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Cretaceous-Paleogene Boundary Clays from Spain and New Zealand: Arsenic Anomalies

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Abstract: Remarkably high arsenic (As) contents have been reported in numerous Cretaceous-Paleogene boundary (KPB) clays worldwide including those from Spain (at Caravaca and Agost) and New (N.) Zealand (at Woodside Creek). Two interpretations have been offered to explain this anomaly. The first one suggests that this As was generated by the combustion of fossil fuels (such as crude oil, coal or oil shales) near the Chicxulub impact site and the second interpretation proposes the post-impact combustion of the global biomass at the KPB. Both types of combustion were presumably triggered by the Chicxulub impactor. This report shows that the estimated surface densities of As in Spain and N. Zealand strongly contradict the fossil fuel hydrocarbons/biomass hypotheses. In addition, we also show that previously reported global abundances of As at KPB are greatly overestimated.

The high abundances of iron (Fe) in the ejecta layers from Spain and N. Zealand lead us to a working hypothesis 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. These were 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 waters.

Keywords: Cretaceous-Paleogene boundary; arsenic; fossil fuel; crude oil; wildfire; iron oxides

1 Introduction

1.1 Iridium

Alvarez *et al.* [1] reported anomalously high iridium (Ir) in the marine Cretaceous-Paleogene boundary (KPB) clays at

Gubbio, Højerup and Woodside Creek, Fig. 1. Simultaneously Smit and Hertogen [2] reported an anomalous Ir in the marine boundary clay at Caravaca, Fig. 1. According to them, this enhanced Ir concentration was triggered by an asteroid impact. Later, it has been suggested that the impact site was at Chicxulub (a village at Yucatan Peninsula, southern Mexico, Fig. 1) [3] and the impactor was a CI carbonaceous chondrite-type body [4]. Since the initial discovery of Alvarez *et al.* [1], Ir anomalies have been found in numerous KPB marine and non-marine clays worldwide [5]. Besides Ir, these clays contain high concentrations of other platinum group of elements (PGE) probably also of chondritic origin [5]. These elements are: ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), Ir and platinum (Pt).

Most of the boundary clays at distal marine sites (more than about 9000 km from Chicxulub) are characterized by a basal (2–4 mm thick) reddish layer (the so called ejecta layer) marking the KPB [6, 7]. This layer contains most of the Ir and other impact-related markers. Typical surface density (or fluence) of Ir in the distal ejecta layer around the globe has been estimated to average $\sim 55 \text{ ng cm}^{-2}$ or around $2.75 \times 10^{11} \text{ g}$ (Table 1). The bulk of this layer consists mainly of submicrometer-size particles (dust) [14, and references therein] and most of them originated from condensation droplets of the impact vapor plume [15].

1.2 Arsenic

Apart from well-known anomalous Ir, the ejecta layers at distal boundary sites show the high concentrations of non-chondritic trace elements such as chalcophiles As, antimony (Sb), copper (Cu), zinc (Zn), molybden (Mo), gallium (Ga), mercury (Hg), rhenium (Re), and selenium (Se). According to [16], these elements represent a primary geochemical signal of the KPB impact.

Gilmour and Anders [13] examined the distribution of Ir and As, Sb and Zn in bulk boundary clays at eight prominent marine sites at Caravaca, Gubbio, Højerup, Woodside Creek, Flaxbourne River (N. Zealand), Zumaya (Spain) and Deep Sea Drilling Project 465A (Central Pacific), Fig. 1. All of these sites are distal (> 9000 km) to the proposed Chicx-

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Figure 1: Geographic locations of the KPB clays in question (see text) enriched with Ir and As, including the Chicxulub impact site, the Pimienta-Tamabra petroleum system, the Cantarell oil field and the Sabinas basin.

ulub impact site. Beside Ir, most of the As, Sb and Zn are situated in their ejecta layers at these sites, with average abundances at the KPB of approximately: $179 \mu\text{g cm}^{-2}$ As (Table 1), $994 \mu\text{g cm}^{-2}$ Zn and $11 \mu\text{g cm}^{-2}$ Sb [13] or about 9×10^{14} g As, 5×10^{15} g Zn and 5.5×10^{13} g Sb. Gilmour and Anders [13] concluded that, in contrast to Ir which is mainly meteoritic, As, Sb and Zn are non-meteoritic in origin and associated in a single, global component of ejecta fallout.

Anomalous As and other chalcophiles found in the ejecta layers of marine and non-marine KPB sections [13, 17] has been attributed to volcanism [18], scavenging from chalcophile-rich pore water [19] and microbial activity [20]. However, these proposed sources of chalcophile enrichments are problematical, with none of these explanation being wholly satisfactory [see [21] for discussion of this subject].

As naturally occurs in crude oil and coal and therefore high temperature processes release As into the atmosphere [22]. For this reason, Gilmour and Anders [23] proposed that combustion (ignited by the Chicxulub impactor) of fossil fuels such as crude oil, coal or oil shales was a possible source of chalcophiles in the boundary clays worldwide. Indeed, chalcophilic elements are low-

boiling trace elements that are volatilized during combustion of fossil fuels and are transferred in the gas phase to the atmosphere, e.g. As.

Wolbach *et al.* [24–26] reported the presence of elemental carbon (mainly acinoform soot) in the boundary clays from the widely separated prominent distal boundary marine sites including Caravaca, Agost and Woodside Creek. The mean global soot abundance at the KPB is estimated to be equivalent to 2.2 mg cm^{-2} to 12 mg cm^{-2} [27]. Wolbach *et al.* [24–26] suggested that this boundary soot originated from global-scale forest wildfires ignited promptly following the Chicxulub impact, arguing that most (~90%) of the Cretaceous forests may have burned down and converted to soot. Wolbach *et al.* [26] also reported that at Woodside Creek soot correlates closely with As. Therefore is a possibility that As in the boundary clays could be derived from the biomass that post-impact forest wildfires burned. It has also been proposed that a high concentration of soot in boundary clays worldwide could be derived from burning crude oil, coal or from the carbonaceous shale beds close to Chicxulub [28, 29, and references therein]. However, this possibility has been recently challenged by Premović [27].

Table 1: The surface densities ($\mu\text{g cm}^{-2}$) of Ir and As in d-RLC, d-RLA, d-RLW and the global boundary layer. The average Ir (ppb) and As (ppm) contents of other geological materials and CI chondrites.

Geological material	Element	RLC ^a	RLA ^b	RLW ^a	Continental crust ^c	Mantle ^c	CI chondrites ^c	Global boundary layer
	Ir		66	20	465	0.1	3.2	481
As		540	360	480	1.0	0.066	1.81	179 ^e

^a[8]; ^b[9]; ^c[10]; ^d[11]; ^e[12]; and, ^e[13].

This report first re-examines each of the above three explanations for the anomalous As in the ejecta layers at Caravaca, Agost and Woodside Creek, Fig. 1. For this purpose, the comprehensive geochemical data for anomalous As and Ir in these clays will be those published by Schmitz [8] and by Smit [9]. Throughout this paper, four reasonable assumptions are made: (i) all Ir found in the boundary clays studied originated from the CI-type of carbonaceous chondrite; (ii) the average content of Ir in the CI chondrites is 481 ppb (Table 1); (iii) Ir and As are located in the non-carbonate fraction of the ejecta layers studied, i. e. the carbonate fraction of this section is essentially their diluents; and, (iv) the assumed density of the ejecta layers, the decarbonated ejecta layers, ejecta fallout and its CI fraction is around 2 g cm^{-3} .

In the final part of this paper, we discuss a possibility that anomalous As of the ejecta layers in Spain and N. Zealand was initially adsorbed on Fe oxides during their passage through the seawater column.

2 Results, interpretation and discussion

2.1 The KPB sections in Spain and N. Zealand

The boundary section at Caravaca consists of a ca. 1 cm-thick Ir-rich dark (almost carbonate-free) marl (BC) overlain by a grey-to-brown marl, Fig. 2A. A basal ~3 mm thick red (ejecta) layer (RLC) of BC enriched with Ir; this layer is underlain with the latest Maastrichtian marl. Terminal Maastrichtian–basal Paleogene marls at Caravaca were deposited in a middle bathyal environment (< 500 m depth) [30]. The abundant presence of goethite ($\alpha\text{-FeOOH}$) in the ejecta layer [8] indicates that its deposition probably occurred under well-oxygenated conditions.

The Ir abundance distribution in the carbonate-free fraction (based on the INAA measurements) across the

boundary section at Caravaca is reported by Schmitz [8]. This distribution is characterized by a sharp increase in the concentration (ca. 110 ppb) in the decarbonated RLC (d-RLC), Fig. 2A. Using the Ir peak concentration, we estimate that d-RLC is derived from about 25% CI. Adopting 0.5 as a chondritic mass fraction globally dispersed after the impact of [31], we estimate that the initial (precursor) RLC could contain about 50% of ejecta fallout which is, after deposition, probably diagenetically transformed and weathered out through various pathways and by various agents. Indeed, this ejecta layer contains numerous presumably impact-derived goethitic microspherules [ca. 10% of the total weight [8]], shocked zircons and Ni-rich spinels. About 19–38 shocked quartz grains per gram were identified in the BC [32].

The Agost boundary section is similar to the neighbouring Caravaca section in lithology, geochemistry and depositional history. This section is also comprised of a dark (about 60-mm-thick) clay (BA) with a basal ~3 mm-thick goethite-rich (ejecta) red layer (RLA), Fig. 2C. RLA is underlain with the latest Maastrichtian marl and BA is overlain by the grey-to-brown marl [33, and references therein]. RLA is deposited in the middle bathyal oxygenated environment, 600–1000 m deep [34].

Smit [9] analyzed Ir (on a whole-rock basis) across the Agosta boundary section. Using their Ir and carbonate content data, we computed Ir concentrations in the non-carbonate (clay) fraction, Fig. 2C. The results show that the highest Ir (ca. 33 ppb) is in the decarbonated RLA (d-RLA); the Ir content gradually decreases upwardly therefrom. I estimate that the d-RLA contains about 6.5% CI. Assuming 50% represents the CI fraction in ejecta fallout [31] then the initial precursor RLA would contain about 13% of this fallout. RLA contains mineralogical evidence of extraterrestrial impact such as Ni-rich spinels and diagenetically altered K-feldspar or Fe oxide microspherules [9].

The KPB section at Woodside Creek is represented by a (ca. 5 mm thick) goethite-rich ejecta layer (RLW), Fig. 2C. This layer is overlain with dark and grey-to-brown marls and underlain by the latest Maastrichtian marl. These lay-

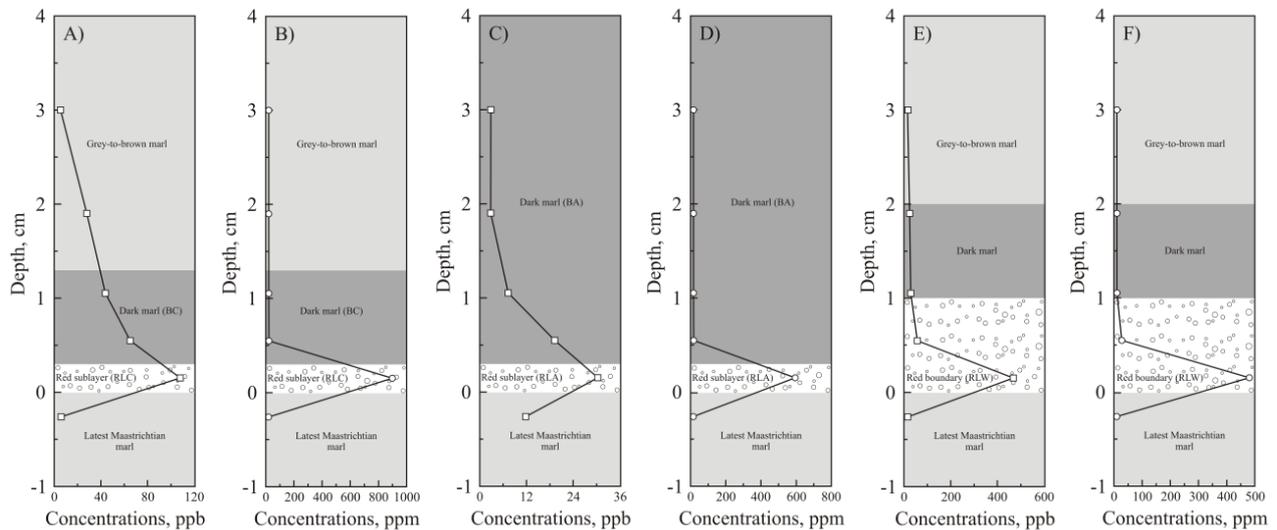


Figure 2: Concentration profiles of Ir and As (on a carbonate-free basis) in the boundary sections: A, B at Caravaca based on data of [8]; C, D at Agost based on data of [9]; and E, F at Woodside Creek based on data of [8]. The section samples were analyzed with instrumental neutron activation (INAA). Relative error in the precision of the analyses ranges from 5% to 10%. Total uncertainties (including accuracy errors) were up to 20% [8].

ers were probably deposited in a shallow marine < 500 m water depth [32] probably also under well-oxygenated conditions.

The INAA data for Ir [8] in the decarbonated fraction of the boundary section at Woodside Creek indicate that the peak concentration of Ir of 465 ppb (Fig. 2E) is located in the RLW which is one of the highest measured to date for any KPB interval. Using Schmitz's data, we estimate that the type CI chondrite input averages about bizarre 100%. Brooks *et al.* [35] reported that decarbonated RLW (d-RLW) (0.8 cm thick) at another site of Woodside Creeks contains about 153 ppb of Ir. This value corresponds to approximately 30% CI.

Based on the Ir data reported by [35] and assuming chondritic mass fraction of 0.5 [31], a simple estimation indicates that the precursor RLW could contain ~60% of ejecta fallout. As in the cases of RLC and RLA, a high percentage of this fallout would have left a residue after diagenesis with high concentrations of the impact indicators in RLW. Specifically, this layer contains numerous goethite-rich and organic microspherules [8]; and, about 2–8 shocked quartz grains per gram [32].

2.2 Distributions of Ir and As

The abundance distributions of As (on a carbonate-free basis) across the boundary sections in Spain and N. Zealand are given in Figs. 2B, 2D and 2F, respectively. Like Ir, As shows a prominent peak at d-RLC (ca. 900 ppm), d-RLA

(ca. 600 ppm) and d-RLW (ca. 480 ppm). 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 [8] and Smit [9] that the surface density of As of d-RBC, d-RBA and d-RBW is, respectively, approximately roughly $540 \mu\text{g cm}^{-2}$, $360 \mu\text{g cm}^{-2}$ and $480 \mu\text{g cm}^{-2}$. By comparison, the mean global surface density of As in the ejecta layer at marine sites is approximately $179 \mu\text{g cm}^{-2}$ (Table 1). This similarity in abundance is rather surprising because of the distant separation (~20,000 km) between the boundary locations in Spain and N. Zealand.

The deposition of RLC and RLA (approximately 3 mm thick, Fig. 2) occurred for several decades up to a century at most [6, 7, and references therein]. The same is probably true for the depositional duration of RLW (ca. 5 mm–8 mm thick, Fig. 2). Adopting the upper value of 100 years for their deposition it is possible to calculate that their accumulation rate of As as being between $4.4 \mu\text{g cm}^{-2}$ per year and $5.4 \mu\text{g cm}^{-2}$ per year.

According to Fig. 2B, the As in d-RLC show, respectively, ca. 180-fold increases in its concentration compared with the decarbonated latest Maastrichtian layer. The analogous increases of d-RLA are about 50-fold, Fig. 2D; this increase of d-RLW is 19-fold, Fig. 2F. These substantial increases of As in the ejecta layers strongly argue against a possibility that a pulse of carbonate dissolution played a major role in the enrichments with As of the RLC, RLA

Table 2: Surface densities ($\mu\text{g cm}^{-2}$) of Ni, Co, Cr, Zn, Cu and Sb in d-RLC and d-RLA, and Ni, Co, Cr in d-RLW. In the brackets are given the Ni, Co, Cr, Zn and Sb concentration increases of RLC and RLW relative to the underlying latest Maastrichtian layer.

Element (increase)	Red layer						
	Ni	Co	Cr	Zn	Cu	Sb	
RLC ^a	1450 (30)	450 (35)	600 (8)	440 (13)	180 (20)	14.5 (44)	
RLA ^b	220	40	480	-	-	5	
RLW ^a	1960 (75)	240 (20)	1200 (15)	800 (20)	240 (8)	23 (40)	

^a[8]; ^b[9].

and RLW after their initial deposition. It is also not possible to explain their anomalous As contents by any enrichment process characteristic for marine sediments (e.g. postdepositional condensation and remobilization, redox-controlled precipitation, chemical diffusion, reworking, bioturbation and local redistribution) of As.

Apart from the enrichments of As, RLC, RLA and RLW show similarly elevated contents of other elements such as Ni, Co, Cr, Zn, Cu and Sb. Table 2 displays the surface densities of these elements in d-RLC, d-RLA and d-RLW, except that the corresponding Zn and Cu data are not available to estimate their surface densities in d-RLA. This table also illustrates the concentration increases of Ni, Co, Cr, Zn, Cu and Sb relative to the underlying latest Maastrichtian layer. These factors show that there are no significant similarities in geochemical behavior of the elements between RLC, RLA and RLW.

Besides, As and other chalcophiles, Strong *et al.* [36] and Gilmour and Anders [13] studied the distribution (on a decalcified basis and whole-rock basis) of Ni, Co and Cr using the available data from the marine boundary sites including Caravaca and Woodside Creek. Their two main conclusions were that these elements are partly meteoritic and were associated in a single component of global ejecta fallout prior to their deposition. The simultaneous presence of extraterrestrial Ir, partly chondritic Ir, Ni, Co, Cr and terrestrial As along with other chalcophiles and soot in these three ejecta layers indicates that these constituents and soot also probably originated simultaneously.

2.3 As, impactor and crater rocks

Using the above estimated values for contribution of ejecta fallout to d-RLC, d-RLA and d-RLW, a simple calculation shows that this fallout should contain As as high as about 0.18% at Caravaca, 0.5% at Agost and > 0.08% at Woodside Creek. This element in ejecta fallout may be derived from

either target rocks or the CI impactor. The target rocks were probably derived from the Earth's continental crust with little contribution of mantle [37] or asteroid [38]. Table 1 shows the average concentrations of As in these terrestrial materials and CI chondrites.

Obviously, none of these are adequate sources for anomalous As in d-RLC, d-RLA and d-RLW. This contention is supported by the various crater rocks and allochthonous impactites at Chicxulub containing extremely low As concentrations < 1 ppm [37, 39, 40]. Exceptionally high As contents of the three ejecta layers is also not consistent with the composition of any chondritic meteorites and therefore with an asteroidal origin in general. Indeed, the As content in chondrites ranges from about 0.9 ppm to 5.5 ppm [41].

Toon *et al.* [14] estimated that the Chicxulub impactor generated about 3×10^{17} g of stratospheric submicron-size particles (hereinafter called impact dust) globally dispersed immediately after Chicxulub. These researchers also suggested that the global ejecta layer at the KPB contains >10% of submicron dust produced by the Chicxulub impact. Even using 50%, basic calculations reveal that the impact dust would still contain extremely high concentrations of Ir ~1.8 ppm, As ~0.6%, Zn ~3.5%, Sb ~0.06% (assuming their average global abundances, as previously indicated.). Later, Pope [15] estimated that the total mass of the impact vapor plume was approximately $2-4 \times 10^{18}$ g containing about $1-3 \times 10^{17}$ g of the impactor material. Pope proposed that the condensates of the impact vapor plume produced minimal amounts of submicron-sized dust 10^{13} g– 10^{14} g. This estimate would imply that the impact dust contained 10^3 to 10^4 times higher concentrations of Ir, As, Zn and Sb than is indicated by the above calculation based on the estimate of Toon *et al.* [14].

2.4 As and the stratosphere

It is likely that the combustion of fossil fuels or biomass, initiated by the Chicxulub impact, would result in a mas-

sive 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 high temperature processes (e.g. crude oil or coal combustion) 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 $1 \mu\text{m}$ are capable of long range (stratospheric) transport [42–44]. Before any further, it would be useful to briefly address this concept as related to As.

As from both natural and anthropogenic sources is released to the present-day atmosphere. The principal natural source is volcanic activity. About 1.7×10^{10} g of As is emitted to the atmosphere by volcanoes, and $< 2 \times 10^9$ g by naturally occurring forest fires [45]. Most of anthropogenic As emitted into the current atmosphere arises from high temperature processes (e.g. coal and crude oil combustion) and occurs only as fine particles (dust) with a mass median diameter of about $\leq 1 \mu\text{m}$ [22, 45–47]. Their residence time in the atmosphere is about 7–9 days, and during that time, the particles may be transported thousands of kilometers (US EPA 1982). Most of As (natural and anthropogenic origin) of the current atmosphere is stored in this particulate (dust) form (ca. 89–99%) and the rest is gaseous [45]. The dust particles and associated As in the atmosphere are transported mainly by wind, and eventually returned to the Earth's surface in wet or dry deposition, leading to their deposition mainly near the source [48].

As generated by the combustion of fossil fuels or biomass ignited by the Chicxulub impact was probably in the elemental form and may have been initially present as the gaseous/vapor emission into the atmosphere. This As would be rapidly oxidized to (highly soluble) oxides and subsequently condensed into the micron and submicron particles (fine dust).

It is highly likely that 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 would be largely removed by the enormous precipitations (probably acid rains). Thus, it appears that only a small fraction of As formed by the fossil fuels or biomass that was burned promptly after the impact could reside in the lower stratosphere and thus be deposited globally.

In the following calculations, f_S is defined as the amount of As dispersed globally through the lower stratosphere to the total As of the crude oil and f_{AS} represents the amount of As distributed over the Earth's surface by the lower stratosphere to the total As emitted by this source

into the atmosphere. It is assumed that f_S and f_{AS} both are equal 1 but this is clearly a high overestimation of their actual values which are likely much lower.

2.5 As and crude oil

As stated above, there are two main potential sources of anomalous As in RLC, RLA and RLW caused by the Chicxulub impact: fossil fuel (such as crude oil, coal or carbonaceous shales) close the Chicxulub impact site or global forests wildfires. This subsection considers a possibility that As was sourced from combustion of crude oil near Chicxulub.

The global surface density of As (d_{As}) derived from crude oil burned promptly after the Chicxulub impact is given by

$$d_{As} = M_O C_O f_S / A_E$$

where M_O is the mass of crude oil burned, C_O is the average concentration of As in crude oil {0.134 ppm: Piver, [49]; Eary *et al.* [50]} and A_E (ca. $5 \times 10^{18} \text{ cm}^2$ is the Earth surface area.

Harvey *et al.* [51] emphasize that the Chicxulub impact crater is located adjacent to the very large Cantarell oil reservoir in the southern Gulf of Mexico, suggesting an abundance of fossil hydrocarbons in the Chicxulub target rocks was likely to have been above global mean crustal abundance. The formation of the Cantarell oil field is a direct consequence of the KPB impact [52] and it belongs to the giant supercharged Pimienta-Tamabra petroleum system, Fig. 1. This system is the most important in the southern Gulf of Mexico and has a cumulative production and remaining reserves of approximately 10^{16} g of petroleum [53]. (The Oil and Gas Journal estimated that as of 2007, there were 12.4 billion barrels of proven oil reserves in Mexico. This corresponds to around 2×10^{15} g of crude oil). The total proven crude oil and natural gas reserves of the world now stand approximately 2×10^{17} g; estimates are that there is about 5×10^{17} g of crude oil and natural gas in the Earth's crust. (World Energy Council-Survey of Energy Resources 2010). Of course, oil reserve estimates cited above all refer to "proven", and there may be much more that has not been found.

Let us assume that the amount of crude oil burned during the Chicxulub impact was equal to the crude oil reserves of the gigantic Pimienta-Tamabra petroleum system. Using this value, I calculate (employing the previous formula) that the upper limit of the global surface density (d_{As}) is 270 pg cm^{-2} compared with the global surface density of As of 179 $\mu\text{g cm}^{-2}$ and with the surface densities of

As of the RLC (540 $\mu\text{g cm}^{-2}$), RLA (360 $\mu\text{g cm}^{-2}$) and RLW (480 $\mu\text{g cm}^{-2}$). Moreover, this estimated value is approximately four millions times less than the present-day mean oceanic value of 922 $\mu\text{g cm}^{-2}$ [54]. As an extreme example, if all the current known reserves of crude oil ($\sim 2 \times 10^{17}$ g) burned d_{As} would be $< 5.4 \text{ ng cm}^{-2}$.

The crude oil of the Pimienta-Tamabra petroleum system derives from Late Jurassic source rock and its expulsion started in the Eocene [53]. The age of reservoir rocks occurs both slightly before and after that of the source beds. Burning of fossil hydrocarbons of Jurassic-Cretaceous carbonaceous shales close to Chicxulub certainly would not serve much better as the source of As in the boundary clays at the Spanish and N. Zealand's sites. Indeed, total world resources of shale oil are conservatively estimated at approximately 10^{18} g [World Energy Council-Survey of Energy Resources 2010]. If all of this oil burned it would create the global surface density of As (d_{As}) of $< 27 \mu\text{g cm}^{-2}$.

An alternative method for estimating d_{As} for crude oil burned is using the following formula:

$$d_{As} = M_O \epsilon_{OfAS} / A_E$$

where M_O and A_E have the same definition and values as those given above, and ϵ_O is the As emission factor (AsEF) for crude oil: $1.6 \times 10^{-4} \text{ g g}^{-1}$ (AP 42, Fifth Edition, Volume I, Chapter 1: External Combustion Sources). AsEF can be defined as the mass of As released into the atmosphere per mass of source material. Simple calculations then show that the upper estimates of d_{As} are $0.32 \mu\text{g cm}^{-2}$ (for $M_O \sim 10^{16}$ g, the Pimental-Tamabra petroleum system), $6.4 \mu\text{g cm}^{-2}$ (for $M_O \sim 2 \times 10^{17}$ g, all worldwide crude oil) and $32 \mu\text{g cm}^{-2}$ (for the world shale oil).

2.6 As and the coal beds in Mexico

It is possible that anomalous As in the boundary clays in Spain and N. Zealand is derived from the combustion of coal bed in the neighborhood of the Chicxulub impact. To estimate the global surface density of As (d_{As}) in this case one can use the following formula:

$$d_{As} = M_C C_{As} f_S / A_E$$

where M_C is the mass of coal combusted, C_C is a mean concentration of As in coal ca. 13 ppm [45, and references therein] and A_E has the same meaning and value as used previously. A simple estimate therefore is that combustion of all proven coal reserves of Mexico about 10^{15} g (Europe's Energy Portal, 2011) would generate a global density of As (d_{As}) $< 2.6 \text{ ng cm}^{-2}$.

To estimate d_{As} for the coal combustion case we can also use the following formula:

$$d_{As} = M_C \epsilon_C f_{AS} / A_E$$

where M_C and A_E have the same meanings and values as before, and ϵ_C is $1.7 \times 10^{-7} \text{ g g}^{-1}$ [55] is A_S EF for coal. It was estimated that d_{As} was less than 34 pg cm^{-2} . One problem with this theory however is that there are no coal bearing rocks in the Chicxulub subsurface with the nearest and most important being the Sabinas basin in northern Mexico (Fig. 1) mostly of the Late Cretaceous period.

2.7 As and the global forest wildfires

It is possible to estimate the global density of As (d_{As}) from biomass burned in the enormous post-impact forest using the following formula

$$d_{As} = M_B \epsilon_B f_{AS} / A_E$$

where M_B is the amount of biomass burned, ϵ_B is $5 \times 10^{-6} \text{ g g}^{-1}$ [56] is the corresponding A_S EF and A_E has the previous meaning and value. Kring [57] estimated that approximately 3.5×10^{18} g to 7×10^{19} g of biomass burned in post-impact forest wildfires. Substituting these values for M_B in the above formula, it is possible to calculate a global surface density of As (d_{As}) ranging between $3.5 \mu\text{g cm}^{-2}$ – $70 \mu\text{g cm}^{-2}$.

There is another method to estimate d_{As} at KPB using the following formula:

$$d_{As} = d_B f_B \epsilon_B f_{AS} A_L / A_E$$

where $d_B \sim 2 \text{ g cm}^{-2}$ is the biomass density estimated by Wolbach *et al.* [26] and based on the assumption that a land area equal to the present had the same biomass density as present-day forests, f_B is a fraction of biomass burned, A_L is the surface area (ca. $1.5 \times 10^{18} \text{ cm}^2$) of the present Earth's land and; ϵ_B and A_E have the same definition and values as those given above. Wolbach *et al.* [26] have used the value $f_B \sim 0.2$, therefore the estimates of the upper limit of d_{As} is $0.6 \mu\text{g cm}^{-2}$.

The global surface density of As (d_{As}) released from biomass burned by the post-impact global forest wildfires can be also estimated using the following equation:

$$d_{As} = M_B \epsilon_F f_{AS} / A_E$$

where M_B and A_E the same as those given above and ϵ_F is A_S EF of for the forest wildfires is $5 \times 10^{-7} \text{ g g}^{-1}$ [55]. The calculation yields d_{As} between $0.35 \mu\text{g cm}^{-2}$ and $7 \mu\text{g cm}^{-2}$.

2.8 Mass of As in the impact dust

As we noted above, Toon *et al.* [14] estimated that the Chicxulub impactor generated about 3×10^{17} g of stratospheric submicron-size particles (the impact dust) globally dispersed for several months immediately after Chicxulub. They also estimated that the global ejecta layer at the KPB contains > 10% of submicron dust produced by the Chicxulub impact. Using conservative estimates (~10%), one may calculate that the concentration of As in the impact dust would be as high as ~3% or 9×10^{15} g (calculated using the average global As abundance as previously indicated).

As we noted above, Pope [15] claims that the vapor condensates of the Chicxulub impact produced 10^{13} g– 10^{14} g of submicron dust. Most of the entire mass of As was likely associated with this dust. If this is correct than similar calculations as those used above, but instead using the Pope's data, indicates that the impact stratospheric dust contained approximate levels of As a hundred to a thousand times higher than calculated above.

As estimated above the impact dust would contain around 9×10^9 t As. For comparison, the total world resources of As are thought to be about 1.1×10^7 t (U. S. Geological Survey, Mineral Commodity Summaries). If the above estimate of As in the impact dust is correct then it is unrealistic to suggest that the Chicxulub impact would completely and instantaneously vaporize an amount of As over two hundred times larger than the Earth's known As resources.

One possible but remote source of the extreme concentrations of As in the impact dust could be a huge As deposit (e.g. a Cu/lead sulfide ore deposit rich in As) under the Chicxulub impact area. However, there appears to be no current geochemical or geological evidence for such a deposit.

A mean As concentration in ocean water is approximately 2 ng g^{-1} [54] and the world's oceans have a volume of $1.4 \times 10^{24} \text{ cm}^3$. Thus, the ocean contains around 2.8×10^9 t As or > 3 times less than that estimated in the impact dust. Again, this highlights the remote possibility that the groundwaters or geothermal waters at Chicxulub (and nearby areas) the source of the enormous As in the impact dust. Indeed, according to [58] the highest As concentrations in these two water sources worldwide are as low as 5 ppm (groundwaters) and 50 ppm (geothermal waters).

It appears that the average global abundance of As at KPB previously reported is highly overestimated. The average global abundances Zn and Sb of the global ejecta layer also show similar discrepancies.

2.9 As and the seawater

The forms or species of dissolved As are mainly limited to As(V) and As(III). As previously explained, RLC, RLA and RLW were probably formed under oxic seawater conditions. As(III) has a thermodynamically unstable oxidation state; the predicted ratio As(III)/As(V) under these conditions is about $10^{-26.5}$ [59].

Furthermore, RLC, RLA and RLW are enriched with the fine-grained goethite. Iron-oxides in general, whether in the bulk or nanoparticulate form, have a strong adsorption efficiency for As. Mamindy-Pajany *et al.* [60] studied the As adsorption by commercially available goethite and haematite. At pH values 5–8 of typical natural (ground and surface) waters, both haematite and goethite were able to adsorb more than 80% of arsenic, regardless of the initial concentration.

Fe-oxide-rich nanophase materials have been previously detected at several KPB sites in Asia, Northern America and Europe (including Caravaca and Agost) and were ascribed to condensates from an impact vapor plume [61, 62]. The presence of Fe oxide nanomaterials in RLC, RLA and RLW may point to the possibility that the nanophase could also partly be a carrier of As. The small size of Fe-oxide nanoparticles is characterized by a high surface area-to-volume ratio which particularly facilitates their adsorption of As from natural (ground or surface) waters.

As noted earlier, the columns of seawater at the KPB site at Caravaca, Agost and Woodside Creek were around 500 m–1000 m. For the average abundance of As in seawater of 2 ppb these columns would contain about 100 μg –200 μg of As. It appears that seawater could be a sufficient source of anomalous As in RLC, RLA and RLW. From early on it has been proposed that the ocean could be an adequate source of As [13, and reference therein] as average abundances at marine boundary sites worldwide (ca. $179 \mu\text{g cm}^{-2}$) are ~20% the current mean oceanic value: $922 \mu\text{g cm}^{-2}$ [54]. Gilmour and Anders [13] hypothesized that the massive amount of ejecta fallout and soot should be able to sweep out this oceanic As.

If the Chicxulub impactor was the CI chondrite, its Fe content would have been roughly 20% [10]. Assuming that all of the impactor's Fe was completely vaporized (and the likely oxidized quickly by atmospheric oxygen to primarily Fe_2O_3) the impact dust may contain approximately 3×10^{16} g of this metal or approximately 1×10^{17} g of Fe-oxides. This assumes that the impactor fraction of this dust is 0.5 as computed by Vickery and Melosh [31]. If about 10% of the impactor dust was deposited at the KPB then the global abundance of chondritic Fe would be roughly 6 g m^{-2} or 0.3% of the global ejecta layer.

Schmitz [8] reported that d-RLC and d-RLW contain about 5% of Fe. A simple calculation based on the data reported by Smit [9] shows that the Fe content of d-RLA is about 15% Fe. The Fe contents of RLC and RLW are roughly 4–5 times higher than in their underlying decarbonated latest Maastrichtian and overlying earliest Danian marls [8]. Estimate that global fluency of Fe-oxides derived from the chondritic Fe were approximately 20 g cm^{-2} . Such a high fluency allows us to formulate a tentative hypothesis that can be explored in more detail in later work. This hypothesis states that the predominant source of this excessive Fe in RLC, RLA and RLW was likely Fe-oxides of ejecta fallout deposited on oxic soils on local topographic highs. Fe of these oxides was probably mostly derived from the vaporized Chicxulub carbonaceous chondrite. The fallout Fe-oxides saturated the nearby surface seawater and adsorbed As (as well Zn, Sb). They were probably transported by the impact-induced-(acidic?) surface waters. Similar explanation is possible to suggest for the anomalous As of the continental boundary clays.

3 Conclusions

From this study, it appears that the As anomaly in the boundary clays at Caravaca, Agost and Woodside Creek (or global at the KPBB, in general) cannot be attributed to the combustion of the fossil fuels close to the Chicxulub impact site or the global biomass burned at KPBB ignited by the Chicxulub impact. We also argue that published estimates of global As fluency at KPBB are likely too high.

We tentatively hypothesize that a major fraction of their anomalous As was adsorbed from seawater by the Fe-oxides. These oxides were probably laterally transported from the local (topographically high) oxic soils to the RLC, RLA and RLW sites by the impact-induced surface waters. The Fe of the oxides was derived from the vaporized (carbonaceous chondrite) impactor.

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