event and that a second large and as-yet unknown impact coincided with the K/T mass extinction. This multiple impact scenario is based on the stratigraphic position of proximal Chicxulub impact ejecta deposits in northeastern Mexico and Texas, where lenses of ejecta spherules are locally embedded within the Maastrichtian marls, for instance, at the Loma Cerca, the El Penon, and the Brazos K/T sections (Keller et al. 2003, 2007). Additionally, Keller et al. (2004) interpreted a 0.66 m thick cross-bedded and dolomitized calcarenite overlying the suevite breccia in the Yaxopoil-1 drill core as a long-term latest Maastrichtian deposit.

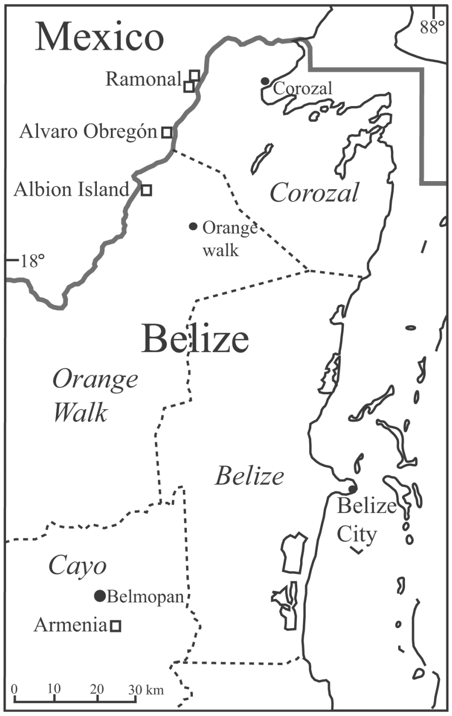


Fig. 1. Map showing the location of the sampled sites in Belize and southern Quintana Roo, Mexico. Ramonal North, Ramonal South, Alvaro Obregón, the Albion Island Quarry, and Armenia are indicated by squares.

In contrast to the multiple-event interpretation, several studies have clearly pointed to Chicxulub as the site of the K/T boundary impact and have invoked a single-event interpretation (e.g., Sharpton et al. 1992; Smit et al. 2004; Arenillas et al. 2006). The multiple spherule deposits in northeast Mexico (La Sierrita) are associated with soft-sediment deformation and have been interpreted to indicate "remolding and reworking" rather than evidence for multiple impacts (Schulte et al. 2003). Similarly, strong sedimentological, mineralogical, and micropaleontological evidences point to reworking of the 0.66 m thick interval in the Yaxopoil-1 drill core, which overlie the impact breccia but predate the K/T boundary (Arz et al. 2004; Smit et al. 2004). However, the proposed multiple impact scenarios for the Central American/Mexican ejecta sediments must be evaluated as an alternative hypothesis.

The proximal ejecta deposits in northern Belize and southern Quintana Roo Mexico (Fig. 1) are characterized by two distinct stratigraphical units; the lower spheroid bed and the upper diamictite bed, both part of the Albion Formation (Fig. 2). The origin and depositional mode of these units remains uncertain. It has been suggested that the spheroid bed represents the initial vapor-plume deposits, whereas the overlying diamictite bed constitutes a debris flow attributed to the collapse of the ejecta curtain (Pope et al. 2005; Ocampo et al. 2006). Smit (1999) alternatively suggested that the sediments in both units were derived from the ejecta curtain, except for some of the components, such as the vesicular clay clasts, which may have derived from the vapor plume.

This study aims to reconstruct the provenance and the sedimentary processes involved in this two-layered proximal ejecta deposit by analyzing the rare earth element (REE) and other trace element concentrations in samples from the northern Belize-Mexico border.

GEOLOGY

The Chicxulub impact structure in Yucatán, Mexico, is a large multi-ringed impact crater with a diameter of approximately 200 km (e.g., Hildebrand 1991; Pope et al. 1991; Morgan et al. 2000; Kinsland et al. 2005). The target rock is composed of a 3 km thick sequence of limestones, marls, dolomite, evaporites, and sandstones overlying a crystalline basement composed of different source terrains with ages that vary from 0.7 to 1.4 Ga (Kettrup and Deutsch 2003). The impactor, proposed to be a carbonaceous chondrite (Shukolyukov and Lugmair 1998), excavated the carbonate/evaporite platform and the underlying crystalline basement, involving material down to the base of the crust (Kring 2005). A globally distributed ejecta layer was produced, which is recognized by shocked quartz, spherules, and geochemical anomalies such as iridium enrichment (Alvarez 1980).

The proximal ejecta deposits were first recognized in a quarry on Albion Island, northern Belize, approximately 360 km southeast from the center of the Chicxulub impact structure; the geographical name subsequently gave name to the strata as the Albion Formation (Ocampo et al. 1996). The deposits are exposed at several places along the Belize-Mexico border, e.g., in Ramonal North, Ramonal South, Alvaro Obregón, the Albion Island Quarry, and Armenia (Fig. 1). The ejecta deposits rest on the fractured and karstified Maastrichtian Barton Creek Dolomite, which was formed on a carbonate platform and has been envisaged to represent a shallow, back-reef lagoon environment (Flores 1952). The ejecta deposits of this region have been described in detail in several studies (e.g., Ocampo et al. 1996; Vega et al. 1997; Pope et al. 1999, 2005; Fouke et al. 2002; Keller et al. 2003; King and Petruny 2003).

The deposits are divided into two units: a spheroid bed and an overlying diamictite bed. Both units are poorly consolidated and include a micritic dolomitic matrix with integrated smectite. The units vary regionally with respect to bed thickness and sedimentary structures compared to the type section at Albion Quarry (Ocampo et al. 1996).

The spheroid bed is 1 to 2 m thick. This unit contains clay and dolomite spheroids. The flattened clay spheroids are 5–10 mm in diameter and occur at the base of the unit. These have been proposed to represent altered impact glass fragments (Pope et al. 1999). The dolomite spheroids are 10–25 mm in diameter with concentric lamination and are regarded as accretionary lapilli (Ocampo et al. 1996). Thin clay layers (ranging from a few millimeters up to 2 cm in

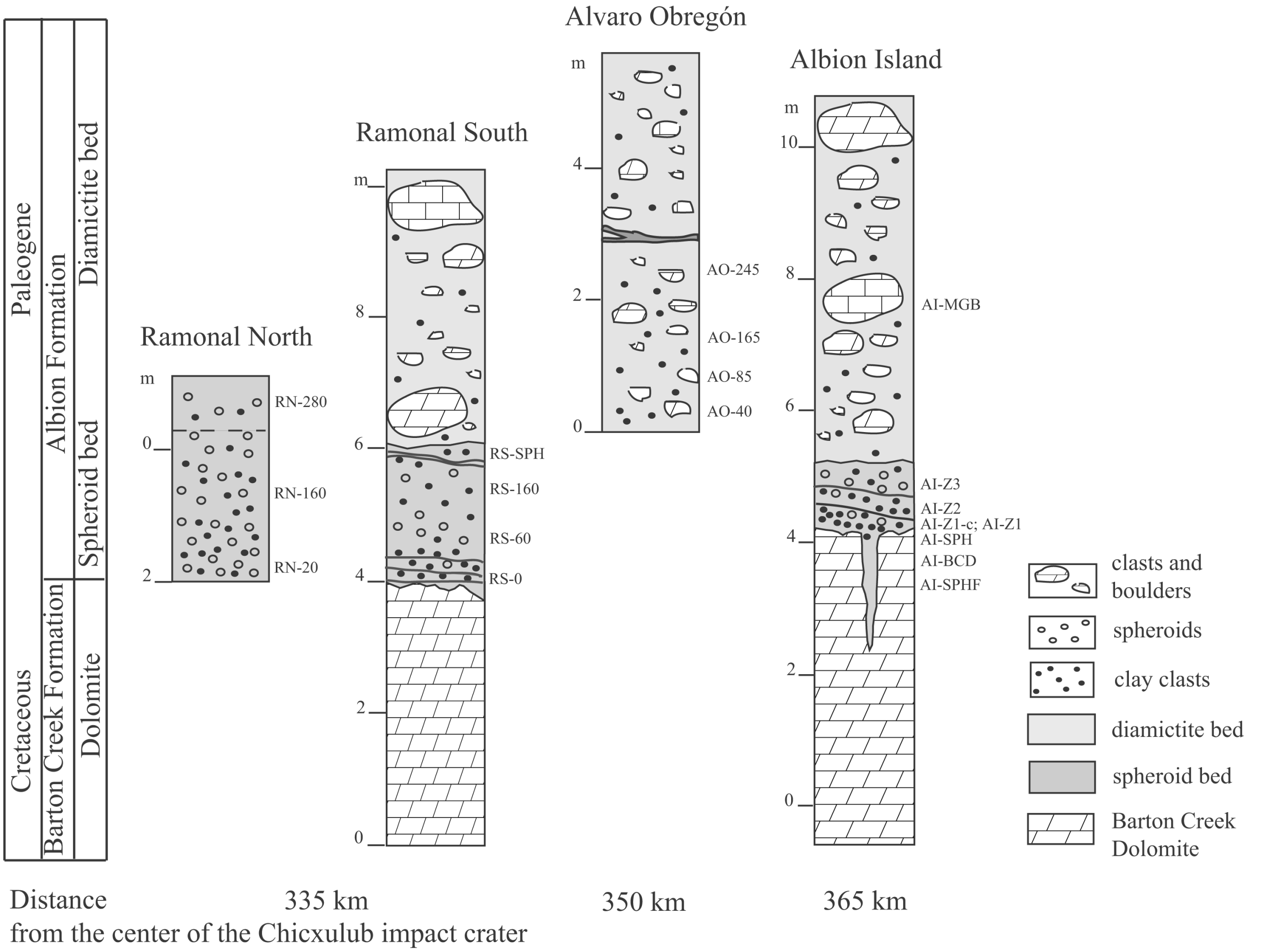


Fig. 2. Schematic geological profiles of the exposed ejecta deposits along the Mexico-Belize border. Sampled levels of the Barton Creek Dolomite, the spheroid bed, and the diamictite bed are shown by sample number.

thickness) with pronounced slickensides constitute the basal contact to the Barton Creek Dolomite and the upper contact to the diamictite bed.

The overlying diamictite bed is approximately 14 m thick. It contains limestone and dolomite clasts and boulders, ranging from millimeters to 10 m in diameter, associated with a sparse occurrence of dolomite spheroids. Many blocks and clasts are mud-coated. There are additional clay clasts composed of smectite and palagonite (cf. Pope et al. 1999) that range from <1 mm to 40 mm in diameter.

SAMPLING AND METHODOLOGY

Four exposed ejecta sequences with increasing distance from the Chicxulub crater center (335–365 km) at the border zone between northern Belize and Mexico were sampled by A. Ocampo from 1994 to 2005. Nineteen samples were selected from Ramonal North, Ramonal South, Alvaro Obregón, and Albion Island (Fig. 1). Additionally, the underlying Cretaceous Barton Creek Dolomite was sampled in the Albion quarry. A red-green clay layer, located at the base of the spheroid bed, was sampled from an exposure in Armenia, central Belize (Fig. 1), approximately 500 km from the center of the impact crater.

For geochemical analyses, bulk powder samples of the matrix in the spheroid bed and the diamictite bed, of clay clast, and of the red-green clay were milled by hand using an agate mortar. Samples of boulders in the diamictite bed and from the Barton Creek Dolomite were pulverized. All samples were sieved using a 250 μm mesh.

The concentrations of major and trace elements, including REEs, were obtained by using inductively coupled plasma–mass spectrometry (ICP-MS). Total carbon (TOT/C) and total sulfur (TOT/S) were obtained by Leco. The analyses were performed by Acme Analytical Laboratories, Vancouver, Canada (see Burman et al. 1978 for details). Iridium analyses were performed by direct irradiation neutron activation by the Becquerel Laboratories, Canada. The Ir content in analyzed samples was below the detection level of 0.5 ppb and will not be discussed further.

Table 1. Abundance of major and trace elements in ejecta deposits from the Belize-Mexico border.

	Ramonal North			Ramonal South				Alvaro Obregón			
	Spheroid bed			Spheroid bed				Diamictite bed			
	Matrix RN-280	Matrix RN-160	Matrix RN-20	Matrix RS-SPH	Matrix RS-160	Matrix RS-60	Matrix RS-0	Matrix AO-245	Matrix AO-165	Matrix AO-85	Boulder AO-40
wt%											
SiO_2	11.46	11.42	15.50	10.75	15.85	10.97	16.67	11.16	18.89	10.87	3.45
Al_2O_3	3.20	2.94	4.26	3.28	4.65	3.40	4.53	2.93	5.13	2.88	0.94
Fe_2O_3	1.12	0.95	1.57	0.90	1.69	0.94	1.76	0.93	1.56	1.02	0.28
MgO	2.41	1.81	2.04	1.52	2.23	1.58	2.23	10.47	13.85	12.91	18.04
CaO	41.29	43.5	38.50	44.21	38.08	43.26	37.50	33.32	21.55	30.13	31.30
Na_2O	0.02	0.02	0.02	0.03	0.01	0.03	0.02	0.03	0.04	0.03	0.05
K_2O	0.41	0.43	0.78	0.15	0.24	0.15	1.04	0.15	0.45	0.15	0.05
TiO_2	0.12	0.11	0.18	0.13	0.18	0.14	0.19	0.11	0.18	0.10	0.03
P_2O_5	0.03	0.02	0.02	0.02	0.02	0.02	0.03	n.d.	0.01	n.d.	n.d.
MnO	0.01	0.02	0.02	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.01
Cr_2O_3	n.d.	n.d.	0.002	0.001	0.008	0.002	0.002	n.d.	0.001	n.d.	n.d.
LOI	39.9	38.8	37.2	39.0	37.2	39.6	36.0	41.0	38.5	42.0	45.9
SUM	99.97	100.03	100.10	100.00	100.17	100.10	99.98	100.11	100.18	100.10	100.05
TOT/C	9.97	9.78	8.49	9.78	8.44	9.68	8.35	9.78	7.93	10.25	11.77
TOT/S	0.03	0.04	0.05	0.02	0.01	0.02	0.07	0.01	0.01	n.d.	0.01
ppm											
Sc	3	4	5	4	5	4	5	4	5	3	1
V	n.d.	11	12	34	63	41	18	34	37	26	12
Co	2.6	2.5	4.0	1.8	2.0	2.1	5.0	1.3	5.4	1.2	0.8
Ni	3.2	2.9	3.9	2.6	3.0	1.9	3.9	3.6	5.0	2.8	2.1
Cu	4.7	4.1	6.1	5.7	3.0	6.3	5.3	4.4	8.5	3.8	2.1
Zn	8	8	11	5	6	5	11	7	12	6	2
As	n.d.	n.d.	n.d.	1.2	0.5	1.9	n.d.	1.0	0.7	0.9	n.d.
Rb	7.1	7.0	12.8	5.1	8.4	4.3	14.0	4.1	7.8	4.3	1.0
Sr	533.0	595.5	568.2	322.7	88.9	305.2	631.2	86.7	104.1	90.0	122.4
Y	4.1	6.1	6.0	7.3	7.1	7.7	6.2	6.1	6.7	6.8	6.3
Nb	1.4	1.1	1.8	1.5	1.9	1.6	2.0	1.2	1.9	1.1	0.5
Sb	n.d.	n.d.	n.d.	n.d.	0.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cs	0.1	n.d.	0.1	0.2	0.2	0.2	0.1	n.d.	0.3	n.d.	n.d.
Ba	81	185	91	17	6	21	1088	28	14	10	15
U	0.5	0.6	0.6	0.5	0.6	0.5	0.6	1.1	1.4	1.5	1.7

RESULTS

Results from major and trace element analyses are presented in Table 1. The variations in trace element concentration are given against a stable element, aluminum, which also is regarded as a proxy for the clay content. The REE abundances were normalized both to chondrite values of Nakamura (1974) (Figs. 3a and 3b) and to the values of North American average shale (NASC) (Gromet et al. 1984) (Fig. 4). A Zr/TiO_2 scatter plot for matrix samples (Fig. 5) is used to constrain the provenance of detrital sediments. Specific trace elements from the spheroid bed at Albion Island were normalized both to Al_2O_3 and to CaO (Fig. 6).

Matrix Samples

The matrix is composed mainly of CaO (21.5–43.5 wt %), followed by SiO_2, Al_2O_3, and MgO in descending order. The Al_2O_3 content (2.9 to 5.1 wt%) shows a fairly consistent negative linear correlation to CaO + MgO. Chondrite-normalized REE abundances (Figs. 3a and 3b) demonstrate that in all four sections the REE in the matrix of the spheroid bed and the diamictite bed have similar distribution patterns and concentrations. A strong linear correlation is evident in the Zr/TiO_2 scatter plot for matrix samples (Fig. 5).

The specific trace elements normalized to Al_2O_3 and to CaO reveal anomalous values of As, Sb, Zn, and of U in the samples from the lower-middle part of the spheroid bed at Albion Island compared to the samples from the top of this unit (Fig. 6). The lowermost sample of the spheroid bed lacks anomalies of these elements but has an elevated concentration of Co and shows a positive anomaly of Eu (Fig. 3a).

At Ramonal South, one sample from the basal part of the spheroid bed shows an exceptionally high content of Ba and elevated values of S (Table 1).

Table 1. *Continued.* Abundance of major and trace elements in ejecta deposits from the Belize-Mexico border.

	Ramonal North			Ramonal South				Alvaro Obregón			
	Spheroid bed			Spheroid bed				Diamictite bed			
	Matrix RN-280	Matrix RN-160	Matrix RN-20	Matrix RS-SPH	Matrix RS-160	Matrix RS-60	Matrix RS-0	Matrix AO-245	Matrix AO-165	Matrix AO-85	Boulder AO-40
REE											
La	4.8	5.2	5.2	6.9	4.5	6.3	5.8	6.3	5.6	6.3	3.3
Ce	7.2	9.5	10.7	12.7	9.9	12.7	11.9	10.4	12.8	9.1	5.6
Nd	3.1	4.8	4.5	5.5	7.1	5.3	6.1	7.1	6.6	6	3
Sm	0.7	0.9	1	1.4	1.8	1.1	1	1.3	1.1	1.1	0.7
Eu	0.16	0.24	0.25	0.3	0.45	0.31	0.24	0.38	0.47	0.34	0.18
Gd	0.66	0.8	0.96	1.23	1.53	0.99	1.04	1.14	1.16	1.07	0.74
Dy	0.63	0.96	0.9	1.19	1.45	1.06	1.11	1.23	1.02	1.09	0.78
Er	0.41	0.59	0.58	0.69	0.68	0.73	0.64	0.7	0.72	0.62	0.74
Yb	0.37	0.71	0.54	0.78	0.33	0.84	0.52	0.75	0.69	0.58	0.73
Lu	0.11	0.09	0.1	0.11	0.08	0.12	0.1	0.12	0.08	0.08	0.22
Σ REE	18.1	23.8	24.7	30.8	27.8	29.4	28.4	29.4	30.2	26.3	16.0
	Matrix RN-280	Matrix RN-160	Matrix RN-20	Matrix RS-SPH	Matrix RS-160	Matrix RS-60	Matrix RS-0	Matrix AO-245	Matrix AO-165	Matrix AO-85	Boulder AO-40
V/Al	–	4	3	11	13	12	4	12	7	9	13
Co/Al	0.8	0.8	0.9	0.6	0.4	0.6	1.1	0.4	1.0	0.4	0.8
Ni/Al	1.0	1.0	0.9	1.0	0.6	0.6	0.9	1.2	1.0	1.0	2.2
Cu/Al	1.5	1.4	1.4	1.9	0.6	1.8	1.2	1.5	1.7	1.3	2.2
Zn/Al	2	3	3	2	1	1	2	2	2	2	2
As/Al	–	–	–	0.4	0.1	0.6	–	0.3	0.1	0.3	–
Rb/Al	2.2	2.9	3.0	1.7	1.8	1.3	3.1	1.4	1.5	1.5	1.1
Sr/Al	166.6	201.9	133.4	109.4	19.1	89.8	139.3	29.6	20.6	31.2	130.2
Y/Al	1.3	2.1	1.4	2.5	1.5	2.3	1.4	2.1	1.3	2.4	6.7
Nb/Al	0.4	0.4	0.4	0.5	0.4	0.5	0.4	0.4	0.4	0.4	0.5
Sb/Al	–	–	–	–	0.2	–	–	–	–	–	–
Cs/Al	–	–	–	0.1	–	0.1	–	–	0.1	–	–
Ba/Al	25	63	21	6	1	6	240	10	3	3	16
U/Al	0.2	0.2	0.1	0.2	0.1	0.1	0.1	0.4	0.3	0.5	1.8

Dolomite Samples

The main constituents of the boulders are CaO and MgO. The Al_2O_3 content is very low, especially in the Barton Creek Dolomite sample, which displays values close to detection level (Table 1). Chondrite-normalized REE values (Fig. 3a) illustrate that the Barton Creek Dolomite and the fracture fill differ from the matrix samples by a flat REE distribution pattern.

The boulders show dissimilar ∑ REE and patterns; the boulder from the diamictite bed at Alvaro Obregón has an REE pattern close to that one for the Barton Creek Dolomite, whereas the ∑ REE is close to the matrix samples (Fig. 3a; Table 1). The boulder from the diamictite bed at Albion Island differs from the Barton Creek Dolomite in that it is significantly depleted in the heavy rare earth elements (HREE): Gd, Dy, Er, Yb, and Lu (Fig. 3a).

Clay Samples

Chondrite-normalized REE values (Fig. 3a) show that the red-green clay has a similar REE concentration and distribution pattern as the NASC, whereas the clay concretion has an REE composition comparable to those for the matrix samples. In the NASC-normalized values, the red-green clay sample is close to 1, whereas the clay clast is depleted in all REEs except for Ce and Eu, which both show positive anomalies (Fig. 4).

DISCUSSION

The depositional processes of the proximal ejecta layer exposed along the Mexico-Belize border are still debated. The ejecta material, which was deposited in a continental environment, is divided into two units separated by a rather sharp contact (Fig. 2). The marked difference in the distribution of detrital components (e.g., boulders, clay clasts and spheroids) between the two units could reflect differences in e.g., provenance or in the depositional processes involved or in the timing of deposition. As stated above, several authors have proposed a multiple-impact scenario for the Central American/Mexican ejecta sediments; these studies have to be considered when analyzing the two layered ejecta deposits in northern Belize-Mexico. This geochemical study,

Table 1. *Continued.* Abundance of major and trace elements in ejecta deposits from the Belize-Mexico border.

	Albion Island								Armenia	
	Spheroid bed					Diamictite bed	Barton Creek		Contact with spheroid bed	
	Matrix AI-Z3	Matrix AI-Z2	Matrix AI-Z1-c	Clay clast AI-Z1	Matrix AI-SPH	Boulder AI-MGB	Fracture fill AI-SPHF	Dolomite AI-BCD	Clay CB-RGC	Detection levels
wt%										wt%
SiO_2	15.26	9.46	10.56	37.84	9.28	3.11	1.28	0.23	39.20	0.01
Al_2O_3	5.03	2.97	3.30	11.65	2.95	0.49	0.41	0.07	13.26	0.01
Fe_2O_3	1.28	1.21	1.31	2.44	0.75	0.08	0.13	0.07	4.41	0.04
MgO	16.23	18.45	18.7	11.08	8.31	20.86	17.83	21.15	2.27	0.01
CaO	21.94	24.90	24.50	7.17	37.41	29.66	33.20	30.82	14.46	0.01
Na_2O	0.03	0.02	0.02	0.04	0.04	0.02	0.04	0.05	0.13	0.01
K_2O	0.07	0.06	0.11	0.27	0.04	0.04	0.04	0.04	0.29	0.01
TiO_2	0.21	0.11	0.13	0.55	0.12	0.02	0.02	n.d.	0.48	0.01
P_2O_5	0.01	n.d.	n.d.	0.02	0.01	n.d.	n.d.	0.01	0.03	0.01
MnO	0.01	0.01	0.01	n.d.	0.01	n.d.	0.01	n.d.	0.04	0.01
Cr_2O_3	n.d.	n.d.	n.d.	0.004	0.001	0.002	n.d.	n.d.	0.012	0.001
LOI	40.1	42.9	42.1	29.3	41.2	45.7	47.1	47.6	25.8	0.1
Sum	100.17	100.10	100.12	100.37	100.12	99.97	100.04	100.03	100.39	
TOT/C	8.70	10.25	9.44	2.51	10.44	13.01	12.25	13.10	2.82	0.01
TOT/S	0.01	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	0.02	0.01
ppm										ppm
Sc	6	3	4	13	3	1	1	n.d.	14	1
V	71	44	149	174	52	16	10	n.d.	64	8
Co	2.5	0.7	2.0	2.3	7.2	0.5	0.5	0.6	9.7	0.2
Ni	6.4	6.8	6.7	8.4	2.9	2.8	2.9	1.5	37.2	0.1
Cu	11.6	3.7	10.1	28.7	2.9	1.4	0.9	1.3	10.3	0.1
Zn	4	10	10	10	4	1	2	5	23	1
As	3.9	8.7	14.9	4.0	3.3	n.d.	n.d.	n.d.	1.6	0.5
Rb	2.0	1.8	3.6	9.3	1.2	0.6	0.8	0.7	33.5	0.1
Sr	71.8	100.5	97.1	45.0	98.8	84.3	90.7	87.0	136.1	0.5
Y	7.6	5.3	5.1	2.8	4.5	0.7	1.4	2.1	28.0	0.1
Nb	2.4	1.3	1.5	5.6	1.4	0.5	0.5	0.5	7.1	0.1
Sb	0.1	0.4	0.5	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	0.1
Cs	n.d.	n.d.	n.d.	0.3	n.d.	n.d.	n.d.	n.d.	4.2	0.1
Ba	9	6	2	4	9	8	6	9	16	1
U	1.0	0.8	2.7	5.4	1.4	1.3	2.1	2.0	1.1	0.1

which compares the trace element abundances in the two stratigraphical layers and the underlying Maastrichtian basement, contributes to the knowledge concerning the genesis of the proximal ejecta deposits in Belize/Mexico.

The REE patterns and concentration of the matrix of both units are very similar (Fig. 3a), indicating a common source and a common geochemical-sedimentological process. The precursor of the dolomitic portion of the matrix is most probably dolomite/lime mud, and as established by Miura and Kwabe (2000), carbonates show no significant change in REE composition during diagenesis and dolomitization. However, the REE signals archived in the matrix of the ejecta deposits display a mixed carbonate-clay signature, and clay diagenesis and acid weathering conditions may lead to redistribution and fractionation of REEs. Even so, the matrix samples show a markedly uniform REE distribution with no significant differences in relative or absolute abundance. Moreover, the REE abundances show the typical pattern for sedimentary rocks with the LREEs relatively enriched compared to HREEs and with negative Eu anomalies. Therefore we propose that the matrix of both beds originated from one source and one process. This is supported by the strong linear correlation of the Zr/TiO_2 scatter plot (Fig. 5), which implies a single source for the material in the matrix. This interpretation agrees with the postulation by Smit (1999) that the basal spheroid bed has the same origin as the overlying diamictite bed. Altogether, this would exclude a multiple impact event for the Albion Formation ejecta layer at the Mexico-Belize border zone.

Compared to the Barton Creek Dolomite, the analyzed dolomite boulders show dissimilar REE concentrations. The boulder from Albion Island is significantly depleted in HREEs. On the other hand, the boulder from Alvaro Obregón shows a flat REE pattern similar to the Barton Creek Dolomite, but has higher $\sum$ REEs (Fig. 3a; Table 1). Owing to the flat REE distribution pattern, a diagenetic modification of

Table 1. *Continued.* Abundance of major and trace elements in ejecta deposits from the Belize-Mexico border.

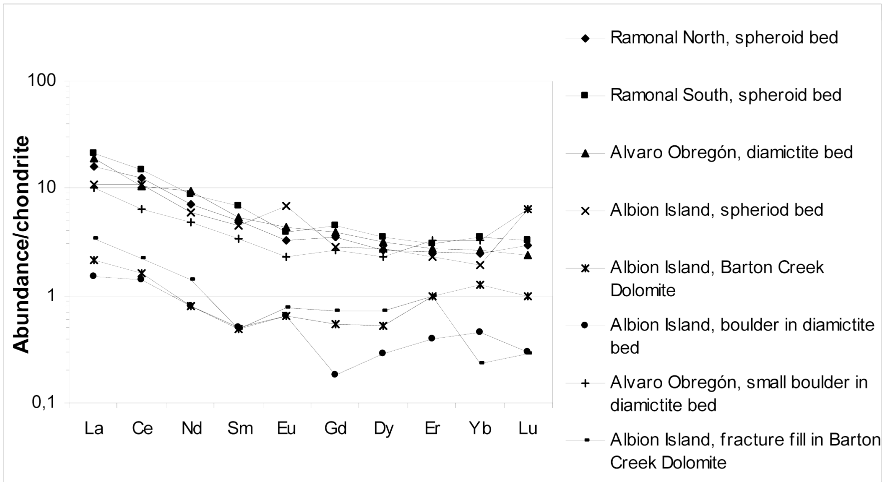
	Albion Island								Armenia	
	Spheroid bed					Diamictite bed	Barton Creek		Contact with spheroid bed	
	Matrix AI-Z3	Matrix AI-Z2	Matrix AI-Z1-c	Clay clast AI-Z1	Matrix AI-SPH	Boulder AI-MGB	Fracture fill AI-SPHF	Dolomite AI-BCD	Clay CB-RGC	Detection levels
REE										
La	6.4	4.2	3.6	2.5	4.7	0.5	1.1	0.7	21	0.1
Ce	12.2	6.6	9.4	20.5	9.1	1.2	1.9	1.4	36.7	0.1
Nd	6.8	4	3.7	2.9	4.2	0.5	0.9	0.5	20.2	0.3
Sm	1.2	0.9	0.9	0.7	0.9	0.1	0.1	0.1	4.7	0.05
Eu	0.37	0.2	0.52	0.24	0.21	0.05	0.06	0.05	0.86	0.05
Gd	1.12	0.79	0.79	0.61	0.76	0.05	0.2	0.15	4.06	0.05
Dy	1.11	0.93	0.93	0.67	0.83	0.1	0.25	0.23	4.56	0.05
Er	0.83	0.43	0.51	0.37	0.46	0.09	0.22	0.22	2.57	0.03
Yb	0.86	0.37	0.42	0.61	0.37	0.1	0.05	0.28	3.09	0.05
Lu	0.12	0.04	0.22	0.07	0.11	0.01	0.01	0.03	0.52	0.01
Σ RE	31.0	18.5	21.0	29.2	21.6	2.7	4.8	3.7	98.3	
	Matrix AI-Z3	Matrix AI-Z2	Matrix AI-Z1-c	Clay clast AI-Z1	Matrix AI-SPH	Boulder AI-MGB	Fracture fill AI-SPHF	Dolomite AI-BCD	Clay CB-RGC	
V/Al	14	15	45	15	18	33	24	–	5	
Co/Al	0.5	0.2	0.6	0.2	2.4	1.0	1.2	–	0.7	
Ni/Al	1.3	2.3	2.0	0.7	1.0	5.7	7.1	–	2.8	
Cu/Al	2.3	1.2	3.1	2.5	1.0	2.9	2.2	–	0.78	
Zn/Al	1	3	3	1	1	2	5	–	2	
As/Al	0.8	2.9	4.5	0.3	1.1	–	–	–	0.12	
Rb/Al	0.4	0.6	1.1	0.8	0.4	1.2	1.9	–	2.53	
Sr/Al	14.3	33.8	29.4	3.9	33.5	172.0	221.2	–	10.26	
Y/Al	1.5	1.8	1.5	0.2	1.5	1.4	3.4	–	2.11	
Nb/Al	0.5	0.4	0.4	0.5	0.5	1.0	1.2	–	0.54	
Sb/Al	–	0.1	0.1	–	–	–	–	–	–	
Cs/Al	–	–	–	–	–	–	–	–	0.32	
Ba/Al	2	2	1	–	3	16	14	–	1	
U/Al	0.2	0.3	0.8	0.5	0.5	2.6	5.1	–	0.1	

LOI = loss on ignition. TOT/C (total carbon) and TOT/S (total sulfur), obtained by Leco is not included in the sum. n.d. = not detected.
Sample abbreviations RN, RS, AO, and Al correspond to sampling localities: Ramonal North, Ramonal South, Alvaro Obregón, and Albion Island.

the REE signature cannot be excluded. Likewise, the low REE concentrations (close to detection limit) in these samples have to be considered. However, by means of cathodoluminecence (CL) petrography, Pope et al. (1999) showed differences in diagenetic pathways for the Barton Creek Dolomite and the boulders. These results demonstrate that the boulders did not originate from the locally underlying Barton Creek Dolomite, but are allogenic.

The REE pattern of the clay concretion and of the lowermost matrix sample from the spheroid bed in Albion Island shows positive anomalies in Eu and Ce (Figs. 3a and 4). This indicates that argillization did not take place in equilibrium with seawater, and seawater did not contribute to the REE budget (cf. Piper 1974). Analogous positive anomalies of Eu and Ce have been recorded in K/T boundary clay samples and potassium feldspar spherules from Agost, Spain. The Eu anomaly was interpreted to indicate a reducing environment (Martinez-Ruiz et al. 1999). However, the Albion Formation ejecta blanket is deposited in a terrestrial environment and the samples in question show no sign of reducing conditions. Eu^{3+} may equally be reduced to Eu^{2+}, allowing for greater substitution and enrichment during very high temperatures. Cesium anomalies are, on the contrary, generated during low-temperature and oxidizing conditions. It is feasible that the Eu and Ce signals reflect a geochemical signature related directly to the processes involved in the impact, as high-temperature and oxidizing conditions are fundamental to impact processes. High temperatures cause melting and vaporization of the impactor and the target rocks, while an oxidizing environment characterizes the vapor plume and the ejecta curtain.

A distinct K/T boundary layer containing shocked quartz, spherules, and iridium enrichment has not been detected in the Mexico-Belize border sections. The red-green clay layer from ejecta deposits in Armenia has an unusually high proportion of Cr (Table 1), but lacks a corresponding Ni anomaly, suggesting a mafic source rather than extraterrestrial input. Furthermore, the strong resemblance to



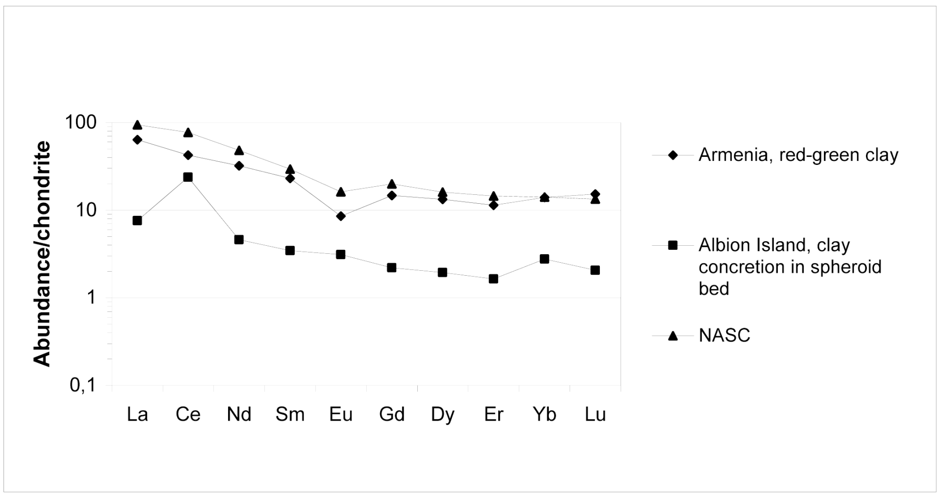


Fig. 3. Chondrite-normalized REE patterns of the clay samples and of the dolomitic phases. a) The REE distribution in the matrix of the two units has similar patterns, with the exception of one sample that shows a positive anomaly of Eu. The boulder from the diamictite bed in Albion Island is depleted in the HREEs compared to the Barton Creek Dolomite. b) The REE distributions in the clay concretion and in the red-green clay differ significantly from each other. The chondrite-normalized NASC values are shown for comparison. The red-green clay from the Armenian section shows strong resemble to the pattern of NASC.

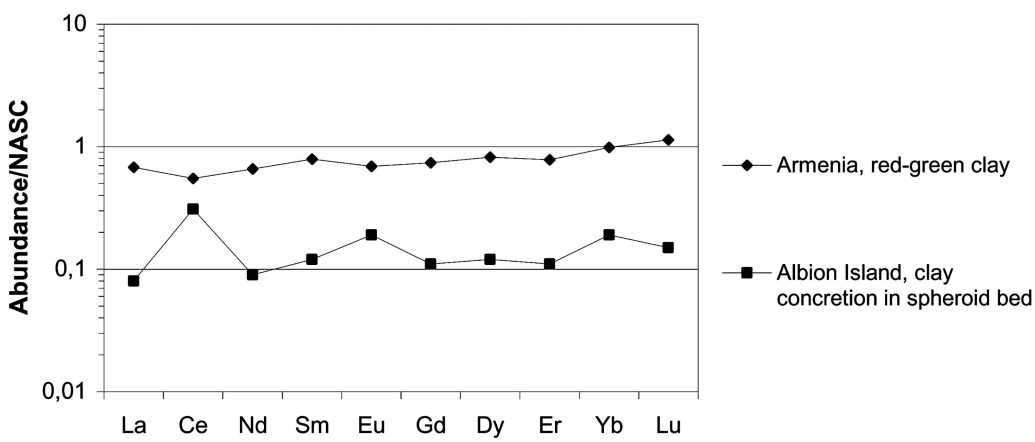


Fig. 4. NASC-normalized (Gromet et al. 1984) REE patterns of the clay samples. The clay from Albion Island displays positive anomalies of Ce and Eu and is depleted in all REEs compared to the clay from the Armenia location.

NASC, both in absolute REE content and in relative abundances (Fig. 4), indicates average marine clay. The elevated concentration of As, Sb, Zn, Co, and U (Table 1; Fig. 6) in the lower part of the spheroid bed in Albion Island is, however, consistent with characteristics of K/T boundary layer elsewhere (e.g., Spain, Denmark, and New Zealand). Various explanations have been provided for the enrichment of the non-meteoritic elements As, Sb, and Zn from the distal K/T boundary layer (Smit and ten Kate 1982; Strong et al. 1987; Schmitz 1992; Martinez-Ruiz et al. 1999). Although elevated values of As and Sb are not ubiquitous at the K/T boundary (Ebihara and Miura 1996), the anomalies are distributed to such an extent that they are most likely linked to a global dispersal event. Major and trace element data obtained from the target rocks at the Chicxulub impact site show that the Cretaceous dolomite, argillaceous limestone, and shale are in fact enriched in As, Sb, U, and Br (Tuchscherer et al. 2005). Thus the elevated concentrations of these elements are likely derived from the target rock, and represent a genetic link between the Chicxulub impact, the proximal ejecta layer exposed in Mexico/Belize, and the global K/T boundary layer.

The sample from the lower part of the spheroid bed at Ramonal South shows an exceptionally high content of Ba and minor, but detectable, elevation in S (Table 1). Investigations of ejecta deposits in northeast Mexico have revealed barium anomalies just below the iridium anomaly (Stüben et al. 2005). In the K/T boundary layer in Agost, Spain, the Ba anomaly occurs within the boundary layer (Martinez-Ruiz et al. 1999). Additionally, at Brazos River, Texas, USA, peaks of sulfur were discovered in a spherule-bearing unit (Heymann et al. 1998). Sulphur-rich sedimentary layers of anhydrite and gypsum are present in the target area, constituting up to one-third of the platform sediments (Ward et al. 1995). At impact, vaporization and dissociation of these rocks caused the release of SO_2 and SO_3 (Gupta et al. 2001). Although the amount of released volatiles is not well constrained (Chen et al. 1994; Agrinier et al. 2001; Ivanov and Deutsch 2002), a significant increase of sulfur aerosols in the atmosphere may be expected in the proximal areas, causing precipitation of $BaSO_4$.

Thus, it is suggested that the spheroid bed and the overlying diamictite bed correspond to a debris avalanche, which is attributed to the collapse of the ejecta curtain following the Chicxulub impact. The differentiation of clay clasts, spheroids, and boulders in the lower and upper beds simply express the different transport mechanisms for the ejecta components. This conclusion is in line with Smit's (1999) interpretation. To explain the partition in two units, Kenkmann and Schönian (2006), after studying the internal structures and sedimentary characteristics of the ejecta blanket, suggested a transition from a noncohesive, turbulent flow to a more cohesive flow. The rather inconsistent occurrence of anomalies of the specific trace elements in the samples collected from different sections of the spheroid bed (Table 1) may be explained by the short distance to the impact site. The contribution of target rocks to the total is of more significance with increasing proximity to the impact site (Smit 1999). In the Mexico-Belize border zone, this high contribution of target rocks would cause a very strong diluting effect on meteoritic components. Furthermore, in such a close position to the impact site the chaotic conditions would cause a complex mixture of ejecta material, whereby a distinct fireball layer as seen in distal areas is not to be expected, as previously pointed out by Schulte (2003). Nor is it fully comparable to the features of marine proximal K/T boundary deposits, which show modification by tsunamis and subsequent marine processes.

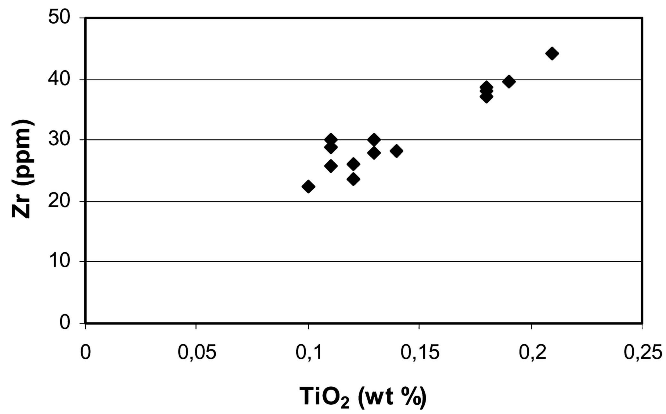


Fig. 5. Plot of Zr and TiO_2 contents in matrix samples from the spheroid bed and from the diamictite bed, the strong linear correlation implies one single source.

SUMMARY AND CONCLUSIONS

Results from this study contribute to the knowledge of the provenance and formation of the proximal ejecta layer produced by the Chicxulub impact. The study was performed on sediments of the Albion Formation along the Mexico-Belize border. The ejecta layer is divided into two separate units, the spheroid bed and the diamictite bed. The main results obtained from this study are:

- The REEs in the matrix of the two units show close to identical distribution patterns and concentrations, suggesting a common provenance and an analogous geochemical-sedimentological process. This supports a single-impact scenario for the Albion Formation ejecta layer exposed along the Mexico-Belize border.
- The REE pattern of boulders within the upper ejecta unit, the diamictite bed, deviates from the REE patterns of the underlying Cretaceous Barton Creek Dolomite by depletion in the HREEs and/or by the $\sum$ REE. This suggests that the boulders do not originate from the Barton Creek Dolomite.

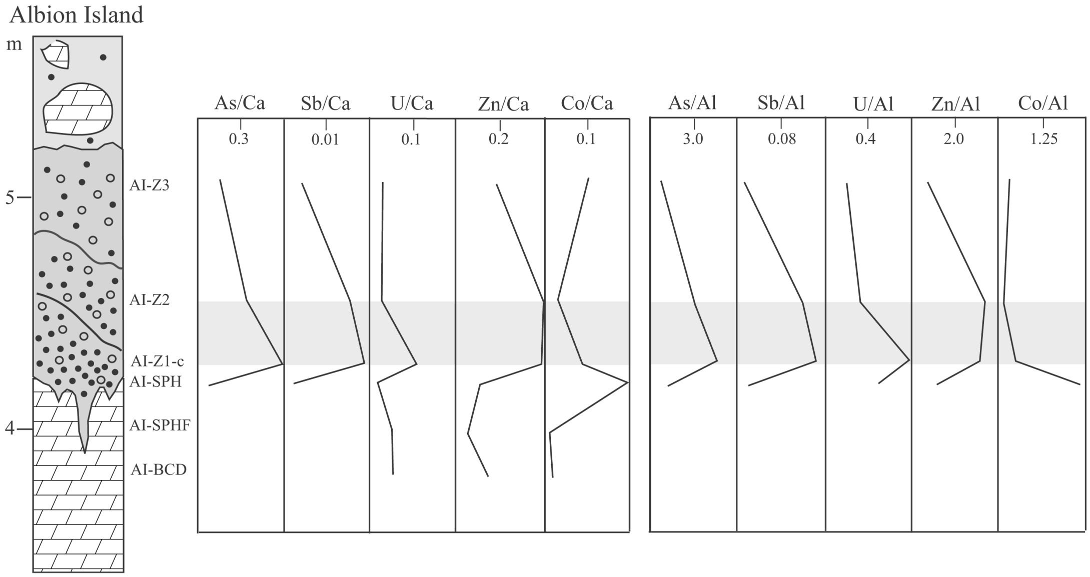


Fig. 6. The graphic presentation of specific elements normalized to CaO and to Al_2O_3 shows elevated concentrations in the spheroid bed from Albion Island.

- The positive Eu and Ce anomalies in a clay concretion and in the matrix of the lower part of the spheroid bed in Albion Island quarry is argued to be related to the high temperature and oxidizing processes involved in the impact. The elevated concentrations of As, Sb, Zn, and U are regarded to have been derived from the Cretaceous sedimentary target rocks. Comparable trace element signals have been recorded in K/T boundary layer worldwide. Thus, a genetic link between the Chicxulub impact, the ejecta deposits in northern Belize–southern Quintana Roo, Mexico, and the global K/T boundary bed is confirmed.

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