

WHAT DO PLATINUM GROUP ELEMENTS REVEAL ABOUT THE FORMATION OF THE

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Introduction: The highly siderophile platinum group elements (PGEs) consist of Ru, Rh, Pd, Os, Ir, and Pt. They have been identified as geologically important for such mechanisms as planetary differentiation, core-mantle signatures in plume volcanism, understanding the effects of meteorite impacts, and their environmental impact from catalytic converters [1 and references therein]. For this study the PGEs and Au (due to its similar geochemical behavior) are being used for their effectiveness in understanding impact processes.

A recent drilling expedition (Expedition 364) from the International Ocean Discovery Program (IODP) retrieved cores from the Chicxulub crater [2]. Of the largest impacts recorded in Earth's geologic record, Chicxulub is the best preserved that offers the perfect setting to study impacts and their effect on a planetary body [2]. The magnitude of the impact that formed the crater was large enough to cause one of the largest mass extinctions on Earth ~65.5 million years ago. Attempts have been made in the past to identify what type of impactor created the Chicxulub crater [3,4]. This methodology has been used to identify impactor compositions that produced impact lithologies on the Moon (e.g., [5]). Impactors carry with them unique signatures that include both elevated PGEs, as well as low ¹⁸⁷Os/¹⁸⁸Os [3]. These signatures between bolides, although distinct from terrestrial signatures, are highly variable. For instance, the Ir concentration for chondrites varies from 760 ppb in CV chondrites, to 360 ppb in L chondrites, which are both above terrestrial values of low-ppb [4]. Using Ir as an indicator of bolide distribution both globally as well as at the Chicxulub crater, has drawn several conclusions. The first is that the bulk of the impactor was distributed globally making it impossible to reconstruct its pre-impact composition [3,4]. The second was the the relatively low abundances of the PGEs in the sample compendium of the time shows that they must have been redistributed to an unsampled reservoir [3,4].

The 2016 IODP drilling expedition 364 has greatly expanded the available samples for analyses. Detailed analyses of the sampled lithologies present in the Chicxulub crater will show where the PGEs have been sequestered and also where they have been mobilized. Post

impact processes such as melt migration, hydrothermal alteration & metasomatism, as well as secondary mineral formation all have the capability of either trapping or remobilizing the PGE suite [6]. Geochemically quantifying the reservoirs present will facilitate the understanding of how the PGEs are transported both during and after the impact event that formed the Chicxulub impact crater.

Samples: Two samples from Expedition 364 were analyzed via inductively coupled plasma mass spectrometry (ICP-MS). They are clustered around two distinct depths; the upper boundary definition of the shallower of the two (40R-1 34.20) is described as the "top of a prominent carbonate cemented surface", the deeper (40R-1 109.4) as the "contact between light green claystone and underlying brown siltstone" [2]. These two depths mark the top and bottom of a unit defined as 1G that is a transitional lithology between post impact sediments above, and upper peak ring material below [2]. A detailed stratigraphic description can be found in [2]. Unit 1G is believed to be the core depth that will contain the most PGEs, and may retain the highest signature of the impactor, assuming there has not been any PGE fractionation during and after deposition. Preliminary isotopic data suggests that the top of unit 1G is more enriched in PGEs than the bottom [7].

Methods: Solution mode ICP-MS was chosen for its broad elemental spectrum, and high resolution capabilities. Roughly 0.1g of each sample was digested using a combination HF-HNO₃ and a high pressure Parr Bomb with aqua regia as is outlined in [8]. The PGEs were separated from the whole rock matrix using cation exchange chromatography [8]. This was necessary due to the very low abundance of the PGEs (low-ppb), and elements present in the matrix could create polyatomic species of the same mass of the elements of interest which would artificially inflate the measured concentration. The samples were analyzed via the standard addition method as outlined in [8,9]. Three aliquots were made of each sample, one with no spike, a second spiked with all elements of interest at 1 ppb, and a third with a spike of 5 ppb. The response of each element of

interest to the spikes is directly correlated to the concentration of that element in the original unspiked sample.

Results and Discussion: This study focuses on the PGEs Ru, Rh, Pd, Ir, and Pt. We do not include Os because the volatile tetrafluoride is lost during the dissolution process. We do include monoisotopic Rh because the method uses standard addition instead of isotope dilution. The data from the intervals here are in good agreement with [7] (Fig. 1; Table 1).

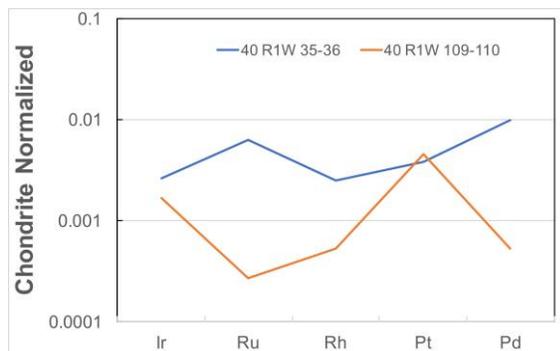


Figure 1: Chondrite-normalized PGE profiles for the base and top of the transition zone in the Chicxulub drill core.

The results presented here are consistent with [6] in that the highly siderophile PGEs appear to be more concentrated at the top of the transition layer rather than at the base. This could be that the 75 cm transition layer represents a short period of time (hours to days) and the top represents the fallout from the impact. This would be the thin Ir anomalous layer seen at the K-Pg boundary around the world.

The PGEs are, however, known to be preferentially mobile in the surface/near surface environment (e.g., [10]), as well as in reducing, sulfide hydrothermal environments (e.g., [6,11]). Future analyses on the sulfide-rich hydrothermal areas of the Chicxulub core will test the mobility of the highly siderophile PGEs in these systems.

Conclusion: The PGEs in the IODP Expedition 364 Chicxulub drill core will in all likelihood not fingerprint the nature of the impactor. This is because of the physicochemical fractionation that occurred because of the impact itself followed by both hydrothermal circulation and low temperature processes that affected the site as the energy from the impact subsided.

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Table 1: Preliminary PGE Concentrations in the Chicxulub Expedition 364 drill core K-Pg transition zone.

| PPB | Ru | Rh | Pd | Ir | Pt | Au |
|----------------|------|------|------|------|------|------|
| 40 R1W 35-36 | 4.50 | 0.32 | 5.44 | 1.19 | 3.87 | 1.23 |
| 40 R1W 109-110 | 0.19 | 0.07 | 0.29 | 0.75 | 4.53 | bdl |

Bdl = below detection limit