Cretaceous-Paleogene boundary clays from Spain and New Zealand: iridium and arsenic anomalies

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ABSTRACT

Remarkably high arsenic (As) contents have been reported in numerous Cretaceous-Paleogene boundary (KPB) clays worldwide including that from Spain (at Caravaca and Agost) and New Zealand (at Woodside Creek). The two interpretations have been offered to explain this anomaly. The first one suggests that this As was generated by combustion of fossil fuels (such as crude oil, coal or oil shales) near the Chicxulub impact site and the second interpretation recalls 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 New Zealand strongly contradict the fossil hydrocarbons/biomass hypotheses. It is also appeared that anomalous As in the boundary clays in these two regions was not sourced by the enormous Deccan Trap volcanism.

Key words: Cretaceous-Paleogene, Caravaca, Agost, Woodside Creek, arsenic, iridium, crude oil, fossil fuel, wildfire, Deccan Traps

1. INTRODUCTION

1.1 Iridium.

Alvarez et al. (1980) reported anomalously high iridium (Ir) in the marine Cretaceous-Paleogene boundary (KPB) clays at Gubbio (central Italy), Højerup (the eastern Denmark) and Woodside Creek (the northern part of the South Island of the New Zealand), Fig. 1. Simultaneously Smit and Hertogen (1980) reported an anomalous Ir in the marine boundary clay at Caravaca (Spain, Fig. 1). According to Alvarez et al. (1980), this enhanced Ir concentration was triggered by an asteroid impact. Later, it has been suggested that the impact site is at Chicxulub (a village at Yucatan Penninsula, southern Mexico, Fig. 1) (Hildebrand et al., 1991) and the impactor was a CI carbonaceous chondrite-type body (Shukolyukov and Lugmair, 1998). Since the initial discovery of Alvarez et al. (1980), Ir anomalies have been found in numerous boundary marine and non-marine clays worldwide (Claeys et al., 2002).

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) redish layer (so called the ejecta layer) marking the KPB (Premović, 2009). This layer contains most of Ir and other impact-related markers. Typical surface density of Ir (or fluence) in the distal ejecta layer around the globe has been estimated to average ~55 ng cm^{-2} (Table 1A). The bulk of this layer consists of micrometer- and submicrometer-size particles (dust) (Toon et al., 1997; Pope 2002, and references therein) and most of them originated from condensation droplets of the impact vapor plume (Pope, 2002).

1.2. Origin of As.

Apart from well-known anomalous Ir, the ejecta layers at distal boundary sites show the high concentrations of (so-called) non-chondritic trace elements such as chalcophiles As, anthimony (Sb), copper (Cu), zinc (Zn), molibden (Mo), galium (Ga), mercury (Hg), rhenium (Re), and selen (Se). According to Hildebrand and Boynton (1989), these elements represent a primary geochemical signal of the KPB impact.

The chalcophiles anomalies has been attributed to the the Chicxulub impactor (Smit and ten Kate, 1982), volcanism (Officer and Drake, 1985), scavenging from chalcophile–rich pore water (Schmitz, 1985), precipitation from seawater (Strong et al., 1987; Schmitz et al, 1988; Gilmour and Anders, 1989; Schmitz, 1992), and microbial activity (Schmitz et al., 1988). However, the source of the chalcophile enrichments remains problematical as none of these possibilities is wholly satisfactory (see Hildebrand, 1992 for discussion of this subject).

Gilmour and Anders (1989) 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 (New Zealand), Zumaya (Spain) and Deep Sea Drilling Project 465A (Central Pacific), Fig. 1**.** These sites are distal (>9000 km) to the proposed Chicxulub impact site. Beside Ir, most of As, Sb and Zn are situated in their ejecta layers. They 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. I readily anticipate their conclusions throughout this report.

As naturally occurs in coal and crude oil and therefore high temperature processes release As into the atmosphere (Pacyna, 1987). For this reason, Gilmour and Anders (1988) also 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 the low-boiling trace elements that are volatized during combustion of fossil fuels and are transferred in the gas phase to the atmosphere, e. g. As.

Wolbach et al. (1985, 1988, 1990) 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} (Premović, 2012). Wolbach et al. (1985, 1988, 1990) suggested that the boundary soot originated from global-scale forest wildfires ignited promptly following the Chicxulub impact, arguing that most (~90 %) of the Cretaceous forests may burned down and were converted to soot. Wolbach et al. (1990) also reported that at Woodside Creek soot correlates tightly with As so there is a possibility that As in the boundary clays could be derived from biomass that the post-impact forest wildfires burned. It has **also** been proposed that a high concentration of soot in the boundary clays worldwide could be derived from burning crude oil, coal or from the carbonaceous shale beds close Chicxulub (Belcher, 2009, and references therein). However, this possibility has been only very recently challenged by Premović (2012).

1.3. 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 (Officer and Drake, 1985). One of the largest basaltic provinces in the world the Deccan Traps (India, Fig. 1) become 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 (Shukla et al., 2001, and references therein).

Deccan Traps (hereinafter Deccan) were created by an enormous volcanic event that originally erupted about 1.2 × 10^6 km^3 of magma (Keller et al., 2012). Recent 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 (Chenet et al., 2007; Keller et al., 2009, and references therein). This phase may have occurred in the short time interval of 10,000 years to 100,000 years (Chenet et al., 2007, 2008) and its effects have been linked to the KPB global faunal extinction (Wignal, 2001; Courtilot and Fluteau, 2010).

In general, volcanic eruptions inject into the atmosphere tens of teragrams of gases, aerosol particles so, for example, the current volcanoes are significant sources of As emissions into the atmosphere (Chilvers and Peterson, 1987). Thus an enormous volcanic source such as Deccan, in principle, could account for the excess of chalcophiles (e. g. As) at the KPB. Indeed, Chenet et al. (2007, 2008) 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 chalcophiles e. g. As.

This report first re-examines each of the above three possibilities for the case anomalous As in the ejecta layers at Caravaca, Agost and Woodside Creek. (India, Fig. 1). For this purpose, comprehensive geochemical data for anomalous Ir and As in these clays will be those published by Schmitz (1988) and at Agost by Smit (1990). Throughout this paper, four reasonable assumptions are made: (a) all Ir found in the boundary clays studied originated from the CI-type of carbonaceous chondrite; (b) the average content of Ir in the CI chondrites is 481 ppb (Table 1A); (c) 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, (d) assumed density of the decarbonated ejecta layers, ejecta fallout and its CI fraction is about 2 g cm^{-3}.

2. EXPERIMENTAL DATA, DISCUSSION AND CONCLUSIONS

2.1 The Caravaca boundary section.

The boundary section Caravaca is among the most continuous and complete marine sections for the KPB transition. The Caravaca section is located in the Betis Cordilleras (southerneast Spain). 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. 2 A. A basal ~3 mm thick red (ejecta) layer (RLC) of BC enriched with Ir (ca. 110 ppb, Fig. 2A); 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) (Smit, 1999). Abundant presence of goethite in the ejecta layer indicates that its deposition probably occurred under well-oxygenated conditions.

The Ir abundance distribution in the carbonate-free fraction across the boundary section at Caravaca is given in Fig. 2A. This profile is based on the INAA measurements performed by Schmitz (1988) and is characterize by a sharp increase in the concentration (ca. 110 ppb) in the decarbonated RLC. This Ir peak has tails both upsection and downsection. The upward tail feature infers a relatively continuous and complete section. Using the Ir peak concentration, I estimate that the decarbonated RLC is derived from about 25 % CI. Adopting 0.5 as a chondritic mass fraction globally dispersed after the impact of (Vickery and Melosh, 1990), I 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: Schmitz, 1988), shocked zircons and Ni-rich spinels. About 19 - 38 shocked quartz grains per gram were identified in the BC (Morgan et al., 2006).

2.2. The Agost boundary section.

The Agost boundary section is similar to the neighboring Caravaca section in lithology, geochemistry and depositional history. As at Caravaca this section is comprised of a dark (about 6-cm-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 (Molina et al., 2005, and references therein). RLA layer is deposited in the middle bathyal oxygenated environment, 600-1000 m deep (Coccioni and Galeotti, 1994).

Smit (1990) analyzed Ir (on a whole-rock basis) across the Agosta boundary section. Using his Ir, As and carbonate content data, we computed Ir concentrations in the non-carbonate (clay) fraction. These calculated concentrations are plotted *vs.* stratigraphic height in Fig. 2 C. The results show that the highest Ir (ca. 30 ppb) is in the decarbonated RLA with an upward gradual decrease from this peak. We estimate that the decarbonated RLA contains about 6.5 % CI. Assuming 50 % represents the CI fraction in ejecta fallout 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 (Smit, 1990).

2.3. 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 and grey-to-brown marls and underlain by the latest Maastrichtian marl, Fig. 2 E. These layers were probably deposited in a shallow marine <500 m water depth (Morgan et al., 2006) probably also under well-oxygenated conditions.

The INAA data for Ir (Schmitz, 1988) in the decarbonated fraction of the boundary section at Woodside Creek studied by Schmitz (1988) are plotted in Fig. 2 E. 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. Using Schmitz's data, we estimate that the type CI chondrite input averages about bizarre 100 %. Brooks et al. (1984) reported that the carbonate-free RLW (0.8 cm thick) at another site of Woodside Creeks contains about 153 ppb of Ir. This value corresponds to about about 30 % CI.

Based on the the Ir data reported by Brooks et al. (1984), a simple estimation indicates that the precursor RLW could contain ~60 % of ejecta. As in the cases of RLC and RLA, a high percentage of the ejecta fallout would have left a residue after diagenesis with high concentrations of the impact indicators in RLW. To express precisely, this layer contains numerous goethite-rich and organic microspherules (Schmitz, 1988); and, about 2 - 8 shocked quartz grains per gram (Morgan et al., 2006).

2.4. Distributions of Ir and As.

The abundance distributions of As (on a carbonate-free basis) across the boundary sections in Spain and New Zealand are given in Figs. 2B, 2 D and 2F, respectfully. Like Ir, As shows a prominent peak at the decarbonated RLC (ca. 900 ppm), RLA (ca. 600 ppm) and 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 instantenous. An estimation from the experimental data of Schmitz (1988) and Smit (1990) that the surface density of As of the decarbonated RLC, RLA and RLW is, respectfully, about 540 µg cm^{-2}, 440 µg cm^{-2} and 480 µg cm^{-2}; by comparison, the mean

global surface density As of the ejecta layer at marine sites is about 179 µg cm^{-2} (Table 1A). This similarity in abundance is rather surprising because of the distant separation (~20,000 km) between the boundary locations in Spain and New Zealand. The deposition of RLC and RLA (about 3 mm thick, Fig. 2) occurred for several decades up to a century at most (Premović 2009, 2011, and references therein). The same is probably true for the depositional duration of RLW (ca. 8 mm - 10 mm thick). If I adopt the upper value of 100 years for their deposition I calculate that their accumulation rate of As lies between 4.4 µg cm^{-2} per year and 5.4 µg cm^{-2} per year.

According to Fig. 2A/B, the Ir and As in the decarbonated RLC show, respectfully, ca. 19- and 180-fold increases in their concentrations compared with the decarbonated latest Maastrichtian layer. The analogous increases of the decarbonated RLA are about 3-(Ir) and 50-fold (As) (Figs. 2C/D); these increases of the decarbonated RLW are 10-(Ir) and 19-fold (As) (Figs. 2E/F). These manifold increases of Ir and As in these ejecta layers strongly argue against a possibility that a pulse of carbonate dissolution played a major role in the enrichments with Ir and As of the RLC, RLA 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 derived from these sources without **some** dubious argumentation.

Apart from the enrichments of Ir and chalcophilic As the decarbonated RLC, RLA and RLW show a similar type of the elevated contents of other elements Ni, Co, Cr, Zn, Cu and Sb. Table 2 displays the surface densities of these elements in the decarbonated RLC and RLW; the corresponding data are not available to estimate their densities for the decarbonated RLA. In this table are also given the concentration increases of these elements relative to the underlying decarbonated late Maastrichtian layer. These factors show that there are no significant similarities in behavior of the elements considered between RLC, RLA and RLW.

Besides, chalcophiles, Strong et al. (1987) and Gilmour and Anders (1989) 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 are that these elements are partly meteoritic and were associated in a single component of global ejecta fallout prior deposition. Simultaneous presence of extraterrestrial Ir, partly chondritic Ir, Ni, Cr, **Co** and terrestrial chalcophilic elements (including As) and soot in these three ejecta layers is rather remarkable in view of their separate origins. This implies that these elements and soot probably resulted from the same event.

2.5. As, impactor and crater rocks.

Using the above estimated values for contribution of ejecta fallout to the decarbonated RLC, RLA and 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 Wodside Creek. This element in ejecta fallout may be derived from either target rocks or the CI impactor. **The target rocks are probably derived from the Earth's continental crust with trivial or no significant contribution of mantle (Koeberl et al., 1994) or asteroid (Tagle et al., 2004).** Table 1a shows the average concentrations of As in these terrestrial materials and CI chondrites.

Obviously, none of these sources is adequate for anomalous As in the decarbonated RLC, RLA and RLW. This contention is supported by the fact that various crater rocks and allochthonous impactites at Chicxulub contains extremely low As concentrations <0.1 ppm (Koeberl, 1993) and <1 ppm (Koeberl, 1993; Koeberl et al., 1994, Tuchscherer et al., 2004), respectfully. Exceptionally high As contents of these three ejecta layers is also not consistent with a composition of any chondritic meteorites and therefore with the asteroidal origin in general. Indeed, the As content in chondrites ranges from about 0.92 ppm to 5.5 ppm (Mason, 1979).

2.6. As and the stratosphere.

It is likely that the combustion of fossil fuels or biomass, initiated by the Chicxulub impact, would result in a massive injection of various chemical elements (including 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. coal and crude oil combustion) very coarse particles with mass diameter >10 µm quickly settle in the vicinity of their sources, whereas particles with diameters between 0.1 µm and 1 µm is particularly suited for long range (stratospheric) transport (Garland, 1983; Müller, 1986; Schroeder et al., 1987). Before any further, it would be instructive to address briefly this question related to As.

As is released to the present-day atmosphere from both natural and anthropogenic sources. The principal natural source is volcanic activity. About 1.72×10^{10} g of As is emitted to the atmosphere by volcanoes, and $<2 \times 10^{9}$ g by naturally occurring forest fires (Matschullat, 2000). Most of anthropogenic As emitted into the atmosphere arises from high temperatures processes (e. g., coal and crude oil combustion) **and occurs and occurs** as fine particles (dust) with a mass median diameter of about 1 µm (Coles et al., 1979; Pacyna, 1987). 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 of the current atmosphere is stored in this particulate (dust) form (ca. 89 – 99 %) and the rest is gaseous (Matshullat, 2000). 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 (Cullen and Reimer, 1989).

As generated by the combustion of fossil fuels or biomass ignited by the Chicxulub impact was probably in the elemental form and may be initially present in in 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). Indeed, most of 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 ≤1 µm (Rahn, 1976; Coles et al., 1979; Pacyna, 1987; **Matschullat,**). Thus, 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 should be largely removed by the enormous precipitations (probably acid rains). Thus, it appears **that** only a notably small fraction of As formed by the fossil fuels or biomass burned promptly after the impact could reside in the lower stratosphere and be deposited globally**.** Similar reasoning is probably also applicable to As generated by Deccan.

In the following calculations, f_S is defined as the amount of As released into the lower stratosphere to the total As of the fossil fuels, biomass or the Deccan magma; f_{AS} represents the amount of As which reaches the lower troposphere to the total As emitted by these sources into the atmosphere. (In fact, f_{AS} is a fraction of f_S). I will assume that both f_S and f_{AS} are equal 1 but this is clearly a high overestimation of their actual values which are probably much lower than 1.

2.7. As and crude oil.

As stated above, there two main potential sources of anomalous As in the decarbonated 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 the 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, 1983; Eary et al., 1990) and A_E (ca. 5×10^{18} cm^2) is the Earth surface area.

Harvey et al. (2008) emphasize that the Chicxulub impact crater is located adjacent to the Cantarell very large oil reservoir in the southern Gulf of Mexico, suggesting that abundance of fossil hydrocarbonas 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 (Grajales-Nishimura et al., 2000) 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 about 10^{16} g of known petroleum (Magoon et al., 2001). (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 at around 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 that much more 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 (ca. 10^{16} g) of the gigantic Pimienta-Tamabra petroleum system. Using these two assumed values, it is estimated that the upper limit of the global surface density (d_{As}) is 270 pg cm^{-2} compared with the surface densities of As of the decarbonated RLC (540 µg cm^{-2}), RLA (440 µg cm^{-2}) and RLW (480 µg cm^{-2}). Moreover, this estimated value is less than about four millions times than of the present-day mean oceanic value, 922 µg cm^{-2} (Quinby-Hunt and Turekian, 1983). To make matters worse, if all world crude oil (~2 × 10^{17} g) burns d_{As} would be <5.4 ng cm^{-2}.

The crude oil of the Pimienta-Tamabra petroleum system derives from the Late Jurassic source rock and its expulsion started in the Eocene (Magoon et al., 2001). The age of reservoir rocks occurs both slightly before and after that of the source beds. For certain, burning of fossil hydrocarbons of Jurassic-Cretaceous carbonaceous shales close to Chicxulub would not serve much better as the source of As in the boundary clays at the Spanish and New Zealand's sites. Indeed, total world resources of shale oil are conservatively estimated at about 10^{18} g [World Energy Council - Survey of Energy Resources 2010]. If all this oil burns it would create the global surface density of As (d_{As}) of <27 µg cm^{-2}.

Another way to estimate d_{As} for crude oil burned is by using the following formula

$$d_{As} = M_O\varepsilon_O f_{AS}/A_E$$

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: 160×10^{-6} 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 µg cm^{-2} (for $M_O \sim 10^{16}$ g, the Pimental-Tamabra petroleum system), 6.4 µg cm^{-2} (for $M_O \sim 2 \times 10^{17}$ g, all worldwide crude oil) and 32 µg cm^{-2} (for the world shale oil).

2.8. As and the coal beds in Mexico.

Let us consider a possibility that anomalous As in the boundary clays in Spain and New Zealand is derived from 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 (Matschullat, 2000, and references therein) and A_E has the same meaning and value as before. One can easily estimate that combustion of all proven coal reserves of Mexico about 10^{15}g **(ref.)** would generate the global density of As (d_{As}) <2.6 ng cm^{-2}.

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

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

where M_C and A_E have the same meanings and values as before, and ε_C (170×10^{-9} g g^{-1}: Walsch et al., 1979) is A_SEF As for coal. I estimate that d_{As} is less than 34 pg cm^{-2}. There is a further difficulty: a quick check shows no coals beds in the area close to

Chicxulub; the nearest and most important Sabinas basin is in the northern Mexico (Fig. 1) mostly of the Late Cretaceous period.

2.9. 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

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

where M_B is the amount of biomass burned, ε_B (5×10^{-6} g g^{-1}: Chilvers and Peterson, 1987) is the corresponding AsEF and A_E has the previous meaning and value. According to Kring (1999), approximately 3.5×10^{18} g to 7×10^{19} g of biomass burned in post-impact forest wildfires. Substituting these values, one can calculate that the global surface density of As (d_{As}) ranges between 3.5 µg cm^{-2} - 70 µg cm^{-2}.

There is other way to estimate d_{As} at KPB using the following formula

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

where d_B = 2 g cm^{-2} is the biomass density [estimated by Wolbach et al., (1990) 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. 1.5×10^{18} 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. (1990) have used the value $f_B = 0.2$ so I estimate that the upper limit of d_{As} is 0.6 µg 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

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

where M_B and A_E the same definition and values as those given above and ε_F is AsEF of for the forest wildfires (0.5 ×10^{-6} g g^{-1}: Walsch, et al., 1979). The calculation yields d_{As} between 0.35 µg cm^{-2} and 7 µg cm^{-2}.

In summary, it appears that the post-impact combustion of fossil fuels close to the Chicxulub impact site or the global biomass cannot be a source of anomalous As in RLC, RLA and RLW. Simple arithmetics reveals that even burning all these materials combined cannot also generated such a high As**..**

Gilmour and Anders (1989) reasoned that the ocean could be an adequate source of As as the average abundances at marine boundary sites worldwide (179 µg cm^{-2}) is ~20 % the current mean oceanic value: 922 µg cm^{-2} (Quinby-Hunt and Turekian, 1983). According to these authors, the massive amount of ejecta fallout and soot should be able to sweep out this oceanic As. By the same process, the oceanic water would be an adequate source for anomalous As in the RLC, RLA and RLW. However, a detailed consideration of such possibility is out the scope of this report.

3. Deccan

3.1. ***Geochemical studies and conclusions.***

Strong et al. (1987) and Gilmour and Anders (1989) 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 (0.006 ppb) determined by Morgan (1978) and assuming that 10^7 km^3 of magma erupted. They also adopted an emission factor of Ir of about 3 g Ir per 10^6 m^3 (or 1 ppt) for magma similar to that at Kilauea volcano (Hawai) (Olmez et al., 1986). This approach is reasonable as the Deccan volcanism shares many volcanological and geochemical features with active volcanic region of modern Hawai. Strong et al. (1987) and Gilmour and Anders (1989) concluded that the Deccan volcanism did not inject significant amounts of chalcophiles and/or Ir in the atmosphere.

Bhandari et al. (1996) 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 750 ppm As comparable with those measured in RLC (ca. 900 ppm), RLA (600 ppm) and RWB (480 ppm), Fig. 2. Bhandari et al. 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 chalcophiles if they are derived from Deccan.

Very recently, Gertsch et al (2011) investigated the biostratigraphy, carbon isotope stratigraphy, sedimentology, clay mineralogy and major and 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., 2009, and references therein).

3.2. Deccan and As.

Adopting the volume of the Deccan magma (1.2×10^6 km^3) estimated by Keller et al. (2012), I calculate that approximately 1×10^6 km^3 or 3×10^{21} g of basaltic lava (assumed density: 3 g cm^{-2}) erupted during the most active phase-2 of the Deccan eruptions. Osae et al. (2005) carried out a geochemical analyses major oxides and trace

elements, including Ir and As, of a numerous target basalt samples from the Lonar impact crater, India; this crater is excavated in the KPB basalts of Deccan. They reported that an 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 (Olmez et al., 1986). (The concentration of As in the continental crust and mantle is, respectfully, 1 ppm and 0.066 ppm, Table 1A). Based on this As concentration, one can calculate that the As content of the phase-2 magma was about 1.75×10^{15} g. The average amount of elemental As at the KPB has been estimated as 179 μg cm^{-2} (Table 1A) implying that the total amount of As at the KPB 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 (Olmez et al., 1986). Assuming that a similar fraction of gaseous As have been released from the phase-2 magma, than the total mass of As released from the phase-2 magma was about 5.25×10^{12} g. If dispersed over the entire Earth, this release of As would create a global surface density of ~1 μg cm^{-2}. This value is conservative 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 (Zoller et al., 1983, Olmez et al., 1986, Finnegan et al., 1990). 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 ng cm^{-2}.

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

$$d_{As} = M_M \varepsilon_M f_{AS} / A_E$$

where M_M (ca. 3 × 10^{21} g) is the mass of the phase-2 magma, and ε_M is AsEF for magma (~ 1.75 × 10^{-9} g g^{-1}: this work). I calculate ε_M by dividing the above estimated total As released by the phase-2 magma (~5 × 10^{12} g) with the mass of this magma. This value should be considered as an upper limit. Using this value for ε_M I estimate that the upper limit of d_{As} is 1 µg cm^{-2}.

Estimates of the current annual input of volcanic As into the atmosphere vary, ranging from 0.280 × 10^9 g per year g to 1.72 × 10^{10} g per year (Chilvers and Peterson, 1987, and references therein), although values seem to be converging on ~7 × 10^9 g per year (Mather et al., 2003) 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 (Chilvers and Peterson, 1987). To make matters worse, the Earth's volcanic emission of As into the atmosphere for the last 100 years could be roughly 10^{12} g As 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 Gilmour and Anders, 1989). As pointed out earlier, the deposition of RLC, RLA and RLW occurred for several decades up to a century at most (Premović 2009, 2011, and references therein) but the duration of the phase-2 far lasted for 10^4 – 10^5 years. Thus, the deposition time of RLC, RLW and RLA is difficult to reconcile with a relatively long duration of the phase-2. In addition, Chenet et al. (2008) 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 litostratigraphic units with a small As spike at or close the KPB instead only one but anomalous.

Finally, if we accepted that 1×10^6 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 New Zealand occurred for 100 years (Premović 2009, 2011) 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 stratosphere and dispersed over the entire Earth this would yield only about 1 - 10 ng cm^{-2}.

In summary, the estimates of the global surface densities of As and other evidence presented here clearly reveal that the Chicxulub impact or Deccan volcanism did not contribute appreciable to the high As in the boundary clays in Spain and New Zealand. In addition, simple arithmetics show that even combination of these two boundary events is also far to be adequate.

4. Conclusions.

From this study, it appears that the As anomaly in the boundary clays at Caravaca, Agost and Woodside Creek (or global at the KPB, in general) cannot be attributed to the combustion of the fossil fuels close to the Chicxulub impact site or the global biomass burned at KPB ignited by the Chicxulub impact. The evidence presented also exclude a possibility that voluminous Deccan volcanism was a source of exceptionally high As in these clays.

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FIGURE CAPTIONS

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, and the Deccan Basin.

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 Schmitz, 1988); C, D at Agost (based on data of Smit, 1990); and E, F at Woodside Creek (based on data of Schmitz, 1988). 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 % (Schmitz, 1988).