

Osmium Isotope Constraints on the Proportion of Bolide Component in Chicxulub
Impact Melts.

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Abstract

The Alvarez team made a rough estimate of the proportion of meteoritic material that would be distributed in the target rocks when they introduced the K/T impact theory in 1980, (Alvarez et. al, 1980). They predicted that though the bolide would have been destroyed on impact, as much as 60% of the impactor would have polluted the atmosphere. The remaining 40% of the bolide would be distributed among the target rocks. Impact craters consist of several types of impactites. These rocks will reflect not only the characteristics of the target rocks, now impact melt breccias, but also reflect the chemistry of the impactor. The amount and distribution of meteoritic material transferred to the target rocks at Chicxulub is still poorly constrained. In this study, rhenium - osmium isotopic analyses of impact melt breccias from the Yaxocopoil – 1 (YAX – 1) borehole were used to determine the distribution and proportion of the bolide component in the samples. The meteorite was assumed to have a $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.127, which reflects the average value of carbonaceous chondrites. The target rocks are assumed to have a value of ~ 1 , the value of seawater 65 at Ma. One of the objectives of this study was to determine how much of the bolide mixed with the target rocks. This was determined by mixing calculations and assumptions regarding the character of the meteorite and the target rocks. Mixing calculations on the proportions of bolide-derived Os mixed with the impact rocks suggest little meteoritic material, only 0.1%, is required to reduce the $^{187}\text{Os}/^{188}\text{Os}$ ratio to a nearly chondritic ratio and significantly change the Os concentration in the composition of the target rocks. None of the samples analyzed exceeded 0.1%. This suggests that while the meteorite did not contribute a significant amount of material to the impactites, the bolide did contribute a considerable proportion of osmium to the target rocks. Another objective was to determine where in the stratigraphy the meteoritic component was most highly concentrated in the Chicxulub structure. No correlation between osmium isotopic composition and stratigraphy or type of impact melt breccia was discovered. It is concluded that most of the samples were variably contaminated with the impactor, $^{187}\text{Os}/^{188}\text{Os}$ ratios ranging from 0.1948 to 2.312, but none have purely chondritic osmium.

Table of Contents:

I.	Abstract	Page 2
II.	Introduction	Page 4
II.	Samples	Page 9
III.	Methods	Page 9
IV.	Data Presentation and Analysis of Uncertainty	Page 10
V.	Discussion of Results	Page 10
VI.	Suggestions for Further Work	Page 14
VII.	Conclusions	Page 15
VIII.	Bibliography	Page 17
IX.	Appendix	Page 19

List of Figures and Tables:**Figures:**

1.	Schematic diagram of impactites within a simple crater.	Page 4
2.	Paleogeography of the late Cretaceous.	Page 5
3.	Schematic diagram of the Chicxulub structure.	Page 6
4.	Osmium and strontium ratios in seawater.	Page 7
5.		
6.	Schematic diagram of a magnetic sector mass spectrometer.	Page 9
7.	Mixing curve of the proportion of meteoritic material in impactites.	Page 12
8.	Meteoritic component as a function of type of impactite.	Page 13
9.	Depth and meteoritic signature.	Page 18

Tables:

1.	Re – Os data for Chicxulub melt rocks from Koeberl et. al, 1994.	Page 7
2.	Uncertainty in type of analysis.	Page 10
2.	Re – Os data (this study).	Page 11

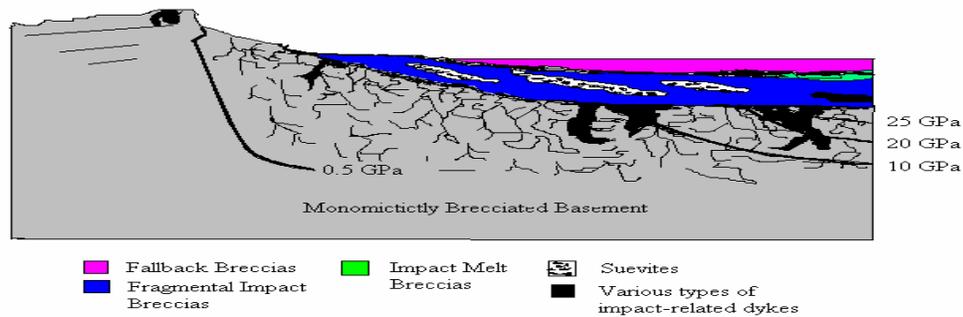


Figure 1: Schematic diagram of a simple crater, (after Koeberl and Anderson, 1996). Shows the different types of impactites and their occurrences.

Introduction:

It has been proposed that the spike in iridium concentration in the clay layer that marks the Cretaceous-Tertiary boundary was caused by a meteorite impact at 65Ma and, consequently, may have caused the mass extinction that occurred concurrently, (Alvarez et. al, 1980). While the cause of the extinctions is still being debated, the theory of a meteoritic impact to explain the iridium anomaly has become well accepted following the discovery of an impact crater of the right size and age to be the impact target.

As part of the theory, Alvarez et. al suggested that approximately 60% of the mass of the bolide would have been injected into the atmosphere. Consequently, 40% of the bolide would have contaminated the crustal rocks it impacted, contaminating them with the composition of the meteorite. Two elements that generally have a high abundance in meteorites relative to crustal rocks are osmium and iridium. Osmium and iridium are both siderophile elements (iron-loving) that are depleted in the Earth's crust. In meteorites, however, Os and Ir have both very high concentrations and Os has a low isotopic ratio. The Chicxulub impact breccias may reflect the enrichment of these elements despite being crustal rocks. Because the difference in Os isotopic ratios is significantly different between crustal rocks and meteorites, the purpose of this experiment is to determine the relative enrichment or depletion of ^{187}Os in the samples of crater ejecta.

The evidence of an impact is overwhelming, but studies examining the meteorite impact site have been limited. For example, it remains unknown how much matter from the impactor was transferred to the impacted rocks. Since the likely bolide was probably destroyed on impact, there are no known direct fragments of the meteorite. This study searched for the bolide component in the target rocks, now largely impact breccias, see Figure 1. There were two main objectives in this study: (1) constrain the proportion of the meteoritic Os isotopic signature present in various types of impactites, and (2) assess any correlation of the depth vs. meteoritic component.

Mixing will most certainly be noted in the chemistry of the rocks. The crustal material that is impacted is ejected out of the crater, mixed with airborne meteoritic material and melted due to the intense energy of the impact before being lithified as an impactite. It is unlikely that pure end-members of either meteoritic material or continental crust will be found as it is suspected that all of the impact breccias will be variably contaminated with the bolide. The energy of the impact will force the large volume of both the disintegrated meteorite and crustal ejecta to mix heterogeneously. The degree of mixing was determined and the probability of the mixing of the

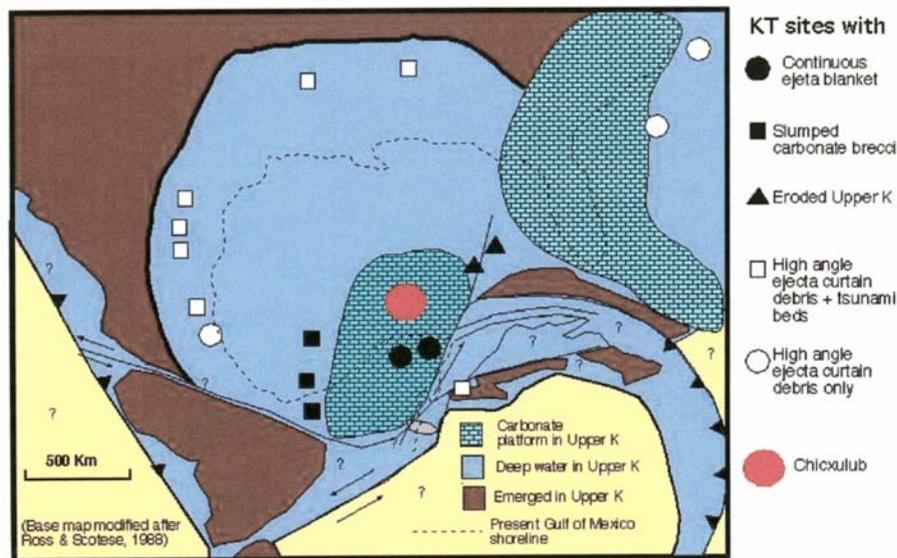
measured Os isotopic ratio being more chondritic or crustal is the determining factor of the conclusion. The hypothesis that was tested is as follows: The Os isotopic ratio, $^{187}\text{Os}/^{188}\text{Os}$, of the impact breccia will be dominated by a meteoritic component. In this study we determined the initial osmium isotopic ratios ($^{187}\text{Os}/^{188}\text{Os}$) (the concentrations of Os and Re) and corresponding γ_{Os} values for the samples. γ_{Os} is large in crustal rocks relative to meteorites.

Background:

The iridium spike that marks the Cretaceous/Tertiary boundary has been identified in over 100 locations around the globe. It is missing elsewhere in the rock record, (Kyte and Wasson, 1986). Ultimately this led workers to discover the crater that had been buried under a kilometer of Tertiary sediments. In 1991, Hildebrand and coworkers (Hildebrand, 1991) identified a suitable crater, having the right age, size, and crustal material, to have been the site of the impactor that could have caused the K/T mass extinction. This structure is located off the Yucatan Peninsula of Mexico, see Figure 2.

Geophysical data indicate that the meteorite produced an ~200 kilometer diameter multi-ring crater (Hildebrand et al., 1991; Sharpton et al., 1996; Penfield and Camargo, 1981) when it dropped onto the continental shelf off the coast of the Yucatan Peninsula. Magnetic and gravity field data suggest a deeply buried circular structure of approximately 65 my age lies on a carbonate platform of the Yucatan. It has been proposed that the bolide hit the platform with a northwest trajectory at an angle of 30 degrees from the horizon, (Powell, 1998 and ref. therein).

Lunar studies have shown that as the size of an impactor increases, the resulting crater morphology tends to change. Multi-ring craters are a result of extremely large meteorites hitting the Earth. The diameter of the crater tends to be influenced by the surface gravity and the target rock composition, (Koeberl and Anderson, 1996). Large meteorites, such as the Chicxulub bolide, produce complex structures with unstable cavity floors causing central uplifts to form. In simple craters produced by smaller meteoritic impacts (e.g. Meteor Crater) produce a cavity where excavated material once was. In larger craters, a central uplift is formed due to the intense energy of the impact. One possible interpretation of the crater structure underlying Chicxulub is shown in Figure 3, (Sharpton et al., 1996). The diameter of the crater is generally assumed to be ~ 200 km. The meteorite excavated approximately 1/3 the volume of the transient crater. The remaining 2/3 of the brecciated target rocks likely mixed with approximately 40% of the meteorite, forming impact melts and various types of breccias.



Late Cretaceous Gulf of Mexico Paleogeography and ejecta distribution

Figure 2: This is a close-up view of the ancient Gulf of Mexico. It describes how the meteorite impacted a shallow marine setting that might have given rise to tsunamis and might have degassed the carbonates it hit. (Kring, 2000)

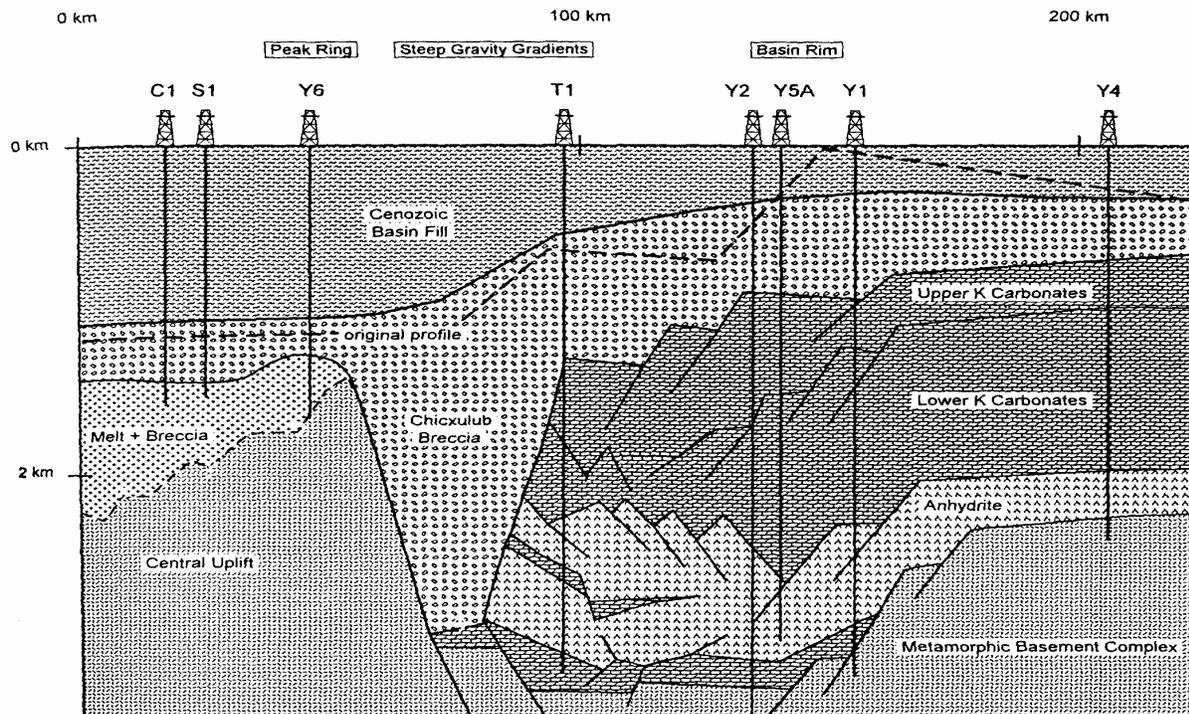


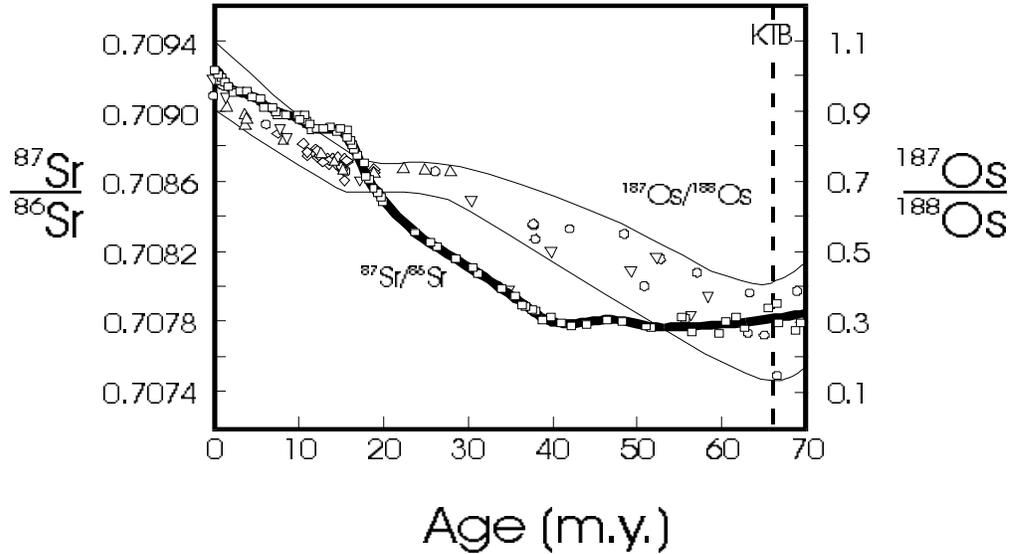
Figure 3: Schematic diagram of the impact crater. It shows the impact rocks, the well sites (note the samples in this study come from Y1). This diagram also demonstrates the differences that are still debated about the impact crater in that this gives a radius of approximately 200 km instead of a diameter of ~200 km. (Sharpton et al., 1996)

The Chicxulub crater has been eroded and its shape is truncated on the northwest end. The structure may be truncated because of tectonic deformation and the rapid influx of seawater following the impact. These waters would have greatly disturbed the original structure causing even more mixing of the meteoritic material and target rocks than a structure that formed on a continent, (Hildebrand et. al, 1991).

A recent study (Shukolyukov and Lugmair, 1998) tried to determine the type of bolide that impacted at the time of the deposition of the K/T boundary. This study used the $^{53}\text{Mn} - ^{53}\text{Cr}$ system, asserting that due to the very short life of ^{53}Mn having completely decayed to ^{53}Cr the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio is distinctive between the different types of meteorites and therefore able to determine the impactor of the Chicxulub event. The authors compared the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio of K/T samples and samples from the Deccan Traps to the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio of various meteorites. They concluded that the most likely impactor was a carbonaceous chondrite. This method was not able to determine whether the impactor was a comet or asteroid since both can be composed of carbonaceous material.

The $^{187}\text{Re}-^{187}\text{Os}$ system has been established as a reliable system for determining if a sample has a meteoritic component, (Koeberl et. al, 1994). This system can be used to distinguish between a carbonaceous chondrite and an ordinary and enstatite chondrites. Carbonaceous chondrites have a $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.1262 ± 0.0006 . Ordinary and enstatite chondrites have isotopic ratios of 0.1283 ± 0.0017 and 0.1281 ± 0.0004 , respectively. While this system cannot distinguish between a chondritic and a mantle source for any samples, can be used to distinguish between a meteoritic source and continental crust. The $^{187}\text{Os}/^{188}\text{Os}$ ratio of modern continental crust is approximately 1.26, (Esser and Turekian, 1993).

Figure 4: Osmium isotopic anomaly at the K/T boundary. Courtesy of D. McDaniel. (Richter et al., 1992, Ravizza, 1993, Pegram et al., 1992, Peucker-Ehrenbrink et al., 1995, and Reush et al., 1998)



It is important to understand that Os isotopic ratios in seawater have changed through time. Figure 4 identifies a negative Os isotopic anomaly at the K/T boundary. Another source of Os in seawater is mid-ocean ridge basalts that succumb to alteration and typically have more chondritic $^{187}\text{Os}/^{188}\text{Os}$, which has been defined as 0.127, (Meisel et al., 1995). Additional sources of Os in seawater are chemical weathering of continental crust and continental/oceanic ultramafic rocks which bring the Os isotopic ratio closer to the modern ratio of 1.04 ± 0.04 (Sharma, 1997). Thus, the impact at the K/T boundary evidently contributed a significant amount of Os and drastically reduced the isotopic ratios of Os in seawater.

A previous attempt has used the Re-Os system to determine if there is a meteoritic component in sample from the K/T boundary as well as samples from the drill core. That study analyzed samples from the C1 borehole and an impact glass from the K/T boundary at Beloc, Haiti, (Koeberl et al, 1994). The samples showed varying $^{187}\text{Os}/^{188}\text{Os}$ ratios, see Table 1, data from Koeberl et al, 1994. C1-N10-1A shows an isotopic ratio that is less than the average value of carbonaceous chondrites, (Walker et al, 2002). C1-N10-2 shows an isotopic ratio of 0.505 ± 15 , which could be due to the mixing that would naturally occur between a relatively small amount of impactor mixing with a large amount of target rocks. The Beloc impact glass also showed an intermediate $^{187}\text{Os}/^{188}\text{Os}$ ratio. Since old crustal rocks tend to have isotopic ratios approaching 1, and there are no known rocks of mantle origin in the vicinity of the crater, they concluded that there was a meteoritic component in the samples.

Table 1: Re-Os data for Chicxulub melt rocks from Koeberl et. al, 1994. High Os concentrations and low Os isotopic ratios indicate that a meteoritic component in the samples analyzed. In C1 chondrites Os = $0.5 \mu\text{g/g}$ and a $^{187}\text{Os}/^{188}\text{Os} = 0.127$. The high abundance of Os in C1-N10-1A is suspected to be due to the higher Ir concentration found in the sample, 6.0 ± 0.7 ppb.

Sample	Re, ppb	^{188}Os , 10^{-15} moles/g	Os, ppb	^{187}Os , %	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Re}/^{186}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}$	$^{187}\text{Os}/^{186}\text{Os}$
C1-N10-1A	1.599	17600	25.2	1.5	0.305 ± 6	2.54	0.113 ± 3	0.941
C1-N10-2	0.952	36.5	0.056	6.3	87.7 ± 1.8	729.1	0.505 ± 15	4.200
Impact Glass Beloc	0.107	65.2	0.095	3.3	5.50 ± 0.16	45.75	0.251 ± 7	2.089

The composition of the abundant K/T tektite spherules found around the world implies that the source rock was dolomitic in nature. Recent drilling of the crater indicates that the target rocks were composed of limestone, dolomite, and anhydrite rocks. With depth in the drill cores the chemistry of the ejecta becomes increasingly more silica rich. This is because the basement rocks are sandstone, which overlies shale, and some crystalline rocks. The

composition of these rocks can be associated with the unique character of the tektites found in Haiti. These spherules are rich in carbonates and typically reveal a feathery calcite texture.

Samples:

Recent drilling has produced the samples of impact melt breccias examined here. Most samples examined here are from the Yaxocopoil-1 borehole (YAX-1), (Kring et. al, 1993, 2003). Two main types of impact breccias have been studied. The first type is a green altered impact meltrock found in the lower portion of the impact sequence. The texture of the rock is microcrystalline and is composed of pyroxene, plagioclase, and alkali feldspars. Its composition is consistent with continental margin rocks. It is generally massive with some flow structure. The rock was brecciated and altered after solidification and contains small amounts of both shocked and unshocked clasts of the impacted lithologies. These lithologies include lithic quartzite, and isolated feldspar crystals. The compositions of these rocks are similar to those seen in meltrocks sampled by the Yucatan-6 borehole, (Kring et. al., 1991; Kring and Boynton, 1992). Our study includes samples YAX-1_861.4, YAX-1_863.51, and YAX-1_876.46, which represent both the top and lower portion of the green impact meltrock. The middle sample in the sequence has the least amount of mineralogical alteration, (Zurcher et. al, 2003).

The second type of melt breccia studied is a brown altered impact meltrock. It also has a microcrystalline texture and both shocked and unshocked clasts of the target material, (Kring et. al, 1991; Kring and Boynton, 1992). Even though this rock type has been altered, remnant schreibersite, metaquartzite, and micritic calcite have been identified. Sample YAX-1_841.32 is representative of this type of rock. It was recovered from a polymict breccia in the middle of the impact sequence.

Three samples of xenoliths have also been included in the analysis. Sample YAX-1 821.76 is a mafic clast containing very fine-grained diorite or basaltic andesite. It contains a minor amount of alteration (~5%) of the chlorite after mafic sites, (Zurcher, 2003). Sample YAX-1 828.28 is a 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, 2003). It should be noted that the numbers following the samples correspond to the depths of the samples in meters.

Additional samples have been obtained from the Universidad Nacional Autonoma de Mexico (UNAM). These samples contain some of the highest recorded iridium concentrations as analyzed by UNAM. They also are green monomictic melt breccias (described previously) and come from the YAX-1 borehole. They are identified as 872.4 and 880.5. Most interestingly, they are suspected to have clasts of the meteorite itself. These small meteoritic clasts are greenish black and compose ~ 15% of the samples.

Methods:

Osmium can attain an oxidation state of +8, the highest of any element observed. Osmium in this state is highly volatile so special precautions must be taken to perform parts of the experiment. Os isotopic ratios are particularly useful in cosmochemistry as they can be precisely analyzed with uncertainties of $\pm 1\%$ or better using negative thermal ion mass spectrometry (NTIMS). This type of mass spectrometry is very sensitive to low concentrations of Os.

The samples were powdered for bulk analysis before being weighed. ^{190}Os and ^{185}Re were utilized for isotope dilution analysis, thereby enriching the sample in these isotopes. This process allows back extraction of the isotopic composition and concentration of the sample by measuring the difference in isotopic composition between that of natural Re or Os and the spike. The crushed impactites and spikes were added to carius tubes and digested via

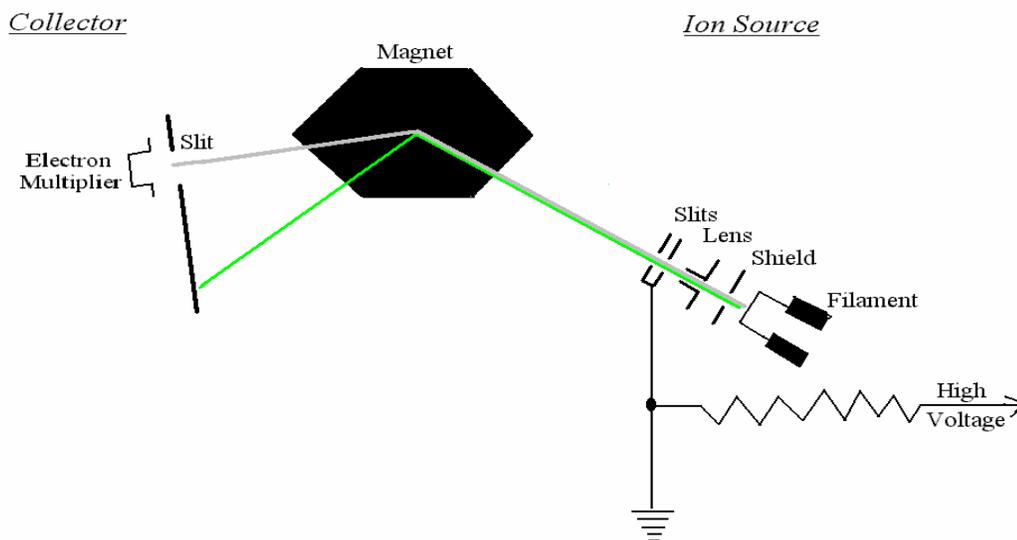


Figure 6: Schematic diagram of a magnetic sector mass spectrometer. Green line represents the light isotopes of an element. Gray line represents the heavy isotopes of an element.

(Walker, 2002)

reverse *aqua regia* at 230°C. Reverse *aqua regia* consists of adding 4 mL of concentrated HCl (aq) and 6 mL of concentrated HNO₃ (aq) to the samples. The Os will enter into the volatile +8 valence during this process so the containers must be placed in a dry ice slush before being sealed and placed into the oven.

After breaking the seal on the tube, the samples were ready for osmium separation. The digested samples were added to liquid CCl₄. Separation of Os from the solution was accomplished by extraction of the CCl₄ under the meniscus following centrifuging for a few minutes. The extracted solution (CCl₄ plus osmium) was then put into concentrated HBr and placed on a hot plate for a couple hours to reduce the Os and drive the Os into the HBr. After cooling, the Os + HBr (a reddish orange solution) was separated from the CCl₄. The HBr was evaporated under a heat lamp, leaving Os in the form of a bromide salt. Osmium was purified further via a mini-distillation process. The Os was then ready for analysis on the mass spectrometer.

Rhenium separation was accomplished by using anion exchange chromatography. A resin (AG-1 X8 estimated, but the similarity in isotopic systematics between the closely spaced YAX-1 861.4 m and 863.51 m samples (combined they define a 65 Ma isochron) suggests minimal open-system behavior. 100-200 mesh anion resin) was put into columns and cleaned by adding successive amounts of stronger and purer HNO₃ (aq). The samples were then added and eluted with HCl (aq) and collected with more HNO₃ (aq). The Re was then cleaned and collected a second time to ensure purification. For more detailed descriptions of all methods and procedures please see the appendix.

The Bobcat, the main instrument used in this experiment, is a type of magnetic-sector mass spectrometer. It was used because of its ability to precisely measure Os isotopic ratios. The process that it uses is as follows, see also Figure: (1) the filament ionizes the sample, (2) the ions are then focused by steering slits and accelerated by high voltage, (3) a magnet is used to separate the beams of ions according to their mass, (4) an electron multiplier is then used to measure the beam of ions selected by the magnet. The intensities of different beams are compared and used to determine the Re/Os isotopic ratios.

The ICP-MS, an inductively coupled plasma mass spectrometer, was used to determine the Re isotopic ratios. The ICP-MS works as follows. (1) A plasma is formed from an inert gas, such as argon. (2) The sample is aspirated into the torch assembly, which has a temperature of about 10,000°C. (3) There it is atomized and ionized. (4) Then, the isotopic ratios are measured using dual electron multiplier and normalized to a Re standard.

The calculation of the mixing curve in Figure 7 was done as follows: (1) the atomic weight of the Os for both the crustal end-member (100% crust) and the meteoritic end-member (100% bolide) was calculated by adding the sum of each isotope multiplied by the percentage of that isotope. (2) The $^{187}\text{Os}/^{188}\text{Os}$ is calculated from the following equation where the “Sum A and Sum B” are the respective end-member isotopic ratios added to 7.4066. (A = crustal component, B = bolide component, Os A = the concentration of Os in component A, Os B is the concentration of Os in component B, OsICA = the isotopic composition of component A, OsICB = the isotopic composition of component B):

$$^{187}\text{Os}/^{188}\text{Os} = \frac{((0.01)(\%A)(\text{Os A})(\text{OsICA/ Atomic Wt. A})) + ((0.01)(\%B)(\text{Os B})(\text{OsICB/ Atomic Wt. B}))}{((0.01)(\%A)(\text{Os A})(1/ \text{Sum A})/(\text{Atomic Wt A})) + ((0.01)(\%B)(\text{Os B})(1/ \text{Sum B})/ \text{Atomic Wt. B})}$$

(3) This procedure was calculated for various values of $^{187}\text{Os}/^{188}\text{Os}$ from 0 to 100% with 99.9% to 100% crustal composition being calculated in 0.01 increments. (4) γOs was calculated from: $((^{187}\text{Os}/^{188}\text{Os} / 0.127) - 1)100$ (5) Os ppb was calculated: $(0.01)(\%A)(\text{Os A}) + (0.01)(\%B)(\text{Os B})$. (5) Re was calculated similarly to (4) by substituting the selected Re components for A and B. These calculations produced a spread of $^{187}\text{Os}/^{188}\text{Os}$ values for 99.9% crust to 100% crust that was used to plot the mixing curve.

Data and Analysis of Uncertainty:

The spike solutions and samples were both weighed to 5 significant figures. The uncertainty in the measurement is in the fifth digit of about ± 0.00003 or ± 0.00005 g. The mass spectrometric uncertainties, however, are normally in the 4th significant digit. This means that the uncertainty in the mass of the sample or spike is relatively unimportant. The sensitivity of this type of mass spectrometry allows both the isotopic ratio and concentration uncertainties to be measured at $\pm 0.5\%$ to 1%. Table 2 shows the reliability of this type of analysis. The standards ran with less than 0.3% uncertainty for the $^{187}\text{Os}/^{188}\text{Os}$ ratios.

Table 2: Reliability of data. 3 standards were run producing data with uncertainties of (2σ) less than 0.3% for $^{187}\text{Os}/^{188}\text{Os}$ ratios.

Standard	Os 7/8	SDM 2-SI	Os 0/8	SDM 2-SI	Os 2/8	SDM 2-SI
1	0.11368	0.000354	1.99215	0.006907	3.07364	0.01281
2	0.11374	0.000277	1.98317	0.001306	3.06983	0.002909
3	0.11330	0.000124	1.98352	0.000882	3.07951	0.001556

Discussion of Results:

The results suggest that the impact breccias from the depths sampled include only moderate to minor Os from the bolide, see Table 3. No samples examined exhibit a pure meteoritic signature. This is consistent with both the low abundances of Os in the rocks, the suprachondritic Re/Os ratios, and the suprachondritic initial $^{187}\text{Os}/^{188}\text{Os}$ ratios.

The maximum proportion of the impactor is estimated at $\sim 0.1\%$, see Figure 7. The mixing model used a $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.9 for the target rocks, similar to the isotopic composition of modern seawater, (Sharma et. al, 1997). 0.9 is used instead of 1.0 ($^{187}\text{Os}/^{188}\text{Os}$ for modern seawater) because it is the best fit for the data. The pure chondritic end-member used the average value 0.127, (Walker et. al, 2002). For reference to the isotopic ratios of Os 65 Ma, refer back to Figure 5. The bolide component in the target rocks could constitute as much as 40% of the Os in the meltrocks, but less than 1% of the total mass of the rock. More likely the isotopic compositions of the target rocks were substantially lower and the percentage of bolide Os is likely $<10\%$. The lower initial ratio of the suevites

and higher Os concentration may suggest either a higher percentage of the bolide component, or a substantially different mix of target lithologies. Effects of subsequent alteration cannot yet be estimated, but the similarity in isotopic systematics between the closely spaced YAX-1 861.4 m and 863.51 m samples (combined they define a 65 Ma isochron) suggests minimal open-system behavior.

In Figure 7, 0% corresponds to 100% continental crust and similarly 0.1% corresponds to 99.9% crustal material. As the concentration of the meteorite in the target rocks increases to 0.1%, the concentration of the Os in the crustal rocks will exponentially increase toward the chondritic end-member, $\sim 0 \gamma$ and > 500 ppb Os. This implies that very little meteoritic material added to the crustal impact rocks is required to drive the Os concentration of the crustal rocks towards the Os concentration for carbonaceous chondrites. Also, $\sim 0.1\%$ of the impactites were originally of meteoritic composition though the meteorite contributed significantly more Os, $\sim 10\%$, to the bulk composition of the impactites.

Table 3: Re-Os isotopic data for Chicxulub Impact Melt Breccias. All samples should be assumed to come from the YAX-1 drill hole except for the sample Sudbury. Uncertainties (2σ) are $< \pm 0.5\%$. The sample numbers are in meters. For instance, the first sample has a depth of 821.76 meters. Within the YAX – 1 samples 841.32 refers to suevites and greater than 841.32 refers to green monomictic impact melt breccias. The * refers to data from the first data set that contains an error due to the small amount of sample and the large blank to spike ratio. The uncertainty in the * values is ± 5 to 10%. Initial $^{187}\text{Os}/^{188}\text{Os}$ ratios are calculated for 65 Ma using a λ for ^{187}Re of $1.666 \times 10^{-11} \text{a}^{-1}$, (Smoliar et. al, 1996). $\gamma_{\text{Os(T)}}$ is calculated as per Shirey and Walker, 1998.

Sample	Weight (g)	Re (ppb)	Os (ppb)	$^{187}\text{Os}/^{188}\text{Os}$	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}_{65}$	γ_{Os}
<i>Xenoliths</i>							
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)	0.543	0.015	0.0212	0.4298	3.56	0.426	237
<i>Suevite</i>							
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
<i>Meltrocks</i>							
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	8.930	0.592	368
YAX-1_861.4 (55,4)	0.11	nd	0.0285	0.5246	nd	nd	314*
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	10.73	1.05	730
YAX-1_872.4 (UNAM 1)	0.80	0.072	0.4445	0.2868	0.795	0.286	126
YAX-1_872.4 (UNAM 1)	0.65	0.048	0.3681	0.2369	0.634	0.236	86.6
YAX-1_872.4 (UNAM 1")	0.72	0.034	0.2606	0.2479	0.637	0.247	95
YAX-1_876.46 (64,3)	0.12	nd	0.0175	0.3289	nd	nd	160*
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 2)	0.86	0.060	0.0285	0.7305	11.0	0.719	468
YAX-1_880.5 (UNAM 2")	0.77	0.141	0.1516	0.1948	4.51	0.190	50

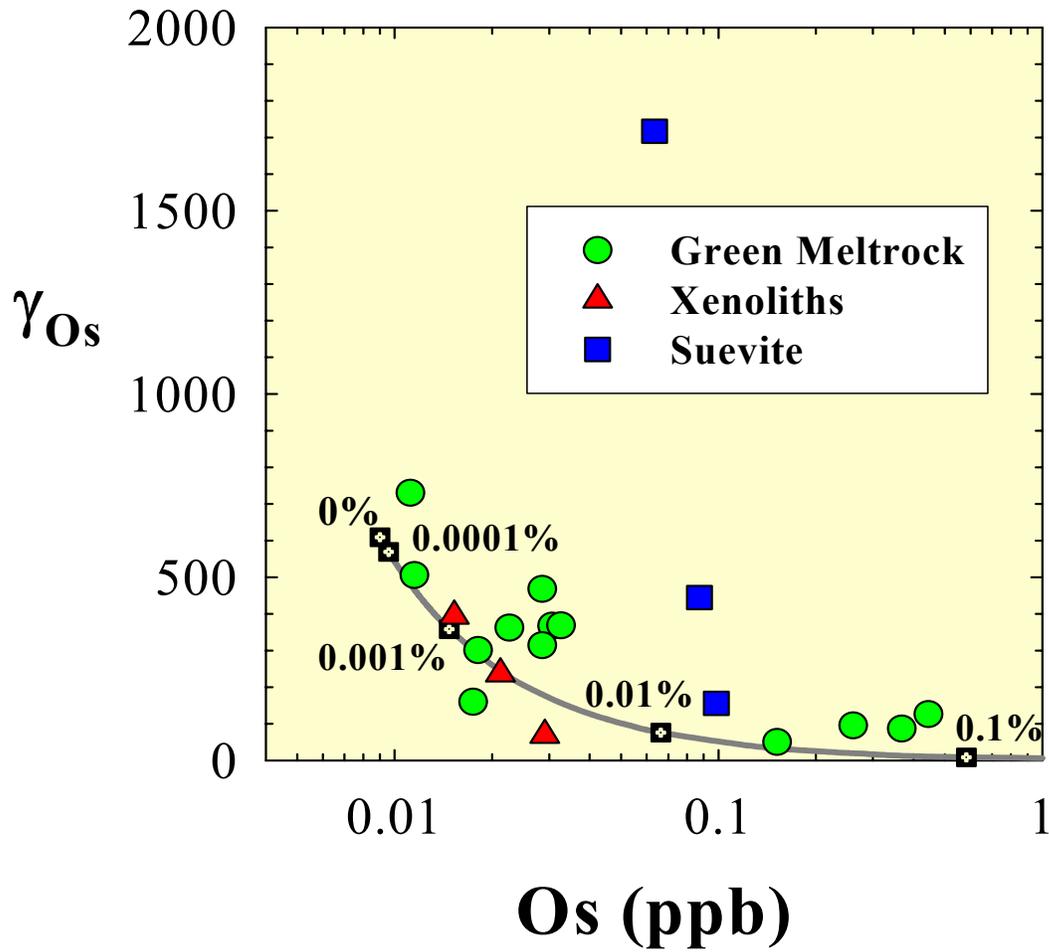


Figure 7: Only minor amounts of meteoritic contamination are required to significantly alter the Os concentration and IC of the target rocks.

The endmembers used in the mixing model are:

Crust: 0.9 ppb Os, $^{187}\text{Os}/^{188}\text{Os} = 0.9$;
 Carbonaceous Chondrite: 573 ppb Os, $^{187}\text{Os}/^{188}\text{Os} = 0.127$.

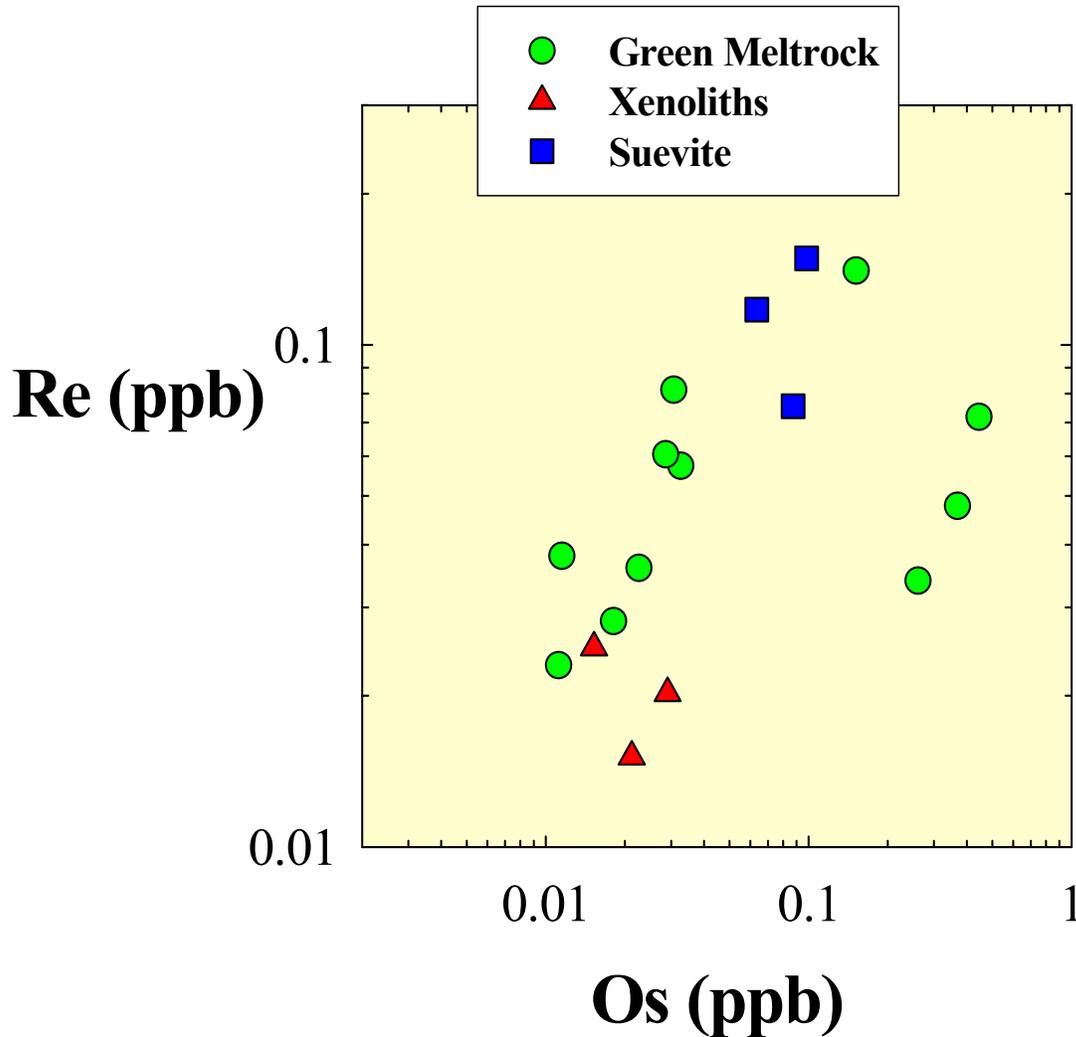


Figure 8: Meteoritic component as a function of the type of impactite. The suevites had the most significant meteoritic contamination followed by xenoliths. The green meltrocks had the most variability. These concentrations suggest that while all of the samples contain a meteoritic component, they were all variably contaminated.

Each type of impactite will reflect the original pre-impact lithics. In Figure 8, it is apparent that there is little correlation between the type of melt breccia and the bolide contamination. All of the samples were variably contaminated, with the green meltrocks showing the most variability. The suevites show the most significant correlation in that they appear to be the most contaminated, followed by the xenoliths. It is also apparent that none of the samples have purely chondritic osmium.

There is also no correlation of a meteoritic signature with depth. Figure 9 is a diagram of the ballistic trajectories of the high-energy ejecta carried into the atmosphere following impact. If each trajectory is considered to be a particle, a significant amount of mixing is occurring before deposition. Even though in the diagram, the Chicxulub structure is represented as a very small dot at the intersection of the trajectories, a more local model can be imagined from this diagram. In this model, a significant amount of mixing of the bolide with the target rocks occurred before deposition. Since there is no correlation of a meteoritic component with depth, the mixing of the bolide and the target rocks would have been heterogeneous.

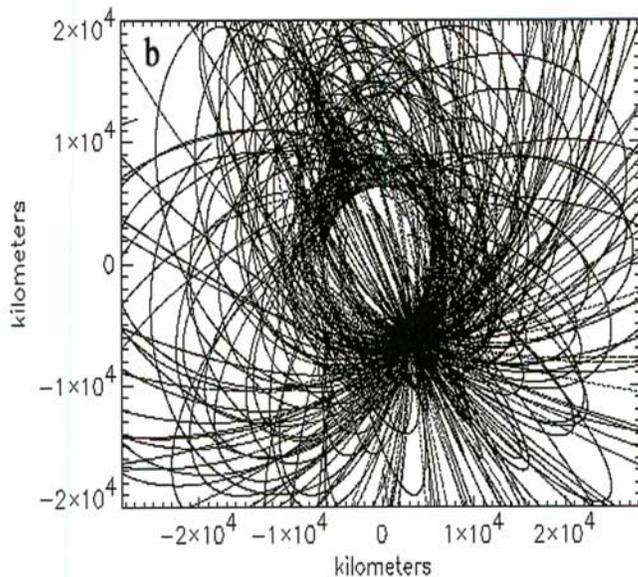


Figure 9: Ballistic trajectories of high-energy ejecta from a model of the Chicxulub event, (Kring and Durda, 2002). The amount of mixing of the bolide with the target rocks that would have occurred would be significant on the local scale. The energy of the particles would cause the disintegrated meteorite's composition to heterogeneously contaminate the ejecta. For scale, the Earth and the impact structure would be a dot at the intersections of the trajectories.

There is a considerable spread of data when considering the depth versus meteoritic component in Figure 10. The UNAM samples that came from the Yax-1 borehole and were recently identified as green monomictic impact melt breccias, generally have the most significant meteoritic component within them. However, these samples, which are purported to have meteoritic clasts within them, mostly have a substantially lower Os isotopic ratio than the other types of samples. The ratios are still suprachondritic, suggesting that the proportion of the bolide within them may be higher than the other samples analyzed.

Suggestions for Further Work:

It would be appropriate to continue analyzing Re-Os data from other boreholes in order to determine if there is a correlation between the meteoritic component and the distance from the center or central uplift of the structure. Data from this borehole revealed no correlation between a meteoritic signature and depth or type of impactite. In order to test the conclusion of this analysis, that the meteoritic component is heterogeneous, further analysis should be done.

Other suggestions would include using this type of analysis on other impact structures, especially continental impact structures. This would determine whether the heterogeneous mixing of the bolide with the target rocks was a function of the mixing effects of the rushing seawater from post-impact disturbances. Tsunamis that are known to have been started following impact could also significantly disturb the distribution of the meteoritic material. Likewise, it would be interesting to verify within other impact structures the mixing component of the meteorite within the target rocks and to determine if it is a function of the size of the impactor.

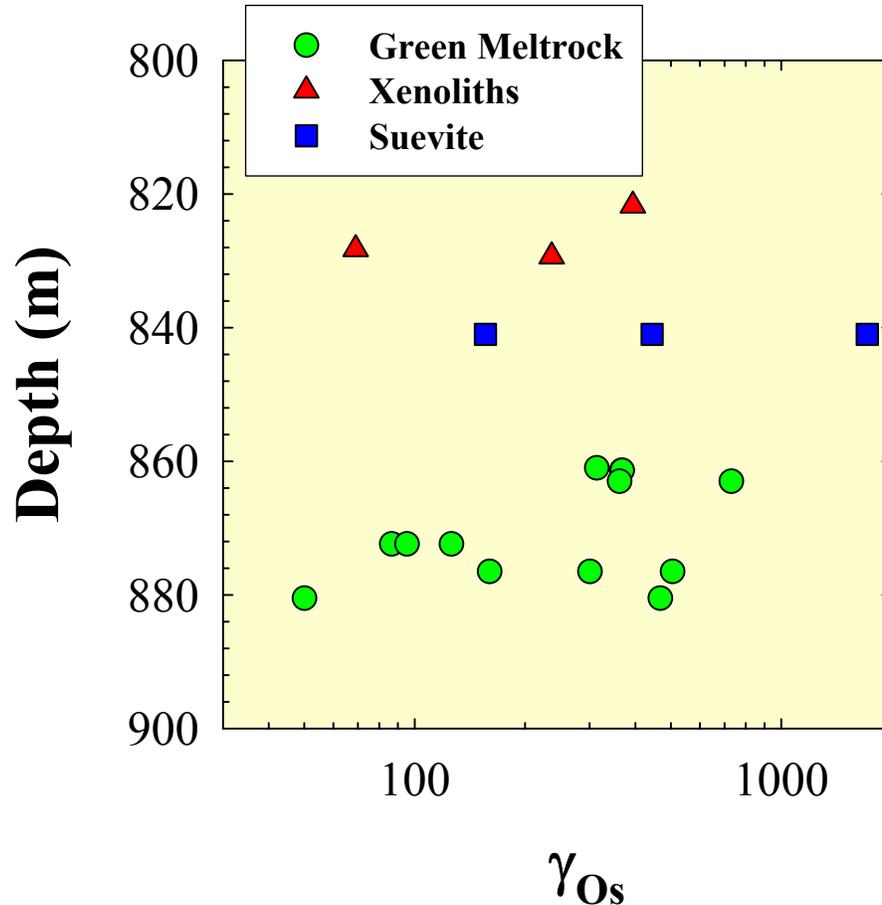


Figure 10: Each of the various types of samples was retrieved from the borehole at approximately the same depths. There is no correlation between depth and meteoritic component.

Conclusions:

The Chicxulub impactor, a carbonaceous chondrite, was heterogeneously mixed with the target rocks. More work is needed analyzing other impact structures to determine if this can be correlated to all large impactors. All of the large craters on Earth have experienced erosional effects from the Earth's atmosphere when impacting continents and displacement of sediments that occurs as seawater floods the crater post-impact when targeting seafloors. Lunar crater studies could ideally be utilized to ascertain this because of the lack of erosional effects of the Earth's atmosphere and seafloor. These kinds of studies would allow the scientific community to better determine the nature of the mixing of the ejecta and bolide.

There is little correlation within the sample from this borehole in the distribution of the impactor among the target lithics. One impactite is just as likely to have a meteoritic signature as another melt breccia is. And, certainly, there seems to be no identifiable chemical stratigraphic layers to the crater, i.e. the meteoritic signature as a function of depth. Though the samples can be differentiated regarding the proportion of clasts to impact glass, the meteoritic component is not eliminated with more or less melting.

The proportion of the impactor among the target rocks is estimated to be a maximum of about 0.1% for most samples. This suggests that only as much as 0.1% of meteoritic material is needed to drive the osmium towards chondritic values and that bolides can significantly alter the chemistry of the impactites. Though the impactor

contributed a significant proportion of the impactor only minor bulk meteoritic material contaminates the impactites. More work can be done to constrain how or if the proportion of the meteorite changes with decreasing radius since the samples in this borehole were near the edge of the crater.

This study determined that there is a variable meteoritic component within the impactites analyzed. The samples were all heterogeneously mixed as a function of depth and the type of impactite. Though the type of impactite tends to occur as a function of depth they do not necessarily occur as a function of the radius. Further work could be done to constrain any relationship between the mixing of the meteorite within the impactites and the radial distance. Following an impact, a maximum of 0.1% meteoritic material is required to drive the Os concentration in the crustal rocks to meteoritic levels. There was only a minor contribution of the bulk composition of the impactor to the target rocks, 0.1%, though the meteorite contaminated the sample with as much as 10% of its osmium content.

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Appendix:

Methods:

Clean Mortar and Pestle:

1. Add a small amount of quartz grains to the mortar and a small amount of distilled water.
2. Use the pestle to grind up the quartz for 2 to 3 minutes or until the quartz has been made into a powder.
3. Wipe the powdered quartz out with a kimwipe and put it in the wastebasket.
4. Rinse the mortar and pestle with distilled water.
5. Dry the mortar and pestle with a kimpwipe.

Pulverize the Samples:

Purpose: To homogenize the samples by pulverizing the samples into a fine powder.

1. Grind up approximately $\frac{1}{2}$ to $\frac{2}{3}$ of the samples with the pestle into a fine powder.
2. Number reagent bottles with the sample number.
3. Put the ground up samples in the appropriate reagent bottle.

Clean Teflonware:

1. Fill a large beaker approximately $\frac{1}{2}$ full with doubly distilled (milli-q) water.
2. Add approximately 300 mL of HCl (aq).
3. Add approximately 200 mL of HNO₃ (aq).
4. Under the hood, wearing gloves and eye protection, slowly add the teflonware to the aqua-rega mixture.
5. Write on the cover (a watch glass), with permanent ink, the name of the reagent (50% AB) and the name(s) of the people using the mixture.
6. Put the beaker on the hotplate under the hood.
7. Set the hotplate at 50%. The goal is to gently boil the teflon. Only a few bubbles should be coming up from the bottom per minute.
8. Clean up any spilled acid.
9. Let it sit on the hotplate for 2 days.
10. Take the beaker off the hotplate and allow it to cool.
11. Drain off the aqua-rega into another large beaker being sure to keep the watch glass over the top. Be sure to give the beaker an extra jiggle or two to free as much of the acid as possible from the insides of the teflon.
12. To rinse the teflon, we filled the beaker with the teflon in it with milli-q water.
13. After the beaker is full, drain the water from the beaker jiggling it a couple of times.
14. The final rinse is accomplished by taking a squirt bottle filled with milli-q water and squirting both the insides and outside of the teflon 3 times.
15. Place on a kimwipe to air-dry.
16. When completely dry, wrap in plastic wrap.
17. Return the watch glass to the beaker of aqua-rega and cleaning up any spilled acid.

Weigh the Samples:

For the purposes of this experiment we want to carefully weigh out no more than 0.1 g of the sample. We want to weigh out the sample to 5 significant figures with the last digit being prone to error.

1. Turn on the scale by pressing on.
2. Set scale to 40 g so that the scale goes from 0.0000 (4 sig. figs.) to 0.00000 (5 sig. figs.) by pressing mode.
3. Cut a piece of weigh paper in half. This is so no paper touches the outer circle of the scale.
4. Fold the paper into a small box to hold the sample.
5. Close the glass door and tare the scale to so that it reads as close to zero as possible.
6. Carefully add sample to the weigh paper on the scale so that the entire sample makes it into the paper box. Close the glass door.
7. After the scale has settled (takes a couple of minutes) record the mass of the sample.
8. Transfer the sample to a funnel inside a carius tube that has been appropriately numbered for the sample. The carius tube is being held upright in a holder that has been placed in a "test tube" tray.
9. Tap down any sample remaining in the funnel by holding the funnel with two fingers and the carius tube with the remaining fingers and bounce gently until most of the sample is inside the carius tube.
10. Cover the samples with plastic wrap.

Determine the Amount of Spike:

Assume that there will be ~0.2 ppb of Os in the sample.

We have ~ 0.1 g of each sample.

$0.1\text{g sample} * 0.2\text{ ng/g Os} = 0.02\text{ ng Os in each sample.}$

The spike selected was: $^{190}\text{Os} - 0.13667\text{ ng/g}$ and $^{185}\text{Re} - 0.03412\text{ ng/g}$

The amount of spike added to the samples will be between 0.1 and 0.2 g.

Make the Spike:

1. Using cotton gloves to avoid charging the teflon place an empty numbered large teflon container on the scale.
2. Tare the scale so that it will show 5 decimal places.
3. Add ~ 0.1 to 0.2 of spike to the teflon. Be careful not to allow the tip of the spike container to touch the teflon and contaminate either the teflon or the spike. Dry off the tip of the spike bottle with a kimwipe when finished so as not to contaminate the next worker's sample.

Make a Dry Ice Slush and Set the Oven:

1. Obtain approximately 1 pound of dry ice from Chemistry Receiving (Rm. 11b)
2. Crush the dry ice with a hammer.
3. Put the dry ice in a green container marked "alcohol".
4. Add ethanol to the container and dry ice until it is ~ 1/3 full.
5. Set oven for about 15° to 20° above the target temperature (200°) and set the shut-off temperature for 15° above that.

Chemistry of the Samples:

1. Add 2.0 g of concentrated HCl 2 x quartz distilled, 1 x teflon distilled to the spike in the teflon.
2. Set up clean carius tubes in a poly stand. Put funnels in each carius tube. Number each carius tube.
3. Add the correct sample to the appropriate carius tube.
4. Add the spike plus HCl acid to the carius tube.
5. Add ~ 4 g of concentrated HNO₃ (2 x quartz distilled, 1 x teflon distilled) to the teflonware that used to have the spike and HCl in it.
6. Put the carius tubes in the dry ice slush.

7. Trying to rinse the funnels of any remaining powdered sample, pour the HNO_3 into the appropriate carius tubes.
8. Rinse the funnel with Milli-Q water slightly.
9. Cover the funnels and carius tubes with plastic wrap.
10. After sealing the carius tubes (see below) place each sample back into the dry ice bath. Fill a large beaker with tapwater. Put the carius tubes into the water to slowly thaw the sample solution.
11. After the samples have thawed place the sealed carius tubes in metal jackets and put in the warmed oven.
12. Turn the oven off after 5 days. Let them cool inside the metal jacket for a day.
13. Take the samples out of the metal jackets, place them in a cup, and put them in the refrigerator for a day.
14. Label 6 large clean teflon containers.
15. Pipette out 4 mL of HBr (aq) and place them in the refrigerator as well.
16. Obtain 6 clean centrifuge tubes and add 3mL of CCl_4 .

Note: the carius tubes contain

sample + 2 g HCl + 4 g HCl + 4 g HNO_3 + 0.1 to 0.2 g of Os/Re spike.

Seal the Carius Tube:

NOTE: Work Quickly! If the mixture thaws it may explode. It is very volatile. Also be sure to be wearing glasses the flame can be very bright.

1. In the mineral separation lab, set up a stand with a clamp to hold a single carius tube.
2. Turn on the gas and the oxygen tank to the blow torch.
3. Strike the flint and light the torch. Adjust the flame appropriately.
4. Pick up the glass rod. Heat the top of the carius tube and the end of the glass rod. Melt the end of the glass rod to the top of the carius tube slightly.
5. Circle the middle of the top of the carius tube with the flame while not moving the glass rod until it melts. See picture.
6. The glass will eventually melt after a minute or two sealing the carius tube.
7. **IMPORTANT:** Be sure not to move the glass rod yourself. An improper seal of the tube could result. This could destroy the sample or cause injuries when opening the carius tube.

Open the Carius Tube:

1. Score the glass tubes.
2. Set up the blow torch and stand as above.
3. Set the carius tubes in the clamps at a 60° angle from the table.
4. Vent the carius tubes by melting a small hole in the top. This degasses the container. You may hear a small pop.
5. Wet the score mark with Milli-Q water.
6. Heat the end of the glass rod and apply the rod to the score mark. You may hear a small crack when the top is unsealed.
7. Snap off the top of the carius tubes under a vented hood.

Osmium Separation:

1. Add the samples from the opened carius tubes to the appropriately marked centrifuge tube. Place the cap on the centrifuge tube.
2. Shake the sample for 1 to 2 minutes by hand. Place in centrifuge for 2 to 3 minutes.
3. Pipette out the lower liquid. This is the portion that contains the Os. The upper portion contains the Re.
4. Place the pipetted liquid into the large teflon containers containing HBr (aq).
5. Turn on the hot plate to 90° to 100° .
6. Repeat procedure by adding 3 mL of CCl_4 to the centrifuge tube. Shake. Centrifuge. Pipette out the lower portion.
7. Repeat once more adding 1 mL of CCl_4 .

8. Set aside the solution contacting the Re for separation.
9. Place the teflon containers onto the hotplate for 2 hours. This will drive the Os from the CCL_4 and into the HBr.
10. The mixture will have separated into 2 liquids. The CCL_4 is reddish orange and the HBr plus Os is yellow.
11. Withdraw the CCL_4 by pipetting out the reddish-orange solution and throwing it away into the organic waste container.
12. Put the remaining samples in the teflon under the heat lamps and dry the solution down to a drop. It should take about an hour to dry. When the solution has dried down to a μL drop, pipette out the drop and place it on the center of the cap to the teflonware.
13. Place the drop of solution back under the heat lamp and allow to dry down completely. This will cause the HBr to be evaporated and the Os will be reduced to a salt.
14. Screw the bottom back on the top when dried down.

Mini-Distillation of Os:

1. Add $15\mu\text{L}$ of concentrated HBr acid to the small teflon container. Tap the drop down into the point at the bottom of the container.
2. Add 20 to $30\mu\text{L}$ to the Os salt speck on the cap of the teflon container.
3. Put the cap on the container and wrap in a small piece of aluminum foil.
4. Place on a hot plate for 2 to 3 hours. The hot plate should be set at 85° .
5. Carefully unwrap the teflon so that the HBr drop, which now contains the Os, does not fall into the bottom.
6. Unscrew the cap. It should still have an orange dot on it. There should be no green. Carefully check the bottom part of the container for contamination as well. If there has been contamination carefully wipe it out with a kimwipe.
7. Check the cap for contamination by pouring a couple drops of Milli-Q water onto the orange speck. You should see no green. Rinse the cap and dry carefully. Screw the cap back on the container.

Rhenium Chemistry:

1. Set up a poly column rack with 6 clean rhenium columns and collection cups under the columns.
2. Fill the column with AG-1 x8 100 to 200 anion resin to 1 or $2\mu\text{L}$ of the top.
3. Add 10 mL of H_2O .
4. Allow the columns to drain between each step hereafter:
 - a. Add 2.5 mL of 0.8 M teflon distilled HNO_3 .
 - b. Add 10 mL of 5 or 6 M 2 x quartz distilled HNO_3 .
 - c. Add 10 mL of 5 or 6 M teflon distilled HNO_3 .
 - d. Add 2.5 mL of 0.8 M teflon distilled HNO_3 .
 - e. Add the sample to the column.
 - f. Add 2.5 mL of 1 N teflon distilled HCl.
 - g. Add 7.5 mL of 1 N teflon distilled HCl.
 - h. Add 2.5 mL of 0.8 M teflon distilled HNO_3 .
 - i. Add 2 mL of 5 M teflon distilled HNO_3 .
5. Add 10 mL of 5 M teflon distilled HNO_3 and collect the Re in the teflonware.
6. Dry down to a drop.
7. Clean up for Re:
 - a. To the column, add 5 mL of H_2O .
 - b. Add 2 mL of 0.8 M teflon distilled HNO_3 .
 - c. Add 10 mL of 5 M teflon distilled HNO_3 .
8. Re-dissolve the sample in 1 mL of 0.8 M teflon distilled HNO_3 .
9. Place the teflon on a 100°C hot plate for an hour.
10. Add 2 mL of 0.8 M teflon distilled HNO_3 .
11. Add the sample.
 - a. Add 1 mL of 0.8 M teflon distilled HNO_3 .
 - b. Add 1 mL of 0.8 M distilled HNO_3 .
12. Elute and collect the Re in mL of 5 M teflon distilled HNO_3 .

13. Dry down.
14. Add a few drops of HCl and HNO₃, dry down again.

Loading the filament for Os:

1. Make a non-fused Pt ribbon filament.
2. Insert the filament into the filament block.
3. Put the filament into the holes of the hot plate. Invert a glass beaker over the top of the filament and heat for 5 minutes at low power until glowing.
4. Meanwhile, add 1.6 μ L of HBr (aq) to the dried sample in the teflonware. Make sure to tap the drop down into the point. This re-dissolves the Os.
5. Take the glass beaker off the filament.
6. Load the filament by pipetting out half the dissolved solution (or 0.8 μ L) and placing it as a small bead on the filament.
7. Turn the power up to dry the solution on the filament.
8. When dry, take a small piece of parafilm and add a small drop of Ba(OH)₂ to the film.
9. Pipette out a small drop of the Ba(OH)₂ and set it aside. This cleans out any acid still remaining in the pipette tip.
10. Pipette out a small drop of Ba(OH)₂. Turn the dial up on the pipetter to suck up a little air. This causes the Ba(OH)₂ to move back a little so that you have more control when applying it to the filament.
11. Apply the meniscus of Ba(OH)₂ to the filament. Try to touch the filament only with the drop of solution and not the pipette tip.
12. Allow the loaded filament to sit for a couple of minutes. The sample will clarify and turn a clear white when ready.

Loading the Filament for Rhenium:

1. Follow general procedure for osmium but use 0.7 μ L of 2% HNO₃ instead of HBr.
2. Always load the entire volume of acid plus Re sample.

Bobcat Instructions:

1. Beam valve should be closed. Filament power supply and high voltage power supply are off. The ion gauge filament can remain on.
2. Press the standby button to bring the turbo pump up to full speed.
3. Close the source valve and turn the red dial on the vacuum gauge all the way to the right.
4. Check the rough pump. It should be off.
5. Open the N₂ tank, the bleed valve, and the needle valve.
6. Close the bleed valve.
7. Loosen the 2 bolts holding the faceplate. Remove the faceplate.
8. Disconnect the filament power wires and remove the bolt holding the filament block in place. Use the specially made hex tool.
9. Remove the filament block with the extraction tool. Put in the new filament block.
10. Replace faceplate and tighten the bolts.
11. Turn on the rough pump.
12. Turn the thermocouple switch to R. Reboot the system if the system trips by pressing the reset button.
13. When the pressure says it is less than 75 millitorrs, close the needle valve.
14. Turn off the rough pump. Turn the thermocouple switch to F.
15. Turn off the ion gauge filament. Open the source valve.
16. Turn the dial on the vacuum gauge to ~500 millitorr.
17. Turn the ion gauge filament on.
18. Add liquid N₂ when the pressure says it is below 5E-6 millitorrs. Make sure there is no water in the cup before adding the N₂.
19. Open the O₂ tank until the pressure reads > 0 then close it tightly. This allows oxygen to get in the line.
20. Bleed in the oxygen to add approximately 1E-7 millitorrs to vacuum.
21. Open the beam valve when it reads 1E -7.

22. Turn on the operate switch.
23. Press the reset button.
24. Turn up the high voltage: Multiplier = 2100 v; Ion optic source = 7120 v.
25. Turn the magnet from internal to external.
26. Turn on the power to the universal counter.
27. Enter the program information into the computer.
28. Check to be sure the ionizing filament is all the way to the left then turn on the filament power.
29. Press the reset button on the universal counter.
30. Slowly bring up the filament until it is slightly glowing. ~ 1.200 or 830° .