

Cretaceous-Paleogene boundary clays from Spain and New Zealand: arsenic anomaly and the Deccan Traps

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Abstract. High arsenic (As) contents have been reported in numerous Cretaceous-Paleogene boundary (KPB) clays worldwide including those from Spain (at Caravaca and Agost) and N. Zealand (at Woodside Creek). The Deccan Traps (India) enormous volcanism is one of the interpretations which have been offered to explain this anomaly. This report shows that the estimated surface densities of As in the boundary clays in Spain and New Zealand strongly contradict that anomalous As was sourced by this volcanic event.

Introduction

Ejecta layer. Alvarez et al. [1] explained the presence of anomalous iridium (Ir) in prominent marine Cretaceous-Paleogene (KPB) clays at three localities (Gubbio in Italy, Stevns Klint in Denmark, and Woodside Creek in N. Zealand) by proposing a late Cretaceous asteroid impact. Around the same time Smit and Hertogen [2] reported an anomalous Ir in the marine boundary clay at Caravaca (Spain). This suggestion was followed by reports of the Ir anomaly in many other marine/continental boundary clays worldwide [3]. These clays mark one of the most significant impact events in the Phanerozoic, one that appears responsible for one of the greatest extinctions in Earth's history.



Figure 1. Geographic locations of the KPB clays at Caravaca, Agost and Woodside Creek enriched with Ir and As, including the Chicxulub impact site and Deccan Traps.

Many researchers think that an extraterrestrial impactor (ca. 10 km in diameter) formed the ca. 180-km crater at Chicxulub (Yucatan Peninsula, Mexico) at the KPB one of the largest impact structures on Earth, Fig. 1. The impactor is postulated to have been a carbonaceous chondrite-type body [4].

A basal (2-4 mm thick) redish layer (so called the ejecta layer) marks the KPB at most of distal marine sites (>9000 km from the KPB impact site at Chicxulub) [5, 6]. This layer contains much of Ir and other impact-related markers. It has been estimated that the global surface density of Ir (or fluence) in the ejecta layers is about 55 ng cm^{-2} [7, 8].

Origin of As. In addition to well-known anomalous Ir, (so-called) non-chondritic trace elements such as As and other chalcophiles are concentrated in the ejecta layers at distal marine boundary sites. According to Hildebrand and Boynton [9], these elements represent a primary geochemical signal of the KPB impact. The chalcophile anomaly of ejecta layers has been attributed to many sources (the Chicxulub impactor, volcanism, seawater and fossil fuels) and associated processes. However, none of these is definitive: see Hildebrand [10] and Premović [11] for discussion of this subject. Moreover, it also appears that the mean global surface density As about $179 \mu\text{g cm}^{-2}$ [12] at KPB previously reported is highly overestimated [11].

Recently, Premović [11] tentatively suggested that the high abundances of iron (Fe) in the ejecta layers from Spain (Caravaca, Agost) and N. Zealand (Woodside Creek) indicates that a major fraction of their anomalous As was adsorbed from seawater by the Fe-oxides. These oxides were mainly derived of Fe from the vaporized (carbonaceous) chondrite impactor.

Deccan volcanic event. An alternative explanation for the cause of Ir anomaly in the boundary clays worldwide is based on the hypothesis that an unusual large volcanic event of short duration that coincides with the KPB is responsible for this anomaly [13]. One of the largest basaltic provinces in the world the Deccan Traps (Fig. 1) becomes the most important when considering the volcanic events implied by this hypothesis though no evidence of high Ir in the Deccan volcanic rocks has yet been found [14].

Deccan Traps (hereinafter Deccan) were created by an enormous volcanic event that originally erupted about $1.2 \times 10^6 \text{ km}^3$ of magma [15]. The studies indicate three main volcanic stages with the most active phase (hereinafter the phase-2) encompassing about 80 % of the Deccan eruptions and coinciding with the latest Maastrichtian [16, 17]. This phase may have occurred in the short time interval of 10,000 years to 100,000 years [16, 18] and its effects have been linked to the KPB global faunal extinction [19, 20].

In general, volcanic eruptions inject into the atmosphere tens of teragrams of gases, dust and aerosol particles so, for example, the current volcanoes are significant sources of As emissions into the atmosphere [21]. Thus an enormous volcanic source such as Deccan, in principle, could account for the excess of As (and other chalcophiles) at the KPB. Indeed, Chenet et al. [16, 18] estimated that the total emission SO_2 emission during the phase-2 is 30 to 100 times that of the Chicxulub impact. This range is probably valid for As (and other chalcophiles).

This report examines Deccan as a possible source of anomalous high As in the ejecta layers at Caravaca, Agost and Woodside Creek, Fig. 1. For this purpose, comprehensive geochemical data for anomalous As (and Ir) in these clays will be those published by Schmitz [22] and at Agost by Smit [23]. Throughout this paper it is assumed that most of As is located in the non-carbonate fraction of the ejecta layers studied, i. e. the carbonate fraction of this section is essentially its diluent.

Results, Interpretation and Discussion

The Caravaca boundary section. The boundary section Caravaca is among the most continuous and complete marine sections for the KPB transition. This section is located in the Betis Cordilleras (southeast Spain). The boundary section at Caravaca consists of a ca. 1 cm-thick Ir-rich dark (almost carbonate-free) marl with a basal ~3 mm thick red (ejecta) layer (RLC), Fig. 2A. RLC is enriched with Ir (ca. 110 ppb) [22].

The Agost boundary section. The Agost boundary section is similar to the neighbouring Caravaca section in lithology, geochemistry and depositional history [24]. As at Caravaca this section is comprised of a dark (about 6-cm-thick) clay with a basal ~3 mm-thick goethite-rich (ejecta) red layer (RLA), Fig. 2B.

The Woodside Creek boundary section. The KPB section at Woodside Creek is represented by a (up to 1 cm thick) goethite-rich ejecta layer (RLW). This layer is overlain with dark marl, Fig. 2C.

The INAA data for Ir [22] in the decarbonated fraction of the boundary section at Woodside Creek shows that the peak concentration of Ir of 465 ppb is located in the carbonate-free RLW which is one of the highest measured to date for any KPB interval.

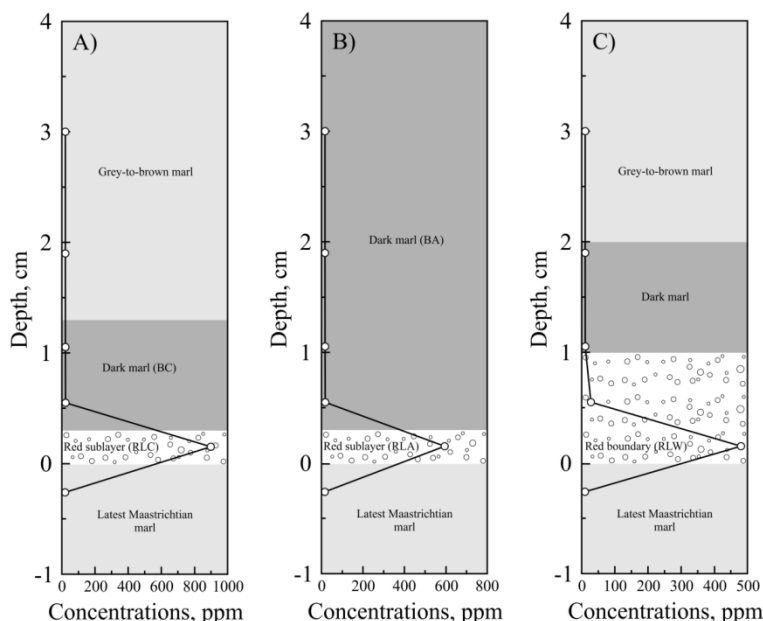


Figure 2. Concentration profiles of As (on a carbonate-free basis) in the boundary sections: (A) at Caravaca: based on data of Schmitz [22]; (B) at Agost: based on data of Smit [23]; and, (C) at Woodside Creek: based on data of Schmitz [22]. The section samples were analyzed with instrumental neutron activation (INAA). Relative error in the precision of the analyses ranges from 5 % to 10 %. Total uncertainties (including accuracy errors) were up to 20 %.

Smit [23] analyzed Ir (on a whole-rock basis) across the Agost boundary section. Using his Ir and carbonate content data, a simple calculation shows the highest Ir (ca. 30 ppb) is in the decarbonated RLA. A similar calculation was performed to estimate an As content in the carbonate-free (clay) fraction of the same section.

Distribution of As. Like Ir, As shows a prominent peak at the decarbonated fractions of RLC: ca. 900 ppm [22]; RLA: ca. 600 ppm [23]; and, RLW: ca. 480 ppm [22]. The duration of the peak in As at Caravaca, Agost and Woodside Creek is similar to that of the Ir anomaly, which would be geologically instantaneous. An estimation from the experimental data of Schmitz [22] and Smit [23] that the surface density of As (on a carbonate-free basis) of RLC, RLA and RLW is, respectfully, about $540 \mu\text{g cm}^{-2}$, $360 \mu\text{g cm}^{-2}$ and $480 \mu\text{g cm}^{-2}$, Table 1; by comparison, as noted above the mean global surface density As of the ejecta layer at marine sites is about $179 \mu\text{g cm}^{-2}$. The deposition of RLC and RLA (about 3 mm thick) occurred for several decades up to a century at most [5, 6]. The same is probably true for the depositional duration of RLW (ca. 8 mm - 10 mm thick).

Table 1. The surface densities [$\mu\text{g cm}^{-2}$] of As in the decarbonated RLC, RLA, RLW and Ir in the global boundary layer. The average As [ppm] contents of other geological materials.

Geological material	RLC ^a	RLB ^b	RLW ^a	Continental crust ^c	Mantle ^c
As	540	360	480	1.0	0.066

^a[22]; ^b[23]; ^c[25].

As and the stratosphere. A volcanic event results in a massive injection of various chemical elements (including As and other chalcophiles) and/or their compounds into the atmosphere. This includes transport of most of their submicron species to the lower stratosphere and their rapid global dispersal. In general, during a volcanic event very coarse particles with mass diameter $>10 \mu\text{m}$ quickly settle in the vicinity of their sources, whereas particles with diameters between $0.1 \mu\text{m}$ and $1 \mu\text{m}$ is particularly suited for a long range (stratospheric) transport [26, 27, 28].

As is released to the present-day atmosphere and its principal natural source is volcanic activity. About 1.72×10^{10} g of As is emitted to the atmosphere by volcanoes [29]. As generated by

Deccan was probably in the elemental form and may be initially present in the gaseous/vapor emission into the atmosphere. This As would be rapidly oxidized to (highly soluble) oxides and subsequently condensed into the micron/submicron particles (fine dust). The As (oxide) species, mainly associated with submicron particles, would rise up to the lower stratosphere and dispersed over the globe. However, a considerable fraction of these particles would fall to the lower troposphere where they should be largely removed by the enormous precipitations (probably acid rains?). Thus, it appears that only a notably small fraction of As sourced by Deccan could reside in the lower stratosphere and be deposited globally.

Deccan Traps

Geochemical studies. Strong et al. [30] and Gilmour and Anders [12] estimated that the Deccan basalts released approximately 6×10^8 g of the gaseous Ir into the atmosphere. This estimation is based on the average Ir content of the Deccan basalts (6 ppt) determined by Morgan [31] and assuming that 10^7 km³ of magma erupted. They also adopted an emission factor of Ir of about 3 g per 10^6 m³ (or 1 ppt) for magma similar to that at Kilauea volcano (Hawaii) [32]. This approach is reasonable as the Deccan volcanism shares many volcanological and geochemical features with active volcanic region of modern Hawaii. Strong et al. [30] and Gilmour and Anders [12] concluded that the Deccan volcanism did not inject significant amounts of chalcophiles (and Ir) in the atmosphere. Indeed, despite emplacing huge magma volumes, flood basalt eruptions (like Deccan) lack obvious eruptive mechanisms to inject huge volumes of fine dust and aerosols directly and quickly into the stratosphere [33], even if they are associated with large gas emissions [34, 35].

Bhandari et al. [36] studied the marine KPB limonitic (carbonate-poor) ejecta layer (<1 cm thick) within the intertrappen sedimentary bed at Anjar in Kutch (western part of the Deccan volcanic region). They reported that this layer is relatively enriched in Ir (1.27 ppb) and contains high chalcophiles including anomalous As (ca. 750 ppm) comparable with those measured in the decarbonated parts of RLC (ca. 900 ppm), RLA (600 ppm) and RLW (480 ppm). Bhandari et al. [36] concluded that Deccan is not likely source of these elements because they did not observe their enrichments in any of a large number of other intertrappen sediments in the Deccan Basin. Accordingly, many of these sediments should be enriched in As (and other chalcophiles) if they are derived from Deccan.

Gertsch et al. [37] investigated the biostratigraphy, carbon isotope stratigraphy, sedimentology, clay mineralogy and major/trace elements geochemistry of the most complete KPB marine sequence known from India along the Ulm Sohryngkew River in Meghalaya. The KPB in this sequence is marked by a 2 cm thick silty (almost calcite-free) boundary layer enriched with extraterrestrial Ir (11.79 ppb) and terrestrial As (162 ppm). These authors reasoned that these two elements were derived from a second major impact postdating the Chicxulub event: see for example Keller et al., [15].

Deccan and As. Adopting the volume of the Deccan magma (1.2×10^6 km³) estimated by Keller et al. [15], a simple calculation shows that approximately 1×10^6 km³ or 3×10^{21} g of basaltic lava (assumed density: 3 g cm⁻³) erupted during the most active phase-2 of the Deccan eruptions. Osaie et al. [38] carried out geochemical analyses major oxides and trace elements, including As (and Ir), of numerous target basalt samples from the Lonar impact crater; this crater is escavated in the KPB basalts of Deccan. They reported that average concentrations of As and Ir in their samples is 0.58 ppm and <1ppb, respectfully. For comparison, the average As content of Kilauea basalts is approximately 0.37 ppm [32]; the concentration of As in the continental crust and mantle is, respectfully, 1 ppm and 66 ppb, Table 1. Based on the As concentration of the Lonar crater basalt, one can calculate that the As content of the phase-2 magma was about 1.75×10^{15} g. Using the average amount of elemental As at the KPB of 179 μ g cm⁻² one can estimate that the total amount of As at this boundary is about 9×10^{14} g. Thus enormous ~50 % of the total As would have had to be released from the phase-2 magma into the atmosphere (stratospheric levels) to account for this amount of As at the KPB.

During eruptions of Kilauea magma emitted 0.3 % of its Ir in gaseous form [32]. Assuming that a similar fraction of gaseous As have been released from the phase-2 magma, than the total mass of As released from this magma was about 5.25×10^{12} g. If dispersed over the entire Earth, this release would create a global surface density of $\sim 1 \mu\text{g cm}^{-2}$. This value is probably too high since the enrichment factor of Ir in gaseous release relative to Kilauea basalt is at least an order of magnitude higher than that of As [32, 39, 40]. Thus, the phase-2 magma probably emitted at least 10 times less As (or <0.03 %) so the upper limit of the global surface density would be $<100 \text{ ng cm}^{-2}$.

In the following calculations, f_s represents the amount of As which reaches the lower stratosphere to the total As emitted by Deccan into the atmosphere. The following calculation assumes that f_s is equal 1 but this is clearly a high overestimation of its actual value which is probably much lower than 1.

The global surface density of As (d_{As}) released from the phase-2 magma can be estimated from the following equation:

$$d_{As} = M_M \varepsilon_M f_s / A_E$$

where M_M (ca. 3×10^{21} g) is the mass of the phase-2 magma, and ε_M is the As emission factor for magma ($\sim 1.75 \times 10^{-9} \text{ g g}^{-1}$: this work). We calculate ε_M by dividing the above estimated total As released by the phase-2 magma ($\sim 5 \times 10^{12}$ g) with the mass of this magma. This value should be considered as an upper limit. Using this value for ε_M we estimate that the upper limit of d_{As} is approximately $1 \mu\text{g cm}^{-2}$.

Estimates of the current annual input of volcanic As into the atmosphere vary, ranging from 2.80×10^8 g per year to 1.72×10^{10} g per year [21], although values seem to be converging on $\sim 7 \times 10^9$ g per year [41] and this value can be regarded as a minimum amount due to the fact that the volcanic emissions were calculated for a year with no large eruptions [21]. Moreover, the Earth's volcanic emission of As into the atmosphere for the last 100 years could be roughly 10^{12} g which is about the amount of As emitted by the phase-2 for its assumed duration of 10^4 years up to 10^5 years. As far as is known, there is no report of any marine clayey section in the last about 12,000 years (the Holocene epoch) and which is a few centimeters thick with a thin red basal layer having a sharp anomalous As spike.

Additional problem is a relatively short time scale of the deposition of the KPB clays which is inconsistent with a relatively long time of the phase-2 event: see also [12]. As pointed out earlier, the deposition of RLC, RLA and RLW occurred for several decades up to a century at most but the duration of the phase-2 far lasted for $10^4 - 10^5$ years. Thus, the deposition time of RLC, RLA and RLW is difficult to reconcile with a relatively long duration of the phase-2. In addition, Chenet et al. [18] claim (based on their paleomagnetic studies) that the lava pile during the phase-2 was erupted in some 30 single eruptive events each in volume from 1000 to 20,000 km^3 and each lasted as short as 100 years. If their claim is correct than we should recognize several lithostratigraphic units with a small As spike at or close the KPB instead only one but anomalous.

If we accepted that $1 \times 10^6 \text{ km}^3$ of the phase-2 basaltic lava was discharged for an extremely short time of $10^4 - 10^5$ years, than the mean eruption rate could have been 10 - 100 km^3 per year. Assuming that the deposition of the boundary ejecta layers in Spain and N. Zealand occurred for 100 years [5, 6] than about 1000 - 10,000 km^3 of the basaltic lava could have been discharged. If 0.3 % of As in this lava was released into the lower stratosphere and dispersed over the entire Earth this would yield only about 1 - 10 ng cm^{-2} . However, as discussed by Sen and Chandrasekharam [42], the mean eruption rate of the Deccan lava could have varied between 1 and 40 km^3 per year. If this true, then the phase-2 for 100 years would released 100 - 4000 km^3 of the basaltic lava or 2.5 - 10 times lower As into the lower stratosphere.

Finally, the highest concentration of As in volcanic gases at Kilauea [31] was about $8 \mu\text{g m}^{-3}$. To yield the global surface fluency of As of $179 \mu\text{g cm}^{-2}$, the amount of As to be transported to the lower stratosphere is about 10^{15} g of gases. This is about 10^{11} km^3 of this material. This is about 2 times the volume Earth's atmosphere ($5.1 \times 10^{10} \text{ km}^3$: the "Karman limit").

In summary, the estimates of the global surface densities of As (and other evidence) presented here clearly reveal that As generated by the Deccan volcanism did not contribute appreciable to the high As in the boundary clays in Spain and N. Zealand.

Deccan and iron. As we noted earlier, Premović [11] hypothesized that the massive amount of Fe oxides of the ejecta fallout generated by the Chicxulub impact should be able to sweep out the oceanic As: the current mean oceanic value: $922 \mu\text{g cm}^{-2}$ [43]. He also speculated that most of these oxides were probably originally deposited on the local (topographically high) oxic soils in Spain and N. Zealand and then laterally transported to the KPB sites by the impact induced surface (acid?) waters.

The most likely mechanism by which Fe of the Deccan volcanism could spread out globally is from degassing magma as it was erupted. Premović [11] roughly estimated that the Chicxulub impactor generated the stratospheric loading containing approximately 3×10^{16} g of Fe (or 6 g m^{-2}). The study of the Kilauea volcano by [31] suggest that the gas phase emitted into the atmosphere contained around $66 \mu\text{g m}^{-3}$ of Fe. Assuming that the Deccan atmospheric gas loading of Fe had a similar amount of Fe as the Chicxulub impact, than the volume of this loading would be roughly $5 \times 10^{11} \text{ km}^3$. This is about 10 times volume of the Earth's atmosphere. The excessive KPB precipitation of oceanic As by stratospheric globally distributed Fe (oxides) generated by Deccan is therefore untenable.

Conclusions

The evidence presented in this report exclude a possibility that voluminous Deccan volcanism was a source of exceptionally high As in in the boundary clays at Caravaca, Agost and Woodside Creek (or global at the KPB, in general). Moreover, an enormous amount of atmospheric gas release is necessary for an anomalous KPB precipitation of oceanic As by Fe (oxides) in the globally distributed fallout (fine dust) produced by Deccan.

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