Detection of a Meteoritic Component in Ivory Coast Tektites with Rhenium-Osmium Isotopes

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Measurement of rhenium (Re) and osmium (Os) concentrations and Os isotopic compositions in Ivory Coast tektites (natural glasses with upper crustal compositions that are ejected great distances during meteorite impact) and rocks from the inferred source crater, Lake Bosumtwi, Ghana, show that these tektites incorporate about 0.6 percent of a meteoritic component. Analysis of elemental abundances of noble metals alone gives equivocal results in the detection of meteoritic components because the target rocks already have relatively large amounts of noble metals. The Re-Os system is ideally suited for the study of meteorite impacts on old continental crust for three reasons. (i) The isotopic compositions of the target rocks and the meteoritic impactor are significantly different. (ii) Closed-system mixing of target rocks and meteorites is linear on Re-Os isochron diagrams, which thus permits identification of the loss of Re or Os. (iii) Osmium isotopic compositions are not likely to be altered during meteorite impact even if Re and Os are lost.

Tektites are natural glasses occurring on Earth in four distinct areas known as strewn fields: the Australasian, Ivory Coast, Central European, and North American fields (1, 2). Tektites occur in various forms on land (1, 2) and as melt rocks in craters (1, 2). Geochronological data show that these melt rocks are derived from terrestrial upper crustal rocks by melting caused by hypervelocity impact (1–4). Although a meteoritic component has been reported for impact glasses, melts, and breccias at several impact craters (5) and meteorite (projectile) compositions have been estimated (6, 7), unequivocal identification of an extraterrestrial component that has not been made for tektites (2). Tektites consist predominantly of terrestrial material (4) because the meteoritic projectile is vaporized on impact (8). The only elements that seem to be diagnostic of a meteoritic component are some siderophile elements, especially members of the platinum group elements (PGEs). Their abundances and interelemental ratios in meteorites are considerably different from those in terrestrial crustal rocks. By using the Re-Os isotopic system, we are trying to characterize the isotopic differences between the source rocks and the tektites and learn more about the impact process. Here, we present Re-Os isotopic analyses of Ivory Coast tektites that show the presence of a meteoritic component (not exceeding 0.6%). This result supports the link between the tektites and their presumed source crater and suggests Re and Os loss during the impact process.

The abundance of PGEs is low in tektites and, as a result, only few tektites have been analyzed for their PGE contents. Morgan (9) analyzed six high-Mg australites by radiocarbon neutron activation analysis; only one showed a distinct PGE enrichment over the typical abundances in upper crustal rocks, but the data did not allow the characterization of the projectile. Palme and co-workers (7, 10) analyzed the PGE content of two Ivory Coast tektites. Abundances of Ir and Os were 0.24 and 0.33 ppb and 0.099 and 0.199 ppb, respectively; the abundances of all other PGEs were below detection limits. Palme et al. (10) suggested that an iron projectile might have been responsible for the Bosumtwi crater, but Jones (11) argued that the target rocks could supply the high Ir content because the Bosumtwi crater is in an area of gold mineralization. Thus, the available data were insufficient to definitely identify the meteorite group of the projectile or its contribution to the tektites. The problem of identification is amplified by unpredictable fractionation between individual PGEs and other siderophile elements during impact (12, 13).

Here, we show that the Re-Os isotopic system can be used to quantify target-bolide mixing during impact and to understand the impact process. Osmium isotopes are able to provide an unambiguous tracer for the presence and proportion of an extraterrestrial component in tektites, impact glasses, and other impact-derived rocks and may help identify the target material. The absolute abundance of Os (and other PGEs) as well as the ratios of 187Re/188Os and 187Os/188Os in meteorites are distinctly different from the values obtained for old continental crustal rocks that make up the target material for tektites. It is unlikely that there is a significant fractionation of Os isotopes during impact. In an earlier study, Fehn et al. (14) determined Os isotopes in suevite and impact melts from the Ries and East Clearwater craters; however, the analytical methods were not yet sensitive enough to allow a quantitative discussion of any meteoritic contamination.

The Re-Os isotopic system has important implications for the study of the mantle-crust system (15) and meteorite chronology (16–18). It is based on the decay of...
$^{187}$Re to $^{187}$Os with a half-life of $42.3 \pm 1.3$ billion years (19). However, it has found wider applications only because of recent analytical improvements that overcome the analytical difficulties posed by the low Re and Os abundances of common terrestrial rocks. During crust formation, Re strongly partitions into the crust, whereas Os stays in the mantle; as a result, the abundance of radiogenic $^{187}$Os is high in old crustal rocks. In general, crustal rocks should have $^{187}$Os/$^{188}$Os ratios that increase with the age of extraction of the crust from the mantle. Meteorites (and mantle rocks) have low $^{187}$Os/$^{188}$Os ratios, between about 0.11 and 0.18. Meteoritic $^{187}$Os/$^{188}$Os ratios are between about 0.95 and 1.5 (20).

We used the sensitive negative thermal ionization technique (21, 22) to determine the abundances and isotope ratios of Os and Re in four Ivory Coast tektites, two impact glass samples, and five different target rocks (including graywackes, microcrystalline granite, and a granodiorite) from the Bosumtwi crater, Ghana. The crater is excavated in metasediments of the Birimian system, comprising mainly phyllites, graywackes, microgranites, and granodioritic rocks (Pepiakese intrusion) (11); the samples selected for analysis are thought to be representative of the variety of target rocks, with emphasis on possible Os-rich rocks.

The Bosumtwi crater was suggested to be the Ivory Coast tektite source crater because the tektites and the crater have the same age (23, 24) and similar chemical composition (11, 25) as well as Rb-Sr (26, 27) and oxygen isotopic characteristics (28, 29). Shaw and Wasserburg (30) showed that the Rb-Sr and Sm-Nd isotopic systems in the Ivory Coast tektites all have large negative $\epsilon_{\text{Nd}}$ values of about $-20$ and positive $\epsilon_{\text{Sr}}$ values from $+260$ to $+300$ (31). Both the Nd and Sr isotopic compositions are typical for old continental crust. The Sm-Nd data yield model ages for the extraction of the crust in the Bosumtwi area from the mantle at about 1.9 billion years ago. This age is in agreement with the whole-rock Rb-Sr ages of the rocks around the Bosumtwi crater, which range from 1.9 to 2.1 billion years (26, 27). The Rb-Sr isotopic characteristics of the Ivory Coast tektites yield a younger age of 0.95 billion years. Shaw and Wasserburg (30) concluded that the decreased Rb/Sr ratio in the tektites compared to that in the crater rocks is the result of sedimentation or metamorphism of the exact tektite source rocks (most likely the uppermost layer of the target) at 0.95 billion years ago.

The tektites have Os concentrations of about 0.06 to 0.30 ppb (Table 1), which is in agreement with earlier data (10). Concentrations of Re vary between 0.004 and 0.016 ppb (32), which is below the detection limit of earlier studies (10). The Os abundances are high relative to normal crustal values (33), whereas the Re abundances are exceedingly low for any rock type, terrestrial or extraterrestrial. Concentrations of both Os and Re in the Bosumtwi target rocks are different from those expect-

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**Table 1.** The Re-Os isotopic data for Ivory Coast tektites and glasses and target rocks from the Lake Bosumtwi, Ghana, impact site. The Re and Os isotopic data were measured with negative thermal ionization mass spectrometry as $^{187}$ReO$_4^-$ and $^{188}$OsO$_4^-$ (21, 22) and corrected for oxygen isotopic composition with the data of Nier (36). The data were corrected for fractionation and normalized to a $^{187}$Re/$^{188}$Os ratio of 3.0826 as given by Nier (37). Total analytical blanks measured during the course of this study were on average, 12 pg for Re and 2 pg for Os. Samples designated "IVC" are from collections at the University of Vienna (24). Those samples designated "BI" are from the Smithsonian Institution. Those samples designated "J" are from the collections of Jones (11).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Re (ppb)*</th>
<th>$^{188}$Os (10$^{-15}$ mol/g)</th>
<th>Total Os (ppb)†</th>
<th>$^{187}$Os (%)</th>
<th>$^{187}$Re/$^{188}$Os</th>
<th>$^{187}$Re/$^{188}$Os‡</th>
<th>$^{187}$Os/$^{188}$Os§</th>
<th>$^{187}$Os/$^{188}$Os∥</th>
</tr>
</thead>
<tbody>
<tr>
<td>IVC 8901</td>
<td>0.0056</td>
<td>177</td>
<td>0.255</td>
<td>2.4</td>
<td>0.1063 ± 0.022</td>
<td>0.8839</td>
<td>0.1819 ± 0.20</td>
<td>1.512</td>
</tr>
<tr>
<td>IVC 8902</td>
<td>0.0078</td>
<td>61.4</td>
<td>0.0889</td>
<td>2.7</td>
<td>0.2766 ± 0.066</td>
<td>3.555</td>
<td>0.2087 ± 0.30</td>
<td>1.734</td>
</tr>
<tr>
<td>IVC 2069</td>
<td>0.0155</td>
<td>89.4</td>
<td>0.129</td>
<td>2.0</td>
<td>0.5841 ± 0.078</td>
<td>4.855</td>
<td>0.1528 ± 0.24</td>
<td>1.270</td>
</tr>
<tr>
<td>(replicate)</td>
<td>0.0153</td>
<td>38.2</td>
<td>0.0551</td>
<td>2.1</td>
<td>1.344 ± 0.11</td>
<td>11.17</td>
<td>0.1616 ± 0.80</td>
<td>1.343</td>
</tr>
<tr>
<td>IVC 3395</td>
<td>0.0041</td>
<td>213</td>
<td>0.307</td>
<td>2.2</td>
<td>0.06403 ± 0.085</td>
<td>0.5322</td>
<td>0.1654 ± 0.14</td>
<td>1.375</td>
</tr>
<tr>
<td>Bosumtwi glasses</td>
<td>0.0727</td>
<td>78.9</td>
<td>0.125</td>
<td>10.8</td>
<td>3.099 ± 0.29</td>
<td>25.8</td>
<td>0.9009 ± 0.49</td>
<td>7.49</td>
</tr>
<tr>
<td>BI 2020</td>
<td>0.112</td>
<td>14.2</td>
<td>0.049</td>
<td>57.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Many of these Re concentrations are so low that in some cases (8 of the tektites) the abundances are only several times higher than our laboratory blank. For these samples, this leads to higher actual uncertainties in $^{187}$Re/$^{188}$Os than the formal uncertainties quoted in column six, which are based on spike calibrations and mass spectrometric uncertainties. This larger uncertainty, which is difficult to estimate accurately, does not affect our conclusions.
†The values for $^{187}$Re/$^{188}$Os and $^{187}$Os/$^{188}$Os are calculated from measured $^{187}$Re/Os (column 6) and measured $^{187}$Os/$^{188}$Os (column 8) with a $^{188}$Os/$^{188}$Os ratio of 0.1203. This $^{188}$Os/$^{188}$Os ratio is the average obtained on Os standards at the Department of Terrestrial Magnetism, Carnegie Institution of Washington, and is within errors of other reported $^{186}$Os/$^{188}$Os determinations on standards (16, 21). Reporting Os isotopic compositions normalized to $^{188}$Os is inherently a better approach than reporting data normalized to $^{186}$Os because $^{188}$Os is a higher abundance isotope on which higher precision data are obtained and is not subject to contributions from the radioactive decay as is $^{186}$Os (from $^{186}$P). Moreover, it is usually measured directly, and $^{188}$Os normalization requires assumptions about which are the best values to use for $^{186}$Os. Normalized data for $^{188}$Os are presented here simply to facilitate comparison to literature data (20).
ed on the basis of published analyses of sedimentary or igneous continental crustal rocks (33). Abundances of Os in the Bosumtwi rocks are relatively high (0.02 to 0.32 ppb), whereas Re abundances are rather low (0.015 to 0.22 ppb) (33, 34). Compared to the target rocks, the tektites have much lower Re abundances but similar Os contents.

Large differences were found for the isotopic ratios between target rocks and the tektites (Table 1). The $^{187}\text{Os}/^{188}\text{Os}$ ratios of the tektites vary from 0.153 to 0.209 (the $^{187}\text{Os}/^{188}\text{Os}$ ratios were 1.34 to 1.73). These values overlap the data field for meteorites (Fig. 1). The ratios are low for all four tektite samples and are inconsistent with values for old silicic continental crust. Carbonaceous chondrites (16, 17) and iron meteorites (16, 18, 35) fall on a data array of 4.56 billion years (Fig. 1). With one exception, the tektites plot on or to the left of the meteorite data array. All target rocks have high (crustal) $^{187}\text{Os}/^{188}\text{Os}$ ratios, ranging from 1.48 to 4.98 ($^{187}\text{Os}/^{188}\text{Os}$ ratios are 12.39 to 41.37) (Table 1). These values are clearly different from those of the tektites (Fig. 2). With one exception (granodiorite sample J 508), the target rocks have remarkably low $^{187}\text{Re}/^{188}\text{Os}$ ratios for their elevated $^{187}\text{Os}/^{188}\text{Os}$ ratios. For the graywacke and microgranite target rocks, a complicated, multistage crustal history is required. They must have had a much higher $^{187}\text{Re}/^{188}\text{Os}$ ratio initially, then lost Re before the present. The $^{187}\text{Re}/^{188}\text{Os}$ ratios in the Bosumtwi graywackes also are lower than expected for closed-system behavior, but Esser (34) found that Re can be mobile during sediment formation. A significant crustal Re and Os contribution from 2-billion-year-old continental crust with typically high Re/Os ratios would have caused elevated $^{187}\text{Re}/^{188}\text{Os}$ ratios coupled with elevated $^{187}\text{Re}/^{188}\text{Os}$ ratios in the tektites so that they would be expected to plot to the right of the meteorite data array.

The Bosumtwi impact glass has an isotopic composition intermediate between the target rock and tektite values. In addition, the tektites also plot off the meteorite data array toward the characteristic low $^{187}\text{Re}/^{188}\text{Os}$ and high $^{187}\text{Os}/^{188}\text{Os}$ values of the target rocks. This overall relation between the samples indicates not only that some of the Os in the tektites is derived from the Bosumtwi country rocks but also that these target rocks in particular can account for the tektite Re-Os isotopic compositions. The large difference in isotopic ratios between the target rocks and the tektites, though, indicates that the fraction of target rock–derived Os in the tektites does not exceed 10% of the total Os content in the tektites (requiring loss of Os during tektite formation), because otherwise the isotopic values would not remain close to meteoritic ratios. From the abundances and isotopic ratios of this study and previously measured values for chondrites (16, 17), we estimate that the total meteoritic contribution to the tektite composition is $\leq 0.6\%$. This amount of meteoritic component would also help to explain the higher concentrations in tektites of elements such as Ni, Co, or Cr compared to their concentrations in the target rocks; however, the enrichment factors and elemental ratios of these elements are quite variable, which makes it difficult to relate them to any specific meteorite class (11) without assuming fractionation of the siderophile elements during impact.

The Re-Os data show (Fig. 3) that during impact, crustal rocks from the Bosumtwi crater were mixed with the meteorite (represented by the meteorite data array). Because of the high abundance of Os in meteorites, incorporation of only about 0.6% of an extraterrestrial component was sufficient to significantly lower the $^{187}\text{Os}/^{188}\text{Os}$ ratio from the values for the crustal ratios of the target rocks (1.5 to 5) to near-meteoritic values in the tektites (0.15 to 0.21). From the data shown in Fig. 3, it seems that the sedimentary rocks from Bosumtwi were more important for the mixture than the rocks from the Pepliase intrusion (sample J 508). Two of the tektites have $^{187}\text{Re}/^{188}\text{Os}$ ratios that are lower than can be explained by mixing. The low Re values could indicate that some Re was lost during the impact (9), and mixing calculations that successfully model the Os isotopic composition of the tektites suggest substantial Os loss. Such Re and Os fractionation during the impact process may be in general agreement with sidereal element fractionation observed at other craters (12, 13).

In conclusion, the low, near-meteoritic $^{187}\text{Os}/^{188}\text{Os}$ ratios in the tektites are unambiguously evidence for an extraterrestrial contribution to the chemical composition of the tektites, which is otherwise indistinguishable from that of old continental crust. We estimate that the meteoritic contribution is 0.6% or less. The Bosumtwi target rocks have variable Os contents that are quite high in some samples, and it appears that both Re and Os were lost during the tektite formation process. As a
greater implication, high abundances of elements such as Ir or Os may therefore be ambiguous as sole indicators of an impact origin or a cosmic component in impact-derived rocks. However, the 187Os/188Os ratios in all rocks from the Bosumtwi crater are high and typical for old continental crust, which supports the conclusion that the bulk of the Os in the tektites is of extraterrestrial, and not crustal, origin. The 187Os/188Os ratios in the Denny Coast tektites are compatible with those in both chondritic and iron projectiles, but the Cr enrichment in the tektites seems to favor a projectile of chondritic composition. These results support the conclusion that no endogenic process can explain the origin of tektites and that the first, high-temperature ejecta formed during impact melting contain a small but significant projectile component.

REFERENCES AND NOTES

4. C. Koeberl, ibid., p. 1033.
20. Most previous studies report Os data normalized to 188Os, for example, 187Os/188Os. In this study, we adopt a conversion of normalization to 187Os [R. M. Slaiman, R. W. Carlson, S. B. Shirley, Nature 359, 718 (1992)]. This normalization is intrinsically better because 187Os, not 188Os, is the nonradiogenically derived Os isotope directly measured by all researchers (Table 1).
31. ε44 and ε48 are defined as the deviation in parts in 10^6 of the 143Nd/144Nd and 87Sr/86Sr ratios, respectively, of a sample compared to a reference reservoir at the same geologic time (in this case, the present). For Nd isotopes, this reference reservoir is usually taken to be a hypothetical mantle growth curve approximated by the isotope evolution of chondritic meteorites. Positive ε44 values are produced by long-term depletion of light rare earth elements; negative ε44 values are produced by long-term enrichment of light rare earth elements. For Sr isotopes, this reference reservoir is usually taken to be a hypothetical “bulk earth” growth curve in part derived from the isotopic composition of mantle-derived rocks. Positive ε85 values are produced by long-term high Rb/Sr ratios; negative ε85 values are produced by long-term low Rb/Sr ratios. See G. Faure, Principles of Isotope Geology (Wiley, New York, ed. 2, 1986).