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# Osmium isotope constraints on the proportion of bolide component in Chicxulub impact melt rocks

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Abstract–The spatial distribution and amount of material transferred from the bolide involved in the Cretaceous/Tertiary (K/T) event to the target rocks at Chicxulub is still poorly constrained. In this study, Re-Os isotopic analyses of impact melt breccias and lithic clasts from the Yaxcopoil-1 (Yax-1) borehole were used to determine the distribution and proportion of the bolide component in the target rocks. Because of the much greater concentration of Os in chondritic meteorites compared to the target rocks, little addition of the bolide component would be necessary to greatly perturb the Os concentration and isotopic composition of target rocks. Hence, this is a very sensitive means of examining bolide contributions to the target rocks. For the examined suite of samples, the initial <sup>187</sup>Os/<sup>188</sup>Os ratios vary from 0.19 to 2.3. Conservative mixing calculations suggest that the bolide component comprised as much as approximately 0.1%, by mass, of some samples. Most samples, however, have negligible contributions from the bolide. No samples have Os that is dominated by the bolide component, so for this suite of samples, it is impossible to fingerprint the chemical nature of the bolide using relative abundances of siderophile elements. These results suggest that the bolide did not contribute a significant amount of material to the target rocks. This may, in turn, indicate that most of the bolide was vaporized upon impact or otherwise ejected without mixing with the melt from the target.

# INTRODUCTION

Large impact melt sheets within impact craters are generally homogeneous mixtures of target lithologies. However, it is not clear how homogeneously distributed traces of the projectile may be in those same melts. It is clear that a large fraction of the projectile was ejected from the Chicxulub crater because it provides the Ir signature of impact at the Cretaceous/Tertiary (K/T) boundary around the world (Alvarez et al. 1980). There have been numerous previous attempts to identify the nature of the projectile that produced the Chicxulub impact crater. Previous analyses of samples from the Chicxulub-1 borehole (Koeberl et al. 1994; Schuraytz et al. 1996) suggest that chemical traces can be found in Chicxulub melt rocks, although, other investigators have reported little or no evidence for the bolide component (e.g., Tagle et al. 2004).

Most evidence regarding the chemical nature of the bolide comes from locations far from the Chicxulub crater.

Kyte (1998) reported a fragment of rock in K/T boundary sediments that had been deposited in the Pacific Ocean. The texture and chemistry of the fragment suggested that it was an altered fragment of carbonaceous chondrite material. Kyte interpreted it to be from the Chicxulub projectile, which he noted would be consistent with computer simulations of the impact that suggested approximately 10% of the projectile may have survived as solid debris (Pierazzo et al. 1998). Shukolyukov and Lugmair (1998) analyzed the chromium isotopes of altered K/T boundary clays and reported an extraterrestrial signature with an isotopic composition similar to that of carbonaceous chondrites. Both types of existing data for distal objects suggest that the projectile had carbonaceous chondrite affinities. It is still unclear, however, whether these materials are remnants of a carbonaceous asteroid or a comet. the latter of which is believed to have rocky components that are similar to carbonaceous chondrites based on studies of interplanetary dust particles. It should be noted that these constraints on bolide composition are based on analyses of materials associated with impact ejecta deposited far from the Chicxulub crater.

Impact melts within craters also often contain traces of the asteroid or comet that produced the craters (e.g., Palme et al. 1978; Morgan et al. 1979). Consequently, impact melts like those recovered in the Yaxcopoil-1 (Yax-1) borehole may provide additional clues about the projectile's composition and the proportion of material transferred to the target rocks from the bolide. The purpose of this Os isotopic study is: 1) by comparison with previous studies, to examine the radial distribution of projectile material. The Yax-1 core represents melt ejected from the transient crater and deposited between the peak ring and final crater rim, while the Chicxulub-1 material remained in the transient crater and was incorporated into the central melt sheet; and 2) to begin to constrain the proportion of the bolide component in the target rocks as a function of position (e.g., depth) within the impact structure. Osmium, a siderophile element, is a good choice for geochemically identifying a meteoritic component because, like Ir, it was undoubtedly highly-enriched in the bolide relative to crustal target rocks (e.g., Koeberl and Shirey 1997). For example, chondrites typically contain 400-800 ppb Os, while most terrestrial crustal rocks contain <0.050 ppb Os (e.g., Morgan and Lovering 1967; Walker et al. 2002). Of

equal importance is that the Os isotopic compositions of the crustal rocks impacted by the bolide were likely very different from that of the bolide. The 187Os/188Os ratios of most primitive meteorites average about 0.13, while continental crustal rocks, although highly variable, average about 1.0 (e.g., Esser and Turekian 1993). Thus, the <sup>187</sup>Os/<sup>188</sup>Os of the Chicxulub breccias should be a very sensitive indicator of the meteoritic component. Studies of siderophile elements from other impact sites have shown that the proportion of a melt derived from the projectile can range from fractions of a percent, the norm, to a few percent (e.g., Koeberl and Anderson 1996). Koeberl et al. (1994) previously reported a  $^{187}$ Os/ $^{188}$ Os ratio of 0.113 ± 0.003 for a melt rock from the Chicxulub-1 borehole. This ratio is actually lower than any known meteorite and is difficult to interpret. Two other samples reported by that study have much higher <sup>187</sup>Os/<sup>188</sup>Os ratio of >0.2, which suggests a modest bolide contribution.

#### SAMPLES

The 0.1–0.8 g sample aliquants examined here are all from the Yax-1 borehole. Two main types of impact breccias have been studied (Table 1). The first type is a green altered impact melt rock found in the lower portion of the impact

Table 1. Rhenium-Os isotopic data for Chicxulub impact melt breccias and lithic clasts.

Sample <sup>a</sup>	Weight (g)	Re (ppb)	Os (ppb)	<sup>187</sup> Os/ <sup>188</sup> Os	<sup>187</sup> Re/ <sup>188</sup> Os	<sup>187</sup> Os/ <sup>188</sup> Os <sub>I</sub> <sup>b</sup>	$\gamma_{Os(T)}^{c}$
Lithic clasts							
Yax-1_821.76 (70, 3)	0.36	0.025	0.0153	0.6340	8.34	0.625	394
Yax-1_828.28 (58, 4)	0.58	0.020	0.0291	0.2169	3.40	0.213	69
Yax-1_829.36 (54, 3)	0.54	0.015	0.0212	0.4298	3.56	0.426	237
Brown melt clasts							
Yax-1 841.32 (65, 4)	0.40	0.149	0.0984	0.3316	7.47	0.324	156
Yax-1_841.32 (65, 5)	0.42	0.117	0.0635	2.312	11.4	2.30	1717
Yax-1_841.32 (65, 4)	0.31	0.075	0.0873	0.694	4.45	0.689	445
Green melt rocks							
Yax-1 861.4 (55, 6+3)	0.73	0.081	0.0307	0.6063	13.6	0.592	367
Yax-1_861.4 (55, 3)	0.51	0.057	0.0326	0.6022	8.93	0.592	368
Yax-1_861.4 (55, 4)	0.11	n.d. <sup>d</sup>	0.0285	0.5246	n.d.	n.d.	314 <sup>e</sup>
Yax-1_863.51 (67, 5)	0.72	0.036	0.0226	0.5932	8.11	0.584	362
Yax-1_863.51 (67, 3)	0.53	0.023	0.0112	1.062	10.7	1.05	730
Yax-1_872.4 (UNAM 2)	0.86	0.060	0.0285	0.7305	11.0	0.719	468
Yax-1_872.4 (UNAM 2")	0.77	0.141	0.1516	0.1948	4.51	0.190	50
Yax-1_876.46 (64, 3)	0.12	n.d.	0.0175	0.3289	n.d.	n.d.	160 <sup>e</sup>
Yax-1_876.46 (64, 4)	0.54	0.028	0.0181	0.5156	7.80	0.507	301
Yax-1_876.46 (64, 6)	0.60	0.038	0.0115	0.7847	17.1	0.766	505
Yax-1_880.5 (UNAM 1)	0.80	0.072	0.4445	0.2868	0.795	0.286	126
Yax-1_880.5 (UNAM 1)	0.65	0.048	0.3681	0.2369	0.634	0.236	86.6
Yax-1_880.5 (UNAM 1")	0.72	0.034	0.2606	0.2479	0.637	0.247	95

<sup>a</sup>The sample numbers refer to depth in m. Uncertainties for all but two samples are approximately  $\pm 0.5$  to 1% for isotopic composition and  $\pm 1-5\%$  and  $\pm 5-30\%$  for Os and Re concentrations, respectively. See text for details.

<sup>b</sup>Initial <sup>187</sup>Os/<sup>188</sup>Os ratios are calculated for 65 Ma using a  $\lambda$  for <sup>187</sup>Re of 1.666  $\times$  10<sup>-11</sup>a<sup>-1</sup> (Smoliar et al. 1996).

 $^{c}\gamma_{Os(T)}$  is calculated for 65 Ma as per Shirey and Walker (1998).

 $^{d}$ n.d. = not determined.

<sup>e</sup>Calculated with no age correction.

sequence (Yax-1\_861.4, 863.5, 872.4, 876.46, and 880.5). Its composition is consistent with continental margin rocks. It is generally massive with some flow structure. The compositions of these rocks are similar to those seen in melt rocks sampled by the Yucatán-6 borehole, (Kring et al. 1991; Kring and Boynton 1992). The green melt rock is dominated by microcrystalline (<50  $\mu$ m) Ca-rich pyroxene (Wo<sub>46-50</sub> En<sub>41-35</sub>Fs<sub>11-15</sub>), plagioclase (An<sub>36-58</sub>Ab<sub>60-40</sub>Or<sub>2-9</sub>), and alkali feldspar (An<sub>0-12</sub>Ab<sub>98-9</sub>Or<sub>2-90</sub>). It also contains primary apatite, primary and secondary magnetite, rutile (or secondary anatase), secondary barite, secondary calcite, and secondary phyllosilicates. Small amounts (<2%) of shocked and unshocked clasts are entrained in the melt, including quartz, feldspar, and mafic xenocrysts, and quartzite and mafic lithics.

The second type of melt sample is from a large browncolored melt clast in a polymict breccia (Yax-1\_841.32) above the green melt unit. While this sample depth may correspond to bulk breccia analyses in other studies, our particular sample was a melt clast separated from the breccia. This melt sample also has a microcrystalline texture and both shocked and unshocked clasts of target material. Even though this rock has been altered, remnant schlieren, metaquartzite, and micritic calcite have been identified. The groundmass of the sample has the same microcrystalline textures and primary minerals as the green melt, although, it was clearly transported differently and, thus, may represent a different mixture of target and bolide components.

Three lithic clasts were separated from suevite. Sample Yax-1\_821.76 is fine-grained, brownish-black diorite or basaltic andesite. Sample Yax-1\_828.28 is coarse-grained, holocrystalline, porphyritic granite. Sample 829.36 is also a granitoid clast of medium- to coarse-grained holocrystalline, equigranular granodiorite. It is significantly altered with carbonate veins, K-feldspar matrix flooding, and shreddy biotite after black biotite (Zurcher and Kring 2003).

#### ANALYTICAL METHODS

Samples were spiked for isotope dilution analysis and digested in Carius tubes in reverse aqua regia at 230 °C. Subsequent separation/purification was accomplished via solvent extraction (Os) and anion exchange chromatography (Re). Osmium analysis was accomplished via negative thermal ionization mass spectrometry using the University of Maryland Bobcat I mass spectrometer. Rhenium was analyzed using the University of Maryland Nu Plasma multicollector ICP-MS. Analysis was done using a triple electron multiplier arrangement for simultaneous measurement of masses 185, 187, and 190 (for <sup>187</sup>Os correction). Additional details regarding chemical separations and mass spectrometry can be found in Walker et al. (2002). Blanks for Re and Os averaged 13 pg and 1.0 pg, respectively. The <sup>187</sup>Os/<sup>188</sup>Os of the blank averaged 0.17. All ratio measurements were better than  $\pm 0.5\%$  (2 $\sigma$ ). Most samples have quite low concentrations, and analytical uncertainties are variable, with the greatest uncertainty resulting from high blank/sample ratios. Our initial two measurements were of sample aliquants of approximately 0.1 g (Yax-1\_861.4; Yax-1\_876.46). Due to low concentrations of Re and Os, uncertainties in Os concentration and isotopic composition are approximately  $\pm 10\%$ . Rhenium quantities were at blank levels and are not reported. More material was digested for subsequent samples and the blank/sample ratios decreased accordingly. Uncertainties for these samples are approximately  $\pm 0.5$  to 1% for isotopic composition and  $\pm 1-5\%$  and  $\pm 5-30\%$  for Os and Re concentrations, respectively.

The <sup>187</sup>Re/<sup>188</sup>Os ratios for all samples are relatively low, so corrections for 65 Ma of <sup>187</sup>Os ingrowth are minor.

### RESULTS

Rhenium and Os concentrations in the lithic clasts range 0.015–0.025 ppb and 0.015–0.029 ppb, respectively, and are generally typical of concentrations reported for rocks of the continental crust (e.g., Morgan and Lovering 1967) (Fig. 1; Table 1). The brown melt rock has significantly higher concentrations of both Re and Os. Rhenium concentrations of multiple aliquants of sample Yax-1\_841.32 range from 0.075 to 0.149 ppb. Osmium concentrations range from 0.063 to 0.098 ppb. The concentrations of Re in the green melt rocks vary significantly from 0.028 to 0.14 ppb. Osmium concentrations for 0.011 to 0.44 ppb. The calculated initial <sup>187</sup>Os/<sup>188</sup>Os ratios for 65 Ma are highly variable among the suite (Table 1). The <sup>187</sup>Os/<sup>188</sup>Os ratios for the lithic clasts range from 0.213 to 0.625 ( $\gamma_{Os}$  = +50 to +730; where  $\gamma_{Os}$  is the percent deviation of

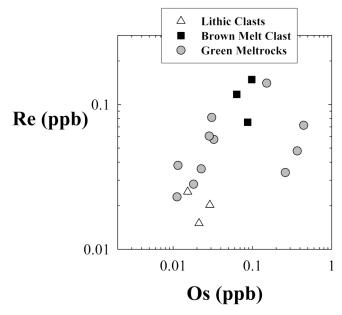


Fig. 1. Concentrations of Re and Os (in ppb) for green melt rocks, brown melt clast, and lithic clasts. Note that this is a log-log plot.

the <sup>187</sup>Os/<sup>188</sup>Os ratio from a chondritic average at the time of comparison) (Fig. 2). Ratios for the brown melt clast range from 0.32 to 2.3 ( $\gamma_{Os} = +156$  to +1720). Such variation in different aliquants of the same powder likely reflects a nugget effect whereby trace phases with high Os concentrations, but different isotopic ratios are unevenly distributed among the aliquants. Open system behavior cannot be appealed to for the variations given the youth of the rocks, coupled with relatively low Re/Os ratios for these and other Chicxulub rocks. The initial isotopic compositions of the green melt rocks are also highly variable, with ratios ranging from 0.190 to 1.05 ( $\gamma_{Os} = +50$  to +730). Two of the three samples examined by Koeberl et al. (1994) have compositions within this range.

## DISCUSSION

In order to place constraints on the proportion of bolide component contained in the rocks, mixing calculations were made. We consider mixing within the context of mixing between a chondritic component and two hypothetical crustal end member components. The crustal components were chosen such that the two mixing curves encompass a majority of the data. The mixing model parameters used for the crustal component are: 1) 0.005 ppb Os,  ${}^{187}$ Os/ ${}^{188}$ Os = 1.1 ( $\gamma_{Os}$  = +766) and 2) 0.025 ppb Os,  ${}^{187}$ Os/ ${}^{188}$ Os = 1.3 ( $\gamma_{Os}$  = +924). The parameters for the bolide are: 573 ppb Os,  $^{187}$ Os/ $^{188}$ Os = 0.126 ( $\gamma_{Os} = 0$ ). The parameter selection for crustal end member 1 reflects a concentration at the lower end of the concentration measured for rocks from the continental crust, and a <sup>187</sup>Os/<sup>188</sup>Os ratio that is equivalent to the modern seawater average (Sharma et al. 1997). This is a very conservative estimate for the crustal component given that Os concentrations for all of the rocks examined here, including the lithic clasts, are  $\geq 0.011$  ppb, and only one sample has an initial <sup>187</sup>Os/<sup>188</sup>Os ratio of >0.9. Crustal end member 2 has a higher Os concentration more typical of continental crustal rocks and <sup>187</sup>Os/<sup>188</sup>Os estimates for upper continental crust (e.g., Peucker-Ehrenbrink and Jahn 2001). The bolide parameters are consistent with the composition of the carbonaceous chondrite Allende at 65 Ma (Walker et al. 2002). Eleven of 19 samples plot within the area defined by the 2 mixing curves on a plot of  $\gamma_{Os}$  versus Os concentration (Fig. 2). Only one aliquant of the brown sample Yax-1 841.32 plots far from the outlined field.

The results of the mixing calculations suggest that the impact breccias from the sampled depths include only minor or no Os from the bolide (Fig. 2). For these mixing models, the samples with the lowest initial  $\gamma_{Os}$  values and the highest Os concentrations could have been produced by additions of only 0.01 to 0.1% of a bolide component. Such limited additions of the bolide component are also supported by the suprachondritic Re/Os ratios of all samples (Table 1).

The maximum proportion of the impactor contained in

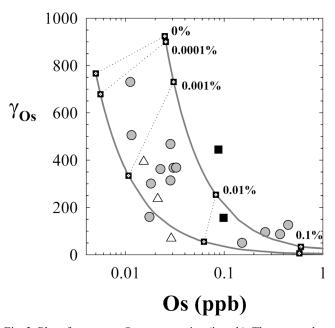


Fig. 2. Plot of  $\gamma_{Os}$  versus Os concentration (in ppb). The curves show mixing between 2 hypothetical crustal end members and bolide with a carbonaceous chondrite composition. The parameters used in the calculations for the crustal end members are: 1) 0.005 ppb Os, <sup>187</sup>Os/<sup>188</sup>Os = 1.1 ( $\gamma_{Os}$  = +766) and 2) 0.025 ppb Os, <sup>187</sup>Os/<sup>188</sup>Os = 1.3 ( $\gamma_{Os}$  = +924). The parameters for the bolide are: 573 ppb Os, <sup>187</sup>Os/<sup>188</sup>Os = 0.126 ( $\gamma_{Os}$  = 0). Mixing curves are shown in dark gray. Percentages (by mass) of the chondritic component are labeled and denoted as black boxes with white crosses. Equivalent percentages are connected for the two curves via dotted lines. Note that the concentration scale is logarithmic.

the target rocks permitted by the mixing models is  $\sim 0.1\%$ (Fig. 1). This means that the percentage of bolide-derived Os contained in this aliquant could constitute as much as 40% of the total Os. More likely, the isotopic compositions of the target rocks were substantially lower than the ratio used in the mixing calculation and the percentage of bolide material was likely <0.1% (and Os <10% bolide-derived). Variability in composition among the different samples, and even among different powder aliquants of the same sample, indicate that the bolide component may have been unevenly mixed into the target lithologies. It is important to note that none of the examined samples are dominated (>50% of the Os derived from the bolide) by a meteoritic signature. Consequently, the relative abundances of other siderophile elements cannot be used here to fingerprint the chemical characteristics of the type of bolide involved in the impact (e.g., Horan et al. 2003).

There is no decipherable correlation between Os isotopic composition and depth (Fig. 3), which suggests that on the limited scale of sampling, no evidence of a stratigraphic control on the distribution of bolide materials exists. This aspect of the distribution of bolide materials, however, will ultimately have to be examined in the context of a much broader areal and stratigraphic sampling of the Chicxulub structure.

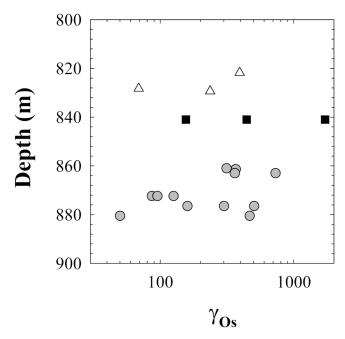


Fig. 3. Plot of  $\gamma_{Os}$  versus depth (in m). No correlation between depth and isotopic composition is noted.

The lack of a substantial bolide component in the target rocks may be reflective of a high velocity impact that resulted in either the nearly total vaporization of the bolide (e.g., O'Keefe and Ahrens 1977), or ejection of bolide solids from the impact without mixing with the melt from the target, perhaps as a result of an oblique angle of impact (e.g., Tagle et al. 2004). Either interpretation is consistent with certain other very large impact events, e.g., Sudbury, where there is little or no evidence of the incorporation of meteoritic material in associated target rocks (e.g., Morgan et al. 2001). This is in contrast to many smaller craters where there is often ample evidence of a meteoritic component, e.g., the Wanapitei Lake crater (Wolf et al. 1980). As noted by Morgan et al. (2001), however, there are exceptions where there is a strong meteoritic component in some large craters and no meteoritic signature in small craters. Issues involved in the injection of meteoritic elements into target rocks have been previously reviewed (e.g., Palme et al. 1978; Grieve 1991).

A major caveat to this Chicxulub study is that only a very narrow range of depths from a single drill core were examined. In addition, the Yax-1 borehole is located between the peak ring and final rim of the crater. This location is beyond the dimensions of the transient crater, so the melts and lithic clasts in the study were excavated and ejected from the transient crater and deposited beyond the peak ring. These melts could potentially have mixed target and bolide components differently than melt that remained within the peak ring to form the central melt sheet. Future studies may reveal more of a meteoritic signature in other parts of the Chicxulub structure.

# CONCLUSIONS

Low <sup>187</sup>Os/<sup>188</sup>Os ratios in several melt rocks from the Yax-1 borehole confirm the presence of an extraterrestrial component in Chicxulub impact melt rocks. The amount of the bolide component, however, is quite limited. Of the studied sample suite, no sample contained more than 0.1% of the bolide component, and no more than 40% of the Os contained in any sample was bolide-derived. At present, this means that the chemical nature of the bolide cannot be constrained via the relative proportions of other siderophile elements. Most samples likely contain none or significantly less of the bolide component. At least with regard to the limited sampling of the Chicxulub structure stratigraphy, the bolide was evidently heterogeneously mixed with the target rocks. The absence of significant bolide material in the target rocks may indicate that it was largely vaporized during the impact, or otherwise, ejected from the crater as a result of an oblique angle impact.

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