PGE CONTENT OF IMPACT MELTS AND SULFIDES IN THE CHICXULUB CRATER; EVIDENCE FOR PGE MOBILIZATION/FRACTIONATION AND THE IMPACTOR SIGNATURE.

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Introduction: The highly siderophile/chalcophile platinum group elements (PGEs) are comprised of Ru, Rh, Pd, Os, Ir, and Pt. They are useful in tracing a variety of geological and environmental processes (e.g., [1] and references therein). This study uses PGEs to trace the heterogeneous distribution of impactor material at the Chicxulub impact crater through analysis of core matrials recovered during the 2016 International Ocean Discovery Program (IODP)/International Continental Scientific Drilling Program (ICDP) Expedition 364 [2].

The impactor that created Chicxulub collided with Earth ~65.5 million years ago and was large enough to have a global effect that caused one of the largest mass extinctions in Earth's history. The PGEs can be used to identify different types of impactors as different bollides have elevated yet variable PGE contents [3-5]. This is only possible if the PGEs remain unfractionated during the impact process and any subsequent impact melt crystallization and hydrothermal activity.

The Chicxulub basin is one of the largest and best preserved impact structures in the geologic record, and provides the opportunity to study impacts and their effects on a planetary body [6]. Previous samples recovered from Chicxulub were analyzed for PGEs, however attempts to identify the impactor were unsuccessful due to differential mobility of these elements [4,5]. The samples from Expedition 364 have provided a new opportunity to define the impactor composition.

The size of the Chicxulub crater makes the process of impactor identification difficult. A large fraction of the impactor was ejected from the crater, distributing material worldwide producing the Ir anomaly that initially triggered the search for the Chicxulub Impact Basin. [7]. This is supported by the mass extinction occurring at the same time that shows that the climatic effects of this impact were global. There is also evidence of hydrothermal systems develeloping post-impact [8] that had the fractionate the PGEs.

We analyzed several Expedition 364 lithologies to quantify PGE mobility and fractionation. The first was the transitional unit (1G) that is located stratigraphically just above the impact horizon [10]. A series of samples was analyzed that extends from the top of 1G down to the base. The second lithology analyzed is two samples of injected impact melt located below section 1G. It was considered that the PGEs could have remained unfractionated within the impact melt. The third is represented by two samples containing sulfides that are the result of secondary mineralization. These samples will give information regarding the extent at which the PGEs were fractionated as impact and post-impact processes occurred. If unfractionated, the type of impactor that created the Chicxulub impact basin could be identified.

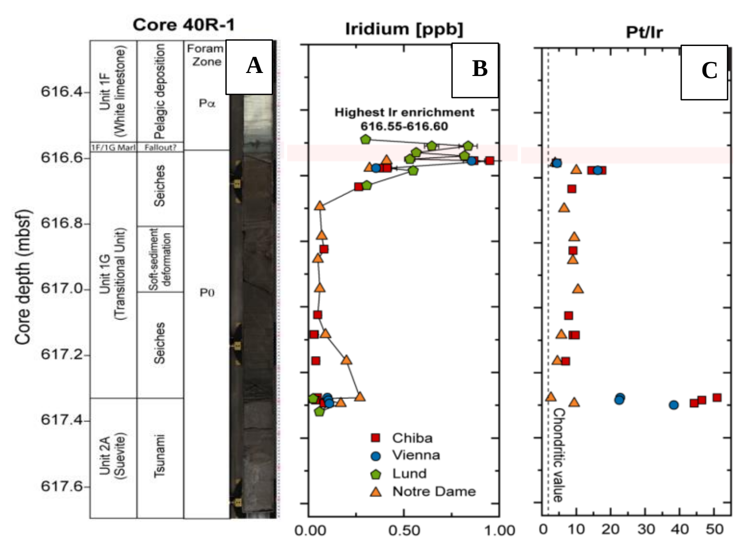

Figure 1: *Ir concentrations (B) and Pt/Ir (C) throughout the transitional unit (A). Ir shows a small anomaly at the base of the transitional unit followed by rapid sedimentation above, and culminating in a high Ir concentration signature at the top. This final signature is interpreted as the atmospheric fallout of the impactor signature when conditions calmed. Pt/Ir shows high variability at the base of the transitional unit which may be a nugget effect providing variable Pt concentrations to the samples allocated to the different labs [10].*

Samples: The transitional unit, 1G, occurs in a section of core 40 R-1 (616.58 to 617.33 mbsf) that bridges upper peak ring material below to post-impact sediments above. Sample 192-2-41.0-43.5 is a suevite breccia with dark melt hosting lithic clasts of granitoid rock, gneiss, and dolerite. Sample 265-2-42-44 is a clast poor impact melt. Sample 294-1-65-67 is an impact melt breccia with coarse clasts of granite, gneiss, and secondary sulfide phases. Samples

303-3-19.5-21 and 303-3-27-29.5 are impact melts from the base of the core with clasts of granite, gneiss, and quartzite. Sulfides (pyrite) from 40-2-105-107 and 297-1-93-95 were isolated from the matrix via hydrogen peroxide digestion. All other samples were digested using HF-HNO_3 followed by aqua regia in high pressure parr bombs. The PGEs were separated via cation exchange chromatography and analyzed using solution mode high resolution ICP-MS. All digestion and analytical procedures are described in [1].

Results and Discussion: The analyses across the impact horizon (unit 1G) of the PGEs show the environmental conditions during and subsequent to the impact event (**Fig 1**). Rapid sediment deposition was followed by atmospheric fallout of the impactor signature. Laboratories from around the world have collaborated in quantifying the PGE signature throught the transition zone [10], which has revealed the fractionated nature of these elements.

In terms of PGE ratios, the impact lithologies plot between chondrites and continental crust (**Fig 2).** The impact melt breccias show a mixing trend between chondritic ratios towards continental crust ratios (**Fig 2**). These impact produced lithologies are a mixture between the impactor and the crustal material that was mobilized during the event. It has been previously suggested that the impactor that created the Chicxulub impact basin was chondritic in nature [9]. This hypothesis is based on a 2 mm clast found in a highly altered clay clod found in the middle of the Pacific ocean [9]. These new data lend creedence to this initial hypothesis in that the PGE ratios overlap, or are quite comparable to, chondritic values (**Fig 2**).

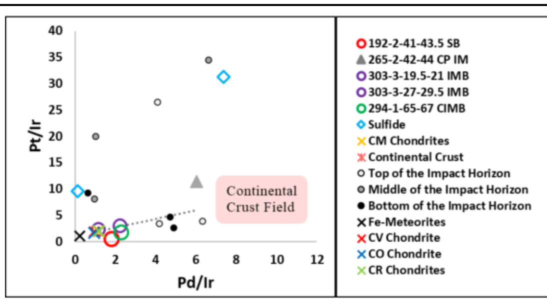

Figure 2: *Pd/Ir vs Pt/Ir. Of the two sulfide samples, the one recovered from core 40 (the transitional unit) shows the lower PGE ratios while the deeper sulfide sample has the higher ratios. The clast-free impact melt is distinct from the other impact melt breccias with a higher clast component. This may be the result of clast-melt interactions depleteding Pt and Pd relative to Ir. Average Continental crust values from [11]*

The sulfide samples are from two different depths; one is from core 40, the transitional unit, while the other is much deeper from core 297. The sulfide sample from core 40 plots above the origin but close to the y-axis, suggesting preferential removal of Pd (**Fig. 2).** The deeper sulfide sample has higher Pd/Ir and Pt/Ir values. This indicates that while Ir may still be present at the transitional unit, the other PGEs may have suffered more mobilization (and fractionation) during hydrothermal activity and be present at higher concentrations in secondary deposits. Overall, the sulfides have more fractionated PGE ratios than the the other impact melt lithologies.Some transition zone samples plot with the sulfides while others plot close to continental crust on the mixing line with chondrites (**Fig. 2**). This may be due to the mobilization of the PGEs via hydrothermal activity which was heterogeneous.

Conclusions: The delivery of PGEs by bolides can reveal the type of impactor depending on how the PGE suite was fractionated. Identifying the impactor that resulted in the 65 Ma mass extinction has been difficult. Hydrothermal circulation conditions produced secondary mineralization in the impact basin. This alone is enough to fractionate the impactor signature. However, impact lithologies injected beneath the transition zone appear to have escaped the post-impact fractionation event(s), and support previous estimates that the impactor is chondritic in composition.

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