



Environmental Science

An Indian Journal

Current Research Paper

ESAJ, 9(3), 2014 [90-94]

Anomalous iridium, arsenic, zinc, antimony and soot in the ejecta layers at cretaceous-paleogene boundary: A mass of submicron fraction in the Chicxulub impact vapor plume

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ABSTRACT

The fireball plume of the Chicxulub impact event at the Cretaceous-Paleogene boundary was probably mostly composed of vaporized material emitted into the atmosphere (stratospheric level) by the impact. Most of this vapor was dispersed globally and condensates, creating a thin so-called ejecta layer. Recent thinking proposes that the impact vapor plume contained minimal amounts of submicron-size particles (dust) 10^{13} g - 10^{14} g insufficient to suppress photosynthesis. However, it seems that the global abundances of the impact-derived iridium, arsenic, zinc, antimony and soot coupled with observations do not support this interpretation.

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KEYWORDS

Cretaceous-Paleogene;
Impact;
Dust;
Iridium;
Soot.

INTRODUCTION

Alvarez et al.^[1] reported anomalous enrichments of iridium (Ir) in Cretaceous-Paleogene boundary (KPB) clays of marine provenance at Gubbio (Italy), Stevns Klint (Denmark) and Woodside Creek (New Zealand). They postulated these enrichments resulted from the impact of achondritic asteroid striking the Earth at that time (about 65 millions years ago). In their initial proposal, these authors also hypothesized that the Ir-enriched boundary clays was once a large quantity of fine dust which was globally distributed in the atmosphere following the impact. Using the Ir anomaly in these clays, Alvarez et al.^[1] evaluated that the mass of the impacting asteroid equals 3.4×10^{17} g, assuming the asteroid mass fraction injected and globally dispersed is 0.22

(Krakatau factor).

Recently, Keller et al.^[2] presented evidence for multiple impacts during K-T transition. The first impact (with no Ir anomaly) occurred at Chicxulub in the latest Maastrichtian (ca. 65.3 Ma). This impact coincided with major Deccan volcanism. According to these authors, the second impact event (with Ir anomaly) occurred at the K-T boundary (ca. 65 Ma) and the third one in the early Danian about 100 ky after the K-T boundary. Their proposal is, however, inconsistent with the currently favored interpretation which supports the genetic relationship between the Chicxulub impact and the deposition of the boundary layers of the KPB sections worldwide^[3].

It is now almost generally accepted that the Chicxulub Crater (the Yucatan Peninsula, Mexico) is

the mark of the impact^[4] and that the asteroid was a (carbonaceous) C1 chondrite-type body^[5]. Since the Alvarez et al. discovery, the KPB has been identified and studied at about 345 (mainly marine) sites worldwide distal or proximal from Chicxulub. Of these, 85 sites, representing all depositional environments, contain an Ir anomaly.

Numerous distal marine boundary clays worldwide (deposited at distances of up to several thousands kilometers from the Chicxulub impact site) are characterized by their 2 - 4 mm-thick basal layer so called the ejecta layer^[6,7]. Early studies assumed that the source of the boundary ejecta layers is created by the stratospheric submicron dust of Chicxulub impact ejecta^[1,8]. It is now generally agreed that this dust originated mainly from condensation of impact vaporized substances in the impact plume and that a contribution from pulverized target rocks to this dust was insignificant. According to Hildebrand^[9], distal KPB contains shocked minerals (mainly quartz and zircon) form around 1 % of the layer. These minerals are thought to originate from Yucatan basement rocks^[4]. Moreover, only a few quartz and zircon grains originated from the Chicxulub basement are found in the prominent distal boundary layers in Spain, Italy and Denmark^[10]. According to these authors, these grains probably arrived at these sites as the low-velocity non-ballistic ejecta. The vapor condensates were composed from the CI impactor and the target rocks (mainly derived from continental crust) and promptly dispersed after the impact over the Earth's surface^[6,11].

RESULTS

Iridium

The Ir anomaly is largely concentrated in the boundary ejecta layers^[7,12]; the mean amount of Ir deposited globally is about (40 – 55) ng cm⁻²^[13-16] or (~ 2.0 - 2.75) × 10¹¹g (using the fact that the Earth's total surface area is about 5.1 × 10¹⁸ cm⁻²). In addition, the Ir-rich global ejecta fallout is probably largely derived from the impact plume^[17]. Ir was found to be enriched in these layers by up to four orders of magnitude compared to average terrestrial crustal abundances. Numerous studies of the boundary ejecta layers worldwide rule out a

terrestrial source for this metal. In the following discussion I will suppose that Ir of these layers is derived from CI type chondrite.

Arsenic, zinc and anthimony

Apart from extraterrestrial Ir, the marine/non-marine boundary clays are enriched with the other trace elements such as typical non-meteoritic chalcophiles: arsenic (As), zinc (Zn) and Sb (anthimony)^[18]. The average abundances of As, Zn and Sb at the KPB are about 179 μg cm⁻², 994 μg cm⁻² and 11 μg cm⁻², respectfully^[18] or about 9 × 10¹⁴g As, 5 × 10¹⁵g Zn and 1 × 10¹³g Sb (the Earth's total surface area is about 5.1 × 10¹⁸ cm⁻²). The As, Zn and Sb anomaly has been attributed to various terrestrial sources (e. g. the Chicxulub impactor, volcanism, scavenging from formation waters by organic redox processes, precipitation from seawater, continental crust or mantle, global oceanic anoxia, and combustion of fossil fuels) but none of these sources is wholly satisfactory. See^[18,19] a for discussion of this subject.

Soot

Wolbach et al.^[20-22] reported the presence of elemental carbon (mainly aciniform soot) in the boundary clays from the widely separated prominent marine boundary sites. The mean global soot abundance at the KPB is estimated to be equivalent to 7 × 10¹⁶g^[22] or 0.014 mg cm⁻² ((the Earth's total surface area is about 5.1 × 10¹⁸ cm⁻²). In addition, Heynmann et al.^[23] reported the presence of fullerene (C₆₀) nanoparticles bonded to the soot at the KPB. They estimated that mean global fullerene (C₆₀) abundance at the KPB is about 7 × 10⁹g or 1.4 ng cm⁻² consistent with the burning carbon-rich materials in air. Wolbach et al.^[20-22] suggested that the soot originated from global-scale forest wildfires ignited promptly following the Chicxulub impact. It has been recently 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^[24] (and references therein). However, this possibility has been challenged by Premović^[25]. According to his calculations, it seems unlikely that fossil hydrocarbons near the Chicxulub impact site contributed significant amounts of soot in the boundary clays worldwide. Previous studies con-

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cluded that Ir, As, Sb and soot were probably associated in a single, global (submicron) component of ejecta fallout^[17,18,22]. I readily anticipate this conclusion.

DISCUSSION

Pope^[6] estimated that the total mass of vapor plume was approximately $2-4 \times 10^{18}$ g containing about $1-3 \times 10^{17}$ g of the impactor material. This impactor fraction represents 0.025 – 0.15 of the vapor plume mass and is significantly lower than estimates of 0.22 by Alvarez et al.^[1] and 0.5 by Vickery & Melosh^[26]. Pope speculates that the most of ejecta fallout worldwide is derived from vapor condensation droplets ~ 200 μ m in diameter though the ejecta layers are characterized only by a few sub-millimeter sized microkrystites^[27]. In general, most of the impact-generated large particles would have a very short residence time in the atmosphere and only the stratospheric portion of fine (submicron) dust from the impact could be deposited globally^[28]. Pope^[6] also proposes that the vapor condensates by Chicxulub produced minimal amounts of submicron-sized dust 10^{13} g - 10^{14} g. This dust would then contain between 10^{11} g - 10^{13} g of the impactor material. It means that almost whole mass of the impactor and its Ir ($\sim 2.0 - 2.75 \times 10^{11}$ g) would be associated with the coarse fraction of the impact vapor plume.

The host of the Ir in the boundary ejecta layers is still not known. Kyte et al.^[29] and Schmitz^[30] hypothesized that Ir in these layers is associated with fine (submicron) dust fraction of ejecta fallout which has since diagenetically altered to clay. For example, a smectite is predominant clay in the ejecta layer of the one most prominent boundary clay so called Fish Clay in Denmark^[31,32]. These authors suggested the Ir is present in the Fish Clay largely associated with the <0.1 μ m clay fraction of this layer and that the main carrier of Ir in the Fish Clay is of submicron size although later^[33] isolated three ~ 30 μ m Ir-bearing particles in this clay by successive splitting of the 200 μ g sample. Korchagin and Tsel'movich^[34] described a numerous metallic microparticles (about 2 μ m to 50 μ m) composed of Fe, Ni, Co and Cr of extraterrestrial origin found in the KPB clay at Højerup. The authors suggest that these microparticles are related to the asteroid fragments or micrometeorites.

To our knowledge, the red ejecta sublayer of the Fish Clay contains no altered meteoritic fragments^[35] and only up to about 6 shocked quartz grains per gram^[10]. Small goethite-rich spherules (mainly ca. 100 μ m in diameter) and large goethite-/FeS₂-rich spherules (125-800 μ m in diameter) show different stratigraphic distribution in this sublayer^[36]. Its aggregate thickness of microspherules is estimated to be 0.2 - 0.4 cm since they make up ca. 10 % of this layer^[10]. These microspherules contain no Ir. It is worth of mentioning here that the thickest known oceanic accumulation of the smectitic microspherules (ca. 100 μ m to 1000 μ m) is about 17 cm thick (Blake Nose, southern Pacific) interpreted as ejecta layer derived from the Chicxulub impact^[37]. This layer contains very low concentration of Ir, reaching a peak or maximum above it. The Blake Nose site was situated about 2000 km from the impact crater at the time of impact.

Very few large Ir-rich particles are only found in the ejecta layers of a few oceanic boundary clays. Robin et al.^[38] described several tens micron size (spinel-bearing) spherules in the boundary clays from DSDP Site 577 (Shatsky Rise, the northwest Pacific Basin); Kyte^[39] identified a few fragments of magnesioferrite spinel (presumably derived from ~ 250 μ m spherules) in the boundary clays from DSDP Site 576 (Shatsky Rise). Although these particles have Ir contents that range up to chondritic values, it appears they are not the principal carrier of Ir at these sites^[40]. Moreover, these oceanic clays have no distinctive Ir-rich ejecta layer and it is still not clear whether their spherules are the impactor ablation droplets^[40], impact melt droplets^[41], or condensates of vapor impact from the Chicxulub impact plume^[42]. Thus, it seems highly unlikely that extraterrestrial Ir was initially associated with the submillimeter portion of the impact plume. The submillimeter particles enriched with Ir probably settled out closer to the Chicxulub impact site though Schuraytz et al.^[33] detected only a few 2-3 μ m size iridium (enigmatic) nuggets from Chicxulub impact melt.

In addition to Ir, the Pope's coarse fraction of the impact plume would also contain all As ($\sim 9 \times 10^{14}$ g), Zn ($\sim 5 \times 10^{15}$ g), Sb ($\sim 1 \times 10^{13}$ g) and soot ($\sim 7 \times 10^{16}$ g). As far as we are aware, no submillimeter-size particles containing anomalous As, Zn, Sb or soot have been detected in the marine or non-marine boundary

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clays. For example, most of As, Zn and Sb (as Ir) in the prominent Fish Clay are associated with a fine smectite particles (with mass diameter $<0.1\mu\text{m}$)^[32]. In general, the boundary soot consists of submicron (0.2 – 0.5 nm) spherules of amorphous carbon linked into characteristic clusters and chains^[20-22].

Finally, the ejecta layers of numerous marine and non-marine boundary clays also show Ni and Cr anomaly. These two metals are partly chondritic in origin but their mean global abundance at the KPB is not known. However, their concentrations in the most prominent of these clays is at least $>100\text{ ppm}$ ^[18] clearly indicating that their mean global abundances must be at least as high. Following the reasoning as above, one may conclude that they must be also associated with the large (submillimeter-size) particles of the ejecta layers for which there is also no evidence whatsoever.

Previously, Toon et al.^[8,11] estimated that the Chicxulub impactor generated about $3\times 10^{17}\text{ g}$ of stratospheric submicron-size particles (dust) globally dispersed which is sufficient to shut down photosynthesis for several months 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% of this (submicron) dust, a simple calculation shows that the impact vapor plume would still contain enormous high concentrations of Ir $\sim 1.8\text{ ppm}$ (assuming its average global abundance as previously indicated) and soot $>30\%$ ^[25].

CONCLUSION

It appears that the estimates of the mass of the submicron-size dust in the Chicxulub impact vapor plume, which are currently available, are inconsistent with the global abundances of Ir, As, Zn, Sb and soot in the ejecta layers of the (distal) marine boundary clays worldwide.

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