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LETTER

Evidence for a meteoritic component in impact melt rock from the Chicxulub structure

CHRISTIAN KOEBERL,[1,2,4] VIRGIL L. SHARPTON,[3] BENJAMIN C. SCHURAYTZ,[3] STEVEN B. SHIREY,[2] JOEL D. BLUM,[4] and LUIS E. MARIN[5]

[1]Institute of Geochemistry, University of Vienna, A-1010 Vienna, Austria
[2]Department of Terrestrial Magnetism, Carnegie Institution, 5241 Broad Branch Road, NW, Washington, DC 20015, USA
[3]Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston, TX 77058, USA
[4]Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, USA
[5]Instituto de Geofisica, UNAM, Mexico City, CP 04510, Mexico

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Abstract—The Chicxulub structure in Yucátan, Mexico, has recently been recognized as a >200-km-diameter multi-ring impact crater of K-T boundary age. Crystalline impact melt rocks and breccias from within the crater, which have compositions similar to those of normal continental crustal rocks and which show shock metamorphic effects, have been studied for trace element and Re-Os isotope compositions. Re-Os isotope systematics allow the sensitive and selective determination of an extraterrestrial component in impact-derived rocks. A melt rock sample shows elevated iridium concentrations, an osmium concentration of 25 ppb, and a low $^{187}Os/^{188}Os$ ratio of 0.113, which are incompatible with derivation from the continental crust. Even though the $^{187}Os/^{188}Os$ ratio is slightly lower than the range so far measured in meteorites, a mantle origin seems unlikely for mass balance reasons and because the cratering event is unlikely to have excavated mantle material. The data support the hypothesis of a heterogeneously distributed meteoritic component in the Chicxulub melt rock. A sample of impact glass from the Haitian K-T boundary at Beloc yielded about 0.1 ppb osmium and an $^{187}Os/^{188}Os$ ratio of 0.251, indicating the presence of a small meteoritic component in the impact ejecta as well.

INTRODUCTION

THE IMPACT MODEL for the Cretaceous-Tertiary (K-T) boundary event initiated the search for a large impact crater of K-T boundary age. Recently, geological, geophysical, and petrological lines of evidence were used to support the identification of the Chicxulub structure in Yucátan, Mexico, as a large buried impact structure. Early arguments, which led to the proposal that Chicxulub is an impact crater, were summarized by HILDEBRAND et al. (1991). Crystalline impact melt rocks and breccias have been recovered from drillcores within the crater. A number of these rocks record a spectrum of shock metamorphic effects, which are characteristic for an impact origin (SHARPTON et al., 1992). Dating of some of the impact melt rocks yielded an age that was indistinguishable from that of the K-T boundary (SWISHER et al., 1992; SHARPTON et al., 1992; KROGH et al., 1993). This age is also identical to that of impact glasses found at the K-T boundary, mainly in Haiti (e.g., SIGURDSSON et al., 1991; SWISHER et al., 1992). The Chicxulub structure has thus emerged as the best candidate for the long-sought K-T boundary impact crater. Recent geophysical studies led to the recognition that the Chicxulub structure is a multi-ring impact crater with a diameter of close to 300 km (SHARPTON et al., 1993). The Chicxulub crater is presently covered beneath 300–1000 m of Tertiary carbonate rocks of the northern Yucatan platform and consequently drilling and geophysical studies are essential for obtaining information on this structure. Some samples are available from exploratory wells drilled by Pemex.

Previously, enhanced levels of iridium of up to 13.5 ppb were found in several fragments of melt rocks from the Chicxulub 1 (C1) and Yucatan 6 (Y6) drill cores (SHARPTON et al., 1992). The C1 well is located near the center of the structure, and the Y6 well is located about 60 km south-southwest of the center. Another study of Y6 melt rocks failed to detect any iridium enrichment (HILDEBRAND et al., 1993).

Enrichment of iridium and other platinum group elements (PGEs) in impact melt rocks is generally regarded as indicative of the presence of a meteoritic component (see, e.g., MORGAN et al., 1975; PALME et al., 1979; PALME, 1982). Tektites, which represent the first high-velocity ejecta, have low levels of meteoritic contamination (MORGAN, 1978; KOEBERL and SHIREY, 1993). On the other hand, impact melts found in situ in a crater may contain up to several percent of a meteoritic component (e.g., PALME et al., 1979; PALME, 1982). However, the PGEs, as well as other siderophile elements, may already be enriched in the target rocks, or may undergo interelement fractionation during the impact event (MITTLEFEHLDT et al., 1992; KOEBERL and SHIREY, 1993), or may be subjected to remobilization effects (WALLACE et al., 1990). Therefore, consideration of elemental abundances alone may yield ambiguous results.

In an effort to confirm the existence of a meteoritic component in Chicxulub melt rocks and to better understand the distribution of extraterrestrial matter in large impacts, we report here the results of additional trace element and Re-Os isotopic analyses on the an impact melt rock from the C1 core. The Re-Os isotopic system allows the detection of a meteoritic component even at low abundance levels and without some of the ambivalence of the elemental concentrations of the PGEs (KOEBERL and SHIREY, 1993; KOEBERL et al., 1994). Because of the similarity between Chicxulub melt rocks and the Haitian impact glass (BLUM et al., 1993), we have also studied the abundances and isotopic composition of rhenium and osmium in a bulk sample of impact glass from the Haitian K-T boundary section.

SAMPLES AND METHODS

Two types of samples have been studied: crystalline melt rock from the C1 drillcore and impact glass from the K-T boundary at Beloc, Haiti. The C1-N10 melt rock (from the depth interval 1393–1394 m below sea level) is a fine- to medium-grained coherent crystalline melt rock composed of subhedral to euhedral pyroxene, feldspar, and a cryptocrystalline to microcrystalline matrix which was once a residual interstitial melt. This rock was selected for our analyses because it shows no indication of undigested clasts or alteration. The major element composition of C1-N10 melt rock is similar to that of average continental crust (SHARPTON et al., 1992). We have analyzed splits of homogenized rock powder from the C1-N10 melt rock, which was described by SHARPTON et al. (1992), who obtained 6.0 ± 0.7 ppb iridium and an age of 65.2 + 0.4 Ma for this sample; our sample has the designation C1-N10-1A. Furthermore, rock fragments (which were also powdered for analysis) from another segment (C1-N10-2) of the same core interval were analyzed. In addition to the Chicxulub melt rocks, we also analyzed impact glass from the K-T boundary at Beloc, Haiti, locality B (JÉHANNO et al., 1992). A bulk sample was repeatedly cleaned ultrasonically and treated with dilute acetic and hydrochloric acids to remove clay, carbonates, and other contaminants, until inspection under the microscope indicated that the sample consisted of glass grains without any other visible contamination.

Trace and some major element abundances (Table 1) in C1-N10-1A and two aliquots of a powdered fragment from C1-N10-2 were determined at the NASA Johnson Space Center by instrumental neutron activation analysis (INAA), following procedures described elsewhere (SCHURAYTZ et al., 1991). Some additional analyses on splits of the C1-N10 powder (C1-10-1B) were done by INAA at the University of Vienna (see footnote to Table 1). The abundances and isotopic ratios of osmium and rhenium were determined using the sensitive negative thermal ionization mass spectrometry technique (NTIMS; CREASER et al., 1991), following methods described by KOEBERL and SHIREY (1993) (see also caption to Table 2).

TABLE 1. COMPOSITION OF CHICXULUB MELT ROCKS FROM THE C1 CORE, AND AVERAGE UPPER CONTINENTAL CRUST.

	Chicxulub C1-N10-1A	Chicxulub C1-N10-2A	Chicxulub C1-N10-2B	Average upper continental crust
Na_2O	4.32±0.05	4.52±0.05	4.53±0.05	3.9
K_2O	2.71±0.23	2.53±0.19	2.68±0.23	3.4
FeO	4.90±0.05	4.77±0.05	4.81±0.05	4.5
Sc	16.6±0.2	16.2±0.2	16.4±0.2	11
Cr	87.9±1.1	118±2	135±2	35
Co	16.2±0.2	13.6±0.2	14.7±0.2	10
Ni	30±8	40±9	50±15	20
As	0.68±0.20	0.63±0.19	0.30±0.13	1.5
Se	<0.4	<0.29	<0.5	0.05
Br	3.1±0.3	3.0±0.4	3.1±0.4	-
Rb	55.4±2.1	52.2±2.2	53±3	112
Sr	336±18	349±24	320±30	350
Zr	155±18	112±19	137±27	190
Sb	0.11±0.01	0.13±0.01	0.12±0.02	0.2
Cs	0.16±0.02	0.21±0.02	0.24±0.03	3.7
Ba	701±17	647±17	657±22	550
La	21.9±0.3	22.0±0.3	21.9±0.3	30
Ce	45.2±0.5	43.8±0.6	44.0±0.7	64
Nd	25.7±2.9	18.7±2.4	16±3	26
Sm	4.53±0.07	4.34±0.06	4.32±0.06	4.5
Eu	1.04±0.02	1.00±0.02	1.03±0.02	0.88
Tb	0.72±0.01	0.67±0.02	0.67±0.02	0.64
Yb	2.69±0.04	2.56±0.05	2.61±0.06	2.2
Lu	0.41±0.01	0.39±0.01	0.41±0.09	0.32
Hf	3.84±0.06	3.69±0.07	3.82±0.09	5.8
Ta	0.62±0.02	0.61±0.02	0.62±0.02	2.2
Ir (ppb)	6.0±0.7	<2.2	<1.7	0.02
Au (ppb)	39.6±1.5	11.2±1.1	13.3±1.4	1.8
Th	7.18±0.09	6.95±0.10	6.84±0.11	10.7
U	2.04±0.10	2.07±0.10	1.93±0.11	2.8

Note: Major element oxide data in wt%; trace element concentrations in ppm, except where noted. Analytical uncertainties are 1σ; 2σ upper limits given for elements below detection limit. Total iron as FeO. An additional split of C1-N10 was analyzed (C1-N10-1B) by INAA at the University of Vienna and found to contain 65 ppm Ni, 15.0 ppb Ir, and 5.3 ppb Au. Data for average continental crust from Taylor and McLennan (1985).

RESULTS AND DISCUSSION

Our results show limited variability for the abundances of most elements between the two drillcore fragments, as well as for the replicate analyses 2A and 2B (see Table 1). The abundances and distribution patterns of the rare earth elements (REEs), and trace element ratios (e.g., Zr/Hf, K/U, Th/U) are characteristic of average continental crust (TAYLOR and MCLENNAN, 1985). The samples yielded depleted mantle neodymium model ages of about 1040 Ma and have ϵ_{Sr}^{65Ma} and ϵ_{Nd}^{65Ma} values of about +58 and −3, respectively (see also BLUM et al., 1993). Such values are not consistent with derivation from the mantle because values for rocks derived from the upper mantle generally fall in a narrow range of ϵ_{Nd} of +4 to +10 and ϵ_{Sr} of −10 to −30. The most significant differences among the three sample splits are the concentrations of chromium and the siderophile elements iridium and gold, and, to a lesser extent, cobalt (Table 1). Nickel, cobalt, and chromium abundances are slightly enriched in the Chicxulub melt rocks compared to average crustal values (TAYLOR and MCLENNAN, 1985), and, more significantly, compared to abundances found in granitic clasts from related impact breccias. These clasts are presumably derived from the crater basement and contain about 14 ppm Cr and 6.4 ppm Co (V. L. SHARPTON et al., unpubl. data). The lack of detectable iridium in C1-N10-2 was noted before (SHARPTON et al., 1992) and attributed to nonuniform distribution of a projectile component.

The Re-Os isotopic system, which is based on the decay of ^{187}Re to ^{187}Os, is uniquely suited to provide an independent test for the presence of a meteoritic component in impact melts (FEHN et al., 1986; KOEBERL and SHIREY, 1993) and impact-derived materials such as K-T boundary clays (LUCK and TUREKIAN, 1983). Mantle-derived melts have substantially higher Re/Os ratios relative to the mantle because during partial melting of the mantle, rhenium is moderately incompatible, while osmium is compatible and retained in the residue. Crustal rocks have elevated Re/Os ratios and accumulate significantly higher abundances of ^{187}Os than the mantle. Crustal rocks have variable osmium isotopic ratios, depending upon crustal extraction age and elemental abundances. $^{187}Os/^{188}Os$ ratios of about 0.67 to 1.61 ($^{187}Os/^{186}Os$ = 5.6–13.4) were reported for various continental river sediments and glacial loess deposits, which are taken to be representative for large areas of continental crust; such rocks also have high $^{187}Re/^{188}Os$ ratios averaging about 40 (ESSER, 1991; ESSER and TUREKIAN, 1993). Meteorites have high

TABLE 2: RE-OS ISOTOPIC DATA FOR CHICXULUB MELT ROCK SAMPLES.

Sample	(1) Re (ppb)	(2) ^{188}Os (10^{-15} moles/g)	(3) Total Os (ppb)	(4) ^{187}Os (%)	(5) ^{187}Re/^{188}Os	(6) ^{187}Re/^{186}Os	(7) ^{187}Os/^{188}Os	(8) ^{187}Os/^{186}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

For Re and Os analyses, about 0.15 g of sample 1A, 1.6 g of sample 2, and 2.8 g of the Beloc glass were spiked with enriched ^{190}Os and ^{185}Re. The measured total procedural blanks for the acid digestion - distillation - anion exchange procedure are 12 pg for Re and 2 pg for Os (Koeberl and Shirey, 1993). Re and Os were measured as ReO_4^- and OsO_3^-, respectively, using negative thermal ionization mass spectrometry (Creaser et al., 1991), using a 15" mass spectrometer. The data were corrected for oxygen isotopic composition (Nier, 1950), and corrected for fractionation and normalized to a ^{192}Os/^{188}Os of 3.0826 (Nier, 1937). Total Os (column 3) includes radiogenic ^{187}Os, the percentage of which is given in column 4. We adopt the convention of normalizing to ^{188}Os because ^{188}Os and not ^{186}Os is the non-radiogenic Os isotope directly measured by all workers. ^{186}Os normalized data (columns 6 and 8) are presented here to allow comparison with earlier literature data. Uncertainties quoted in columns 5 and 7 refer to the last digits and are taken to be ±3rel.% based on the uncertainty in the spike calibrations; mass spectrometric uncertainties are usually <1rel.%.

*Two additional Re analyses on different aliquots of the rock powder gave 0.952 and 0.956 ppb, respectively, showing very good reproducibility.

osmium abundances, low Re/Os ratios, and therefore low ^{187}Os/^{188}Os ratios of about 0.11 to 0.18 and ^{187}Os/^{186}Os ratios of 0.95 to 1.5 (see, e.g., WALKER and MORGAN, 1989; MORGAN et al., 1992; HORAN et al., 1992). Such ratios are distinctly different from those of old continental crust.

Thus, the Re-Os isotopic system can be used to identify extraterrestrial components in impact-derived rocks, such as melt rocks, glasses, and breccias, because the absolute abundances of osmium and, more importantly, the ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios in meteorites are distinctly different from those in old crustal target rocks. The mixing systematics inherent to the Re-Os isochron diagram can show whether rhenium and/or osmium were lost during the impact (cf. KOEBERL and SHIREY, 1993). It is furthermore unlikely that osmium isotopic ratios will be altered during impact (cf. KOEBERL and SHIREY, 1993). Measurements of Ivory Coast tektites and impact glasses from the Bosumtwi crater and impact breccias from some other craters (KOEBERL and SHIREY, 1993; KOEBERL et al., 1994; KOEBERL et al., unpubl. data) show the feasibility of the Re-Os method as a new tool for impact crater studies.

For sample C1-N10-1A we measured 25.2 ppb Os, whereas C1-N10-2 contains only 0.056 ppb (Table 2). The higher osmium abundance in C1-N10-1A relative to C1-N10-2 is in agreement with the higher iridium contents found in C1-N10-1A (Table 1). Different iridium values have been found for splits of the *same powder* of C1-N10-1A (6.0 and 15.0 ppb), while most other elements have very similar chemical abundances. The fact that only some highly siderophile elements show a significant difference may be explained by a nugget effect, possibly due to a low-abundance host phase of the PGEs. Such a nugget effect could also be responsible for the higher osmium abundance relative to the iridium content in C1-N10-1A. This observation is in agreement with a heterogeneous distribution of siderophile elements in the melt rock. Even more significant differences exist for the isotopic ratios (Figs. 1 and 2). The high-Os sample (1A) has extremely low ^{187}Os/^{188}Os and ^{187}Re/^{188}Os ratios of 0.113 and 0.305, respectively, which are inconsistent with those of old continental crust. In contrast, C1-N10-2 has high ^{187}Os/^{188}Os and ^{187}Re/^{188}Os ratios of 0.505 and 87.7, respectively, similar to values typical of old continental crust (ESSER and TUREKIAN, 1993).

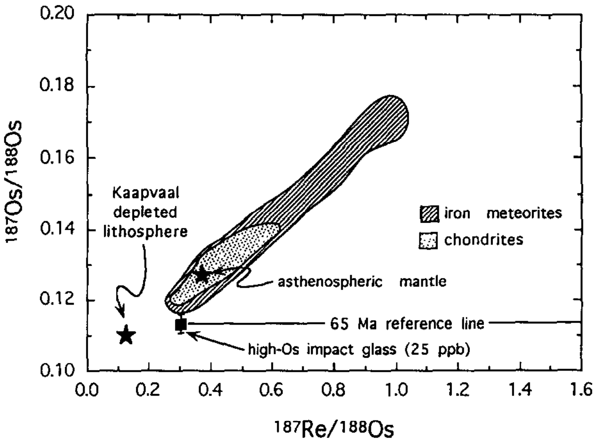

FIG. 1. Re-Os isotopic composition of Chicxulub melt rock samples compared to iron meteorites, chondrites, and lithospheric and asthenospheric mantle. Chicxulub data and Kaapvaal depleted lithosphere plotted as measured, normalized to ^{188}Os. Meteorite data and asthenospheric mantle calculated from reported ^{186}Os normalized data using an ^{186}Os/^{188}Os ratio of 0.1203. This value is an average of repeated measurements of standards and samples at DTM (S. B. Shirey, unpubl. data) and agrees with reported ^{186}Os/^{188}Os (LUCK and ALLÈGRE, 1983; CREASER et al., 1991). Meteorite data from ALLÈGRE and LUCK (1980), LUCK and ALLÈGRE (1983), WALKER and MORGAN (1989), MORGAN et al. (1992), and HORAN et al. (1992). ^{187}Re/^{188}Os isotopic composition of asthenospheric mantle estimated from MORGAN (1986) and ^{187}Os/^{188}Os estimated from HATTORI and HART (1991) and MARTIN (1991). Kaapvaal depleted lithosphere is derived from the average of typical kimberlite-hosted mantle xenoliths from the Kaapvaal craton, South Africa, that have escaped subsequent melt enrichment (G. PEARSON et al., unpubl. data), and is shown to demonstrate the lowest osmium isotope ratios measured so far in mantle rocks.

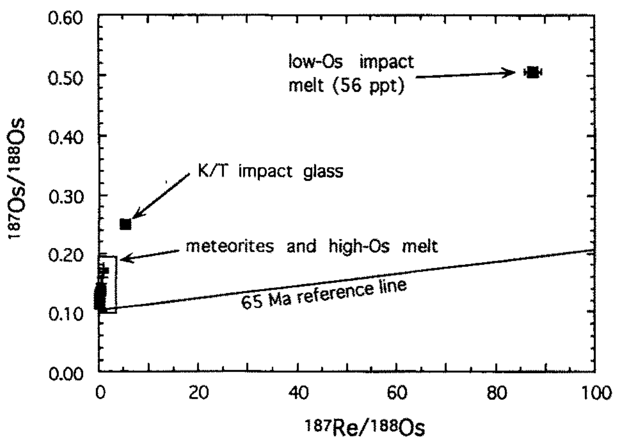

FIG. 2. Same as Fig. 1 but with different scale to include the low-Os Chicxulub melt rock and the impact glass from the Haitian K-T boundary at Beloc. The box on the left side marks the ranges of Fig. 1. Normal continental crustal rocks have $^{187}Os/^{188}Os$ ratios of about 0.7 to 1.6 and $^{187}Re/^{188}Os$ ratios of about 10 to 60 and would plot outside the top of the figure. This indicates that the Re-Os isotopic composition of the Haiti glass could be derived by mixing a meteoritic component with crustal material.

Geophysical studies (SHARPTON et al., 1993) indicate that the Chicxulub-forming impact event excavated to a depth of 17–20 km, well within the upper part of the crust (the depth of the transient crater, about 45–60 km, includes excavation plus downward displacement of the target beneath the impact point). Hence, it is unlikely that the crater-forming event could have mixed mantle material into the Chicxulub melt rocks. In addition, trace element, Rb-Sr, and Sm-Nd isotopic characteristics of the samples are typical of rocks from the continental crust, and exclude any major contribution from basaltic, ultramafic, or other mantle-derived material. MORB and related basalts contain only sub-ppb osmium abundances and $^{187}Os/^{188}Os$ ratios (MARTIN, 1991) that are slightly higher than that observed in the Chicxulub melt rock. Depleted lithospheric mantle xenoliths are the only terrestrial rocks known with subchondritic $^{187}Os/^{188}Os$ ratios (WALKER et al., 1989; G. PEARSON et al., unpubl. data). However, osmium abundances in xenoliths are too low (2–3 ppb) to account for the high abundances observed here. In addition, occurrences of depleted continental lithosphere are unknown from this area, and none of these basalts or ultramafic bodies have been observed in the Chicxulub target area or in impact breccias (SHARPTON et al., 1992, 1993). Consequently, we consider the presence of a mantle component in the Chicxulub samples to be an unlikely explanation for osmium abundance and isotopic composition.

As mantle sources require implausible excavation depths or rocks not known to be present at Chicxulub, we conclude that an extraterrestrial source is the more likely explanation for the observed values although the $^{187}Os/^{188}Os$ ratio in C1-N10-1A is slightly below the range so far measured in meteorites. This difference could be due to analytical uncertainties in the analyses of meteorites and the Chicxulub melt rock (i.e., the data overlap within the error given by the spike calibration), or it could be due to the peculiar nature of the impactor. For example, we can speculate that a comet or a differentiated asteroid may have isotopic characteristics slightly different from those of known chondrites or iron meteorites. Based on our results for iridium and osmium abundances and the osmium isotopic ratio, compared to average chondritic osmium abundances (about 700 ppb), we estimate a maximum of 3% chondritic contribution in the samples analyzed. This percentage is well within the range of meteoritic components reported for large craters (e.g., up to 10% at East Clearwater; PALME et al., 1979). However, we have no good explanation for the nonchondritic ratios of nickel, cobalt, and chromium in the Chicxulub melt rock. From abundance data for these elements and iridium, as well as isotopic ratios for osmium, we conclude that the meteoritic component is heterogeneously distributed in the Chicxulub melt rock; similar nonuniform distributions have been reported at other impact craters (PALME et al., 1979; PALME, 1982). Variations in the abundances of chromium and some siderophile elements between different splits of the melt rocks may be due to formation, separation, and selective inclusion of Cr-Ni-spinels and/or siderophile element-rich sulfides which were found in Chicxulub melt rocks (SCHURAYTZ and SHARPTON, 1994).

We have also measured rhenium and osmium concentrations and isotopic ratios in a sample of impact glass from the K-T boundary at Beloc, Haiti (SIGURDSSON et al., 1991). The Haitian K-T boundary impact glass is indistinguishable from the Chicxulub C1-N10 melt rock in Rb-Sr and Sm-Nd isotopic characteristics, supporting the notion that the impact glass was derived from the Chicxulub impact crater (BLUM et al., 1993). The glass contains 0.095 ppb Os which is elevated compared to average crustal abundances, 0.02 to 0.05 ppb (TAYLOR and MCLENNAN, 1985; ESSER, 1991; ESSER and TUREKIAN, 1993). The $^{187}Os/^{188}Os$ ratio in the Haitian glass is 0.251 which is somewhat higher than the values for chondrites and iron meteorites (Fig. 2); however, it is considerably lower than the average crustal ratio of 1.23 (ESSER, 1991) or the ratio of 0.505 found for the low osmium melt rock, C1-N10-2, which may represent background values at Chicxulub. The major and trace element composition (SIGURDSSON et al., 1991; KOEBERL and SIGURDSSON, 1992) and the Rb-Sr and Sm-Nd isotope systematics (BLUM et al., 1993) of the Haitian impact glass are indistinguishable from that of crustal rocks and thus do not show any significant mantle component. The enrichment in osmium, and the low $^{187}Os/^{188}Os$ ratio in the Haitian glass can thus be best explained by the presence of meteoritic material. The iridium content resulting from the small amount of meteoritic material that is required to lower the osmium isotopic ratio is too low to be detected by standard INAA procedures. If the low-Os melt rock is assumed to be typical of the target composition, then the Haitian impact glass plots slightly to the left of a mixing field between target and meteorite values. This is in agreement with observations for some Ivory Coast tektites and Bosumtwi crater impact glasses which show the same trend (KOEBERL and SHIREY, 1993) and is indicative of rhenium depletion during impact (MORGAN, 1978).

SUMMARY AND CONCLUSIONS

The high osmium abundance (25 ppb), as well as the low $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ ratios in the Chicxulub C1-N10-

1A impact melt rock, show that the osmium (and, by inference, the iridium) in this rock is not of crustal origin. Such values can be explained either by mantle or meteoritic components. The observed $^{187}Os/^{188}Os$ ratio is slightly below the range presently known for meteorites and is in better agreement with depleted lithosphere. However, the low PGE abundances (relative to chondrites or most iron meteorites) observed in mantle xenoliths, the absence of any such rocks in known Chicxulub breccias, and excavation depths within the crust make it difficult to reconcile the observed values with a mantle source. A meteoritic source seems the more plausible explanation, even though the siderophile elements do not show strictly chondritic relative elemental abundance ratios. Fractionation of PGEs and other siderophile elements have been observed in glasses at smaller impact craters (e.g., MITTLEFEHLDT et al., 1992), and partitioning and redistribution of trace elements is an expected consequence of protracted cooling and differentiation within impact large melt sheets (SCHURAYTZ and SHARPTON, 1993). We also analyzed a composite sample of impact glass from the Haitian K-T boundary at Beloc to determine the possible presence of a meteoritic component in analogy to tektite studies (KOEBERL and SHIREY, 1993). This sample yielded about 0.1 ppb Os and a $^{187}Os/^{188}Os$ ratio of 0.251, indicating the presence of a small meteoritic component.

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