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Review Paper

Re–Os isotope systematics as a diagnostic tool for the study of impact craters and distal ejecta

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Abstract

The Re–Os isotopic system is based on the β-decay of ^{187}Re to ^{187}Os (half-life = 42.3 ± 1.3 Ga). During partial melting of mantle rocks, Os remains in the residue but Re is enriched in the melt. Thus, crustal rocks have high Re and low Os concentrations and the crustal ^{187}Os/^{188}Os ratio increases rapidly with time. The present-day ^{187}Os/^{188}Os ratio of mantle rocks is about 0.13. Meteorites also have low ^{187}Os/^{188}Os ratios of about 0.11–0.18. Osmium is much more abundant in meteorites than Re, leading to only small changes in the meteoritic ^{187}Os/^{188}Os ratio with time.

Old continental crust has ^{187}Os/^{188}Os ratios of about 0.67–1.61, which are distinctly different from the meteoritic values. This allows the use of Re–Os isotope systematics for the study of impact craters and ejecta. Impact melts, breccias, and different materials in ejecta consist of terrestrial target rocks, in some cases mixed with a very small ($<1\%$) admixture of recondensed projectile material, the so-called meteoritic component. Up to the 1990s, this component has been identified in the form of significantly enhanced abundances of some siderophile elements. Because of the high Os abundances in meteorites, the admixture of only a small meteoritic component to crustal target material will drastically change the Os isotope characteristics of the resulting breccias or impact melt rocks.

The recent development of negative thermal ionization mass spectrometry allowed the determination of abundances and isotopic ratios of Os and Re at low abundance levels and using relatively small amounts of material. We review the results of Re–Os isotope studies of material from various impact craters, e.g., Bosumtwi (Ghana), Kalkkop, Saltpan, and Vredefort (South Africa), Chicxulub (Mexico), Manson (U.S.A.), Sudbury (Canada), and at the K–T boundary. Re–Os isotope systematics allow the determination and quantification of the meteoritic component in impact-derived materials (in comparison to target rocks) and may help to understand the mixing between the bolide and target rocks. An interesting application of this method is the confirmation of an impact origin for unusual sedimentary layers of possible impact origin or structures of doubtful geological origin (which may be of importance for eroded structures). The study of Os isotopes may become a tool of similar diagnostic power as the study of shock metamorphism in confirming impact structures. © 1997 Elsevier Science B.V.

Keywords: Re/Os; isotope ratios; impact craters; ejecta; K–T boundary

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1. Cratering and detection of meteoritic components

Impact cratering is one of the most important geological processes that shape and modify the surfaces of terrestrial planets, asteroids, and satellites. However, while impact craters are relatively easy to discern on the surface of the Moon, terrestrial processes, such as volcanism, tectonics, and erosion, conspire to obliterate the impact cratering record on the Earth, and make detection of impact craters difficult. About 150 impact structures are known on Earth. Details of the formation of impact structures, the variety of impact lithologies, and the use of shock metamorphism to identify them, are described in the literature (see, e.g., French and Short, 1968; Stöffler, 1972; Melosh, 1989; Stöffler and Langenhorst, 1994; Koeberl, 1994a).

The detection of meteoritic components in impact-derived rocks, directly at the crater (e.g., in autochthonous and allochthonous impact breccias and melt rocks) or in distal ejecta, is of great diagnostic value. The presence of such a meteoritic component can be decisive in assigning an impact origin for a certain structure or an ejecta layer. The discovery of a possible extraterrestrial component in the Cretaceous–Tertiary (K–T) boundary clay prompted Alvarez et al. (1980) to postulate that a large asteroid or comet impact was responsible for the environmental catastrophe at 65 Ma that led to one of the largest mass extinctions in Earth history. In impact crater research, the evidence for an impact origin is ambiguous for a number of structures. While there are various criteria for the identification of impact craters, only one criterion has been accepted as providing unambiguous evidence for an impact origin: the discovery of shock metamorphic effects, as no such effects have ever been confirmed in nature related to non-impact processes (see, e.g., Sharpton and Grieve, 1990; Stöffler and Langenhorst, 1994; Koeberl, 1994a, for reviews of this topic). However, many craters are deeply eroded, obscuring any shock record, or, in the case of ejecta layers, shocked rocks and minerals are very rare, making their discovery unlikely. Thus, the detection of a clear extraterrestrial component can provide decisive evidence for the impact origin of a structure.

However, the detection of a meteoritic component in most impact glasses, melt rocks, and breccias, is not without problems. Impact-derived rocks (impactites) form from terrestrial target rocks, while the impactor (the so-called projectile) is completely vaporized as a result of the enormous temperatures that are released during a hypervelocity impact. Strictly speaking, this is true only for craters that are larger than about 1.5 km in diameter; in smaller craters a minor part of the impactor may survive. Minor amounts of the recondensed meteoritic vapor may be mixed with the vaporized, molten, or shocked and brecciated target rocks. The first studies of meteoritic contamination at terrestrial impact craters were the result of an attempt to provide ground truth for our understanding of meteoritic admixtures observed in lunar rocks (e.g., Morgan et al., 1975; Palme et al., 1978, 1979; Palme, 1982).

It is extremely difficult to differentiate this minute meteoritic contamination from the compositional signature of the normal terrestrial target rocks, which make up usually >99% of the impactites. However, as some characteristic siderophile trace elements are much more abundant in meteorites than in terrestrial crustal rocks, they can be used to identify the presence of an extraterrestrial component in impact rocks. A strong enrichment in siderophile elements in impact melts is usually indicative of the presence of either a chondritic or an iron meteoritic component. Achondritic projectiles are much more difficult to detect, because they have significantly lower abundances of the key siderophile elements. Among the elements commonly used for these studies are Ni, Co, Cr, and interelement ratios. Chondrites have high abundances of Cr (typically about 0.26 wt%), whereas iron meteorites have Cr abundances that are much more variable, but typically about 100 times lower than those of chondrites. Enrichments in Cr and low Ni/Cr or Co/Cr ratios can, thus, be used to distinguish between iron and chondritic projectiles (e.g., Evans et al., 1993), but, as Co, Cr, and Ni are rather common elements on the Earth, their enrichments may be ambiguous.

Better suited for the identification of a meteoritic component are the platinum-group elements (PGEs: Ru, Rh, Pd, Os, Ir, Pt) and Au (e.g., Morgan et al., 1975; Palme et al., 1978, 1979; Morgan and Wandless, 1983; Evans et al., 1993). The abundances of the PGEs in chondrites and iron meteorites are several orders of magnitude higher than those in terrestrial crustal rocks. Chondrites contain about 400–800 ppb Ir and Os (depending on the chondrite type), whereas the abundances of Ir and Os in the continental crust are on the order of 0.02 ppb (e.g., S.R. Taylor and McLennan, 1985; see Table 1). Thus, the signal to background ratio is very high for the PGEs, and the addition of only minor amounts of chondritic material to crustal target rocks will result in significantly elevated abundances of the PGEs in the melt rocks or breccias. For example, mixing of as little as 1 wt% of a chondritic meteorite with average terrestrial crustal rocks will result in an Ir content of 4 ppb in the impactite. The enrichment of Ir and other PGEs in specific impactites is, thus, often taken as good evidence for the presence of a meteoritic component (see, e.g., Morgan et al., 1975; Palme et al., 1978; Palme, 1982; Evans and Chai, 1997-this issue). In a number of these studies, PGE abundances and interelement ratios were used in an attempt to resolve the type or class of meteorite (e.g., Morgan et al., 1975; Palme et al., 1978, 1979; Evans et al., 1993). The projectile type was determined in such way for about one dozen terrestrial craters (e.g., Grieve, 1991).

The abundance of Au and the Au/Ir ratio has also often been used to distinguish between cosmic and terrestrial signature (Palme, 1982). However, Au is much more mobile than Ir under most conditions, which may lead to non-chondritic Ir/Au ratios even if a meteoritic component is present in impact-derived rocks. Specifically, Au often shows high indigenous abundances in some terrestrial rocks, yielding low (non-chondritic) Ir/Au ratios. Matters are further complicated by the fact that PGEs are enriched in certain terrestrial rock types (see Section 3.2 on Ivory Coast tektites). The PGE patterns of the mantle and in some mantle-derived rocks may be similar to those of chondrites, and the PGE abundances in mantle rocks are also higher than those in the crust by factors of about 10^2–10^3, making a distinction between an exposed mantle section or a component in the impactites derived from an ultramafic precursor rock and a meteoritic component quite difficult, if not impossible.

For unambiguous identification of a meteoritic component, abundances of PGEs and other sidero-

Table 1
Average abundances of Re and Os in terrestrial and extraterrestrial materials

Rock [Reference]	Re (ppb)	Os (ppb)	Re/Os
CI chondrites [1]	36.5	486	0.075
Allende (CV3 chondrite) [2]	68.6	851	0.081
Ordinary chondrites [3]	57	660	0.086
IIAB iron meteorites [4]	1.39–4799	12.7–65270	0.073–0.11
IIIAB iron meteorites [4]	2.83–1444	17.1–18430	0.078–0.202
Juvinas eucrite [5]	0.01	0.018	0.55
Moore County eucrite [5]	0.06	0.44	0.136
Peridotite [3]	0.43	5.3	0.081
Tholeiite basalt [3]	0.84	0.03	28
Amphibolite [6]	0.44	0.011	40
Gneiss [6]	0.049	0.011	4.45
Granite (U.S.A.) [6]	0.077	0.033	2.33
Granite (Australia) [6]	0.22	0.007	31.4
Sandstone [7]	0.033	0.019	1.74
Avg. Upper Continental Crust [8]	0.5	0.02	25

Data from: [1] Anders and Grevesse (1989); [2] Walker and Morgan (1989); [3] Allègre and Luck (1980); [4] Morgan et al. (1992); [5] Mason (1979); [6] Walker et al. (1991); [7] Koeberl et al. (1994a); [8] S.R. Taylor and McLennan (1985).

phile elements in impactites need to be compared with those in the target rocks. Ideally, the indigenous concentrations should be subtracted from the abundances found in the impact melt rocks, and yield the "pure" meteoritic abundance ratios (e.g., Morgan and Wandless, 1983). This is often difficult, because the target rocks are not always exactly known, or because of very low or highly variable indigenous PGE concentrations (see, e.g., Schmidt and Pernicka, 1994; Pernicka et al., 1996).

Another complication is introduced by complex fractionation processes that seem to take place during the formation of impact glasses and melts. In recent studies of impact glasses from some small craters for which the meteorite has been partly preserved (e.g., Meteor crater, Wabar, and some Australian craters), it was found that the siderophile elements show strong fractionations that do not show any obvious correlations with any physical or chemical properties of the elements (Attrep et al., 1991; Mittlefehldt et al., 1992a,b). Mittlefehldt et al. (1992b) proposed that the siderophile elements may have been fractionated from each other during the early phases of the impact, while the projectile was undergoing decompression and before mixing with the target materials, although they were unable to explain the fractionations with any single model. Other fractionation effects have been documented for distal ejecta from the K–T boundary impact at various localities around the world (see Evans et al., 1993; Evans and Chai, 1997-this issue).

A further complication is the possibility of siderophile element fractionation in the impact melt while it is still molten. This effect may be significant in larger craters, because there the melt can stay hot for many thousand years. Different mineral phases, such as sulfides or oxides (e.g., magnetite, chromite), may take up various proportions of the PGEs or other siderophile elements, leading to an irregular distribution of these elements and possibly fractionated interelement ratios and patterns. Such irregular distribution of siderophiles is known from, for example, the East and West Clearwater impact structures (Palme et al., 1979), or the Chicxulub impact structure (Koeberl et al., 1994d). Hydrothermal processes associated with the hot impact melt may also change PGE abundances. All these problems can make an identification of a meteoritic component, and, especially, of a specific projectile type, very difficult and can yield fortuitous results. Thus, a more selective method of the identification of a meteoritic component would be very valuable.

2. The Re–Os isotope system

The study of the isotopic composition of Os, together with Re and Os abundance determinations, provides such a selective method as mentioned above. The effectiveness of this method is based on some characteristics of the Re–Os isotopic system and the geochemical behavior of these elements (see, e.g., Faure, 1986; Shirey, 1991).

The element rhenium has two naturally occurring isotopes, ^{185}Re and ^{187}Re, with abundances of 37.4% and 62.6%, respectively. ^{187}Re is radioactive and decays via β-decay into ^{187}Os with a half-life of 42.3 ± 1.3 Ga (Lindner et al., 1989). Osmium has seven naturally occurring isotopes, which are all stable. The isotopes and their abundances (in parentheses; given in %) are: ^{184}Os (0.024), ^{186}Os (1.600), ^{187}Os (1.510), ^{188}Os (13.286), ^{189}Os (16.252), ^{190}Os (26.369), and ^{192}Os (40.958) (Faure, 1986).

The amount of ^{187}Os increases with time as a result of the decay of ^{187}Re. This decay can be described by normalizing to an Os isotope not affected by radioactive decay:

$$^{187}\mathrm{Os}/^{188}\mathrm{Os} = (^{187}\mathrm{Os}/^{188}\mathrm{Os})_{\mathrm{i}} + {}^{187}\mathrm{Re}/^{188}\mathrm{Os}(e^{\lambda t} - 1)$$

where ^{187}Os/^{188}Os and ^{187}Re/^{188}Os are the measured ratios of these isotopes; (^{187}Os/^{188}Os)$_{\mathrm{i}}$ is the initial isotopic ratio at the time when the system became closed for Re and Os; λ is the decay constant ($\ln 2/t_{1/2}$); and t is the time elapsed since system closure for Re and Os. Normalization to ^{188}Os is preferred over ^{186}Os, because ^{188}Os is the isotope actually measured by most workers. With this equation it is possible to calculate an "age" if the initial isotopic ratio of Os is known. Alternatively, it is possible to calculate the initial Os isotopic ratio from a suite of samples with the same age, in analogy to the Rb–Sr method (Faure, 1986; Shirey, 1991). It was not until the early

1980s, that advances in analytical techniques (Allègre and Luck, 1980) made it possible to use the Re–Os method for dating of meteorites (e.g., Luck and Allègre, 1983). The Re–Os isotopic method is particularly useful for studying meteorites (e.g., Walker and Morgan, 1989; Horan et al., 1992; Morgan et al., 1992) or the evolution of the Earth's mantle (e.g., Allègre and Luck, 1980; Walker et al., 1989; Martin, 1991; Ellam et al., 1992; Hauri and Hart, 1993; Carlson and Irving, 1994).

The geochemical behavior of Re and Os sets the Re–Os system apart from all other radioactive isotope systems, where parent and daughter elements are incompatible in mantle rocks. In contrast, Os is strongly retained in the mantle during partial melting of mantle rocks and remains in the residue, while Re is moderately incompatible and is, therefore, enriched in the melt. This behavior results in high Re, but low Os, concentrations in most crustal rocks. Present-day mantle has a low ^{187}Os/^{188}Os ratio of about 0.13, and meteorites also have low ^{187}Os/^{188}Os ratios of about 0.11–0.18 (^{187}Os/^{186}Os = 0.95–1.5) (see, e.g., Walker and Morgan, 1989; Martin, 1991; Horan et al., 1992; Morgan et al., 1992; Smoliar et al., 1996). Most meteorites, especially chondrites and iron meteorites, have relatively high Re and Os contents. An exception are the achondrites (e.g., eucrites), which are the product of magmatic differentiation on asteroidal bodies, and which have low Re and Os abundances. The Earth's mantle has Re and Os abundances that are much lower than those in meteorites, but a Re/Os ratio that is indistinguishable from that of meteorites. The abundances of Os in crustal rocks are much lower than even in mantle rocks and the Re/Os ratios are significantly different from those of mantle rocks or meteorites (see Table 1 for data).

Differences in the Re/Os ratio between meteorites and continental crustal rocks lead to differences in the increase of the radiogenic isotope ^{187}Os, as shown in Fig. 1. The ^{187}Os/^{188}Os ratio in meteorites and mantle rocks changes relatively slowly with time, whereas the crustal ^{187}Os/^{188}Os ratio increases more rapidly with time because of the high Re abundances. ^{187}Os/^{188}Os ratios of about 0.67–1.61 (with an average of about 1.2) are thought to be representative of upper continental crust (e.g., Esser, 1991; Esser and Turekian, 1993), although it should be noted that the continental crust has a highly variable age and possibly a variable Re/Os ratio.

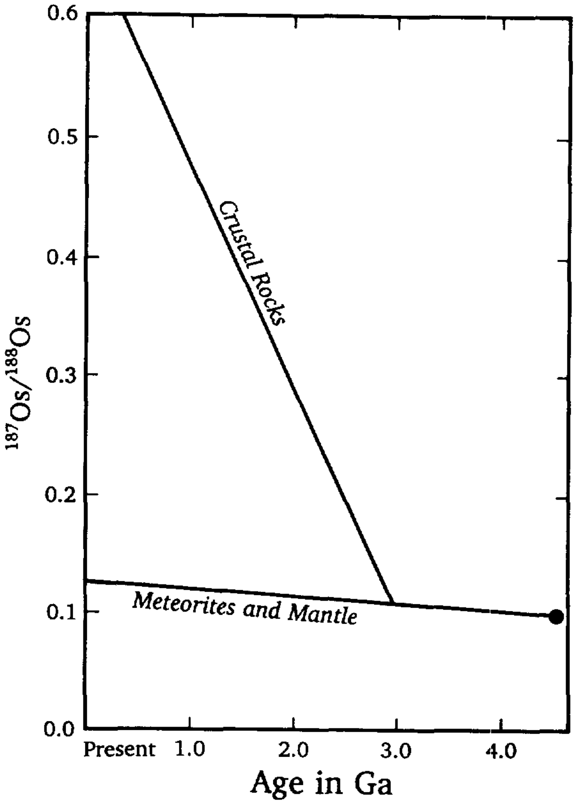

Fig. 1. Schematic evolution of the ^{187}Os/^{188}Os ratio of meteorites and the Earth's mantle and crust, after Faure (1986). The *solid dot* on the right-hand side of the diagram marks the estimates of the isotopic starting composition ($[^{187}\mathrm{Os}/^{188}\mathrm{Os}]_{4.56\mathrm{Ga}} = 0.0965$; Walker and Morgan, 1989) of the Earth's mantle and meteorites 4.56 Ga ago. Due to the relatively low Re/Os ratio of <0.1, the ^{187}Os/^{188}Os ratio increases only slightly with time, as indicated by the *Meteorites and Mantle* line. The *Crust* line follows a hypothetical crustal extraction event 3 Ga ago. During most magmatic processes, including crustal extraction, Os strongly retained in the mantle, while Re partitions somewhat into the melt, leading to Re/Os ratios $\gg 1$ in many crustal rocks. Thus, the ^{187}Os/^{188}Os ratio of crustal rocks increases rapidly with time due to the production of radiogenic ^{187}Os by decay of ^{187}Re, as indicated in the diagram (^{187}Re/^{188}Os ≈ 12). Therefore, many old crustal rocks have ^{187}Os/^{188}Os ratios (and absolute Re and Os abundances) that are distinctly different from those of mantle material and meteorites.

In addition to elemental abundance enrichments, the Re–Os isotopic system adds the Os isotopic composition as a distinguishing factor between terrestrial and meteoritic components in impact craters and ejecta. While high abundances of Os could be due to crustal enrichment processes and incorporation of ore minerals, noncrustal Os isotopic compositions unambiguously indicate the presence of a meteoritic or mantle component. When mantle sources can be excluded on the basis of other evidence, non-crustal Os isotopic ratios provide very good evidence for a meteoritic component in impact-derived rocks. This concept was first suggested by Turekian (1982) for distinguishing between a cosmic and a terrestrial component in Cretaceous–Tertiary (K–T) boundary clays.

Even though the Os isotopic composition adds a new level of discrimination, careful petrologic studies, as well as detailed major- and trace-element analyses, and, if possible, supplementary Rb–Sr and/or Sm–Nd data are essential for complete sample characterization, as components derived from ultramafic precursor rocks may mimic the presence of a meteoritic contribution. From these studies, the presence of an ultramafic component can be detected or excluded, because the much lower Os abundances in mantle rocks compared with meteorites require a much larger ultramafic contribution (compared to meteorites) to explain elevated Os abundances and lower ^{187}Os/^{188}Os ratios (see Section 3.7).

During the first 10 years following Turekian's (1982) suggestion, only a small number of studies of the Os isotopic composition in K–T boundary sediments were performed, mostly because analytical difficulties made the effort truly heroic. The K–T boundary studies are discussed below. The first application of the Re–Os isotopic system in the investigation of impact craters was attempted by Fehn et al. (1986), who used accelerator mass spectrometry (AMS) and found some evidence for a meteoritic component in melt rocks from the East Clearwater crater. Their method, however, had relatively low precision, did not allow the measurement of all relevant Os isotopes or of Re, and required large amounts of sample. No further Os analyses by AMS have been published.

While the number of Re–Os isotopic studies increased after the work by Allègre and Luck (1980), the low Re and Os abundances in impact-derived rocks, and the large amount of sample necessary, prevented wider application for impact crater studies. The situation changed with the development of the negative thermal ionization mass spectrometry (NTIMS) technique for Os isotope measurements (Creaser et al., 1991; Völkening et al., 1991). This method allows the determination of abundances and isotopic ratios of Os and Re at the low abundance levels found in target rocks and in impact-derived rocks while using relatively small amounts of material. The availability of limited amounts of sample material is a problem for many impact glasses or impact melt rocks.

For analysis, after a high-temperature acid digestion step for dissolution of the rocks and isotope equilibration between the spike and the sample Re and Os, Os is separated by double distillation from sulfuric acid, and Re is isolated by anion exchange chromatography (see, e.g., Walker et al., 1989; Ellam et al., 1992; Koeberl and Shirey, 1993b). However, the complete digestion of mineral constituents, as well as the achievement of isotope equilibration between spike and sample Re and Os, have been problematic. Only recently have these problems been solved by the application of the so-called Carius tube digestion method (Shirey and Walker, 1994, 1995).

3. Examples of Re–Os studies of impact craters and distal ejecta deposits

3.1. K–T boundary

The possibility of using Os isotopes to distinguish an extraterrestrial component in the PGE signature at the K–T boundary from simple concentration of crustal PGEs by terrestrial processes was the subject of initial proposal by Turekian (1982). The first such study was that by Luck and Turekian (1983), who analyzed marine manganese nodules and two K–T boundary clay samples. The manganese nodules were found to have ^{187}Os/^{188}Os of about 0.7–1, showing a clear continental crustal signature, while the K–T boundary samples from Stevns Klint (Denmark) and Starkville South (Colorado, U.S.A.) yielded values of 0.200 and 0.155, respectively (Table 2). These results indicate clearly that the enrichment of PGEs at the K–T boundary is not the result of the concentration of PGEs from a crustal source by terrestrial processes (e.g., by elemental mobility; Colodner et al., 1992). Luck and Turekian (1983) concluded that a meteoritic origin of the Os is the most likely explanation.

Subsequently, Lichte et al. (1986) analyzed a sample from the Woodside Creek (New Zealand) K–T boundary clay and found a $^{187}Os/^{188}Os$ ratio of 0.135 (Table 2). Further short reports in abstract form by Krähenbühl et al. (1988), Esser and Turekian (1989), Schmitt (1990), Meisel et al. (1993), and Yin (1995) found comparable values, ranging from 0.137 to 0.212, for K–T boundary samples from Starkville South, Madrid and Berwind Canyon (Colorado, U.S.A.), Raton (New Mexico, U.S.A.), Shatsky Rise (DSDP Leg 577), Stevns Klint, and Sumbar (Turkmenistan); see Table 2. Pegram and Turekian (1993) and Peucker-Ehrenbrink et al. (1994) inferred a sharp decrease in the $^{187}Os/^{188}Os$ ratio of seawater at the K–T boundary (from measurements of the presumed hydrogenous fraction of Os in ferromanganese crusts — at that time there were no direct measurements of the Os isotopic composition of seawater, but cf. Koide et al., 1996), which they attributed to input of a large quantity of exogenous Os from the impactor. The long-term trend of the $^{187}Os/^{188}Os$ ratio of seawater shows a gradual increase over the last 70 Myr from values of about 0.42 to a present-day value of about 1.03 (Pegram et al., 1992), with exception of the minimum at the K–T boundary (0.15). Pegram et al. (1992) also found a decrease of the seawater $^{187}Os/^{188}Os$ ratio at around 34–35 Ma, which could be related to the end-Eocene impact that formed the North American tektite strewn field [see Koeberl (1994b) for a discussion of the North American tektites, and Poag et al. (1994) and Koeberl et al. (1996b) for a discussion of the possible source crater].

The study by Meisel et al. (1995) is the only one, in which the variation of the $^{187}Os/^{188}Os$ ratio across a K–T boundary section (at Sumbar, Turkmenistan), not just in the boundary clay, was actually measured. The results are shown in Fig. 2. A significant and sudden decrease of the

Table 2
Osmium abundances and isotopic data for K–T boundary samples

Boundary locality [Reference]	Os (ppb)	$^{187}Os/^{188}Os$	$^{187}Os/^{186}Os$
Stevns Klint, Denmark [1]	n.r.	0.200 ± 3	1.660 ± 27
Starkville South, CO, U.S.A. [1]	n.r.	0.155 ± 5	1.29 ± 4
Starkville South, CO, U.S.A. [2]	25	0.14	1.2
Starkville South, CO, U.S.A. [3]	21.2	0.148 ± 2	1.232 ± 16
Starkville South, CO, U.S.A. [3]	12.6	0.147 ± 2	1.224 ± 13
Madrid, CO, U.S.A. [3][a]	12.2	0.140 ± 1	1.167 ± 8
Berwind Canyon, CO, U.S.A. [3][b]	18.2	0.140 ± 1	1.164 ± 8
Raton, NM, U.S.A. [3]	36.6	0.138 ± 1	1.145 ± 12
Woodside Creek, New Zealand [4]	60	0.135	1.12
Shatsky Rise (DSDP 577[c]) [5]	n.r.	0.212 ± 8	1.76 ± 7
Stevns Klint, Denmark [6]	n.r.	0.17587 ± 4	1.4618 ± 3
Stevns Klint, Denmark [6]	110	0.1668 ± 3	1.386 ± 3
Sumbar, Turkmenistan [7]	40	0.1369 ± 7	1.138 ± 6

n.r. = not reported. References: [1] Luck and Turekian (1983); [2] Krähenbühl et al. (1988); [3] Esser and Turekian (1989); [4] Lichte et al. (1986); [5] Schmitt (1990); [6] Yin (1995); [7] Meisel et al. (1995). Earlier authors reported only $^{187}Os/^{186}Os$ ratios; data recalculated to $^{187}Os/^{188}Os$ by assuming $^{186}Os/^{188}Os = 0.12031$. Uncertainties quoted in the $^{187}Os/^{188}Os$ ratios refer to the last digits, as given by the respective authors. Some authors did not quote uncertainties.

[a] Madrid: $^{187}Re/^{186}Os = 6.91 \pm 29$ ($^{187}Re/^{188}Os = 0.83 \pm 3$), Re = 2.09 ppb.

[b] Berwind Canyon: $^{187}Re/^{186}Os = 4.51 \pm 25$ ($^{187}Re/^{188}Os = 0.54 \pm 3$), Re = 2.05 ppb.

[c] DSDP 577 locality is in the Pacific Ocean, about 2200 km ESE of Japan and at 2680 m depth.

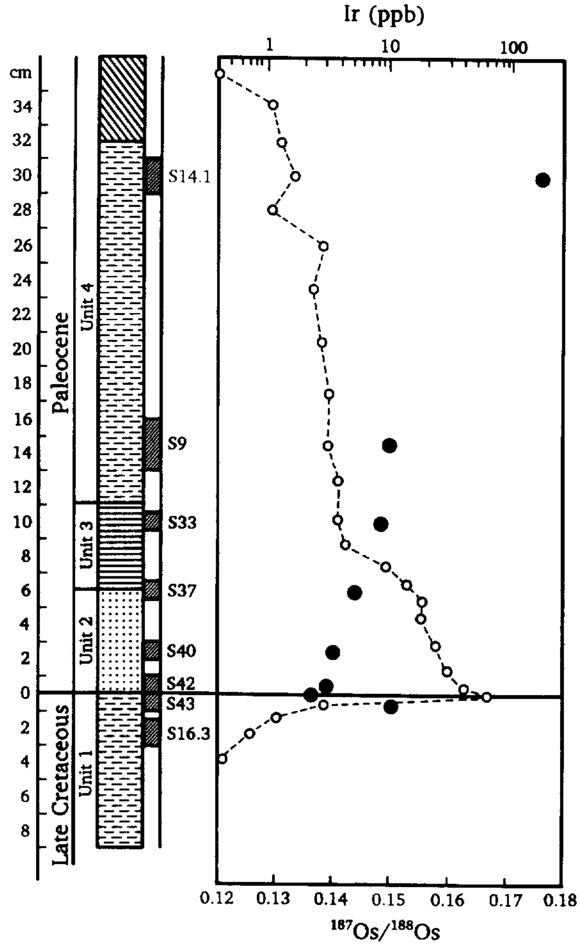

Fig. 2. The variation of the $^{187}Os/^{188}Os$ ratio (*solid dots*) across the Sumbar (Turkmenistan) Cretaceous–Tertiary (K–T) boundary (after Meisel et al., 1993, 1995). The drop in the $^{187}Os/^{188}Os$ ratio at the K–T boundary coincides with the maximum in the Ir distribution (top scale, *open circles*). The low Os isotopic ratio at the K–T boundary is indicative of admixture of extraterrestrial material. The scale on the left gives the distance (in cm) in the section from the K–T boundary clay.

$^{187}Os/^{188}Os$ ratio from the end-Cretaceous rock layers to the actual K–T boundary clay is obvious and correlates with the maximum Ir and Os concentrations; in the early Tertiary rocks, the $^{187}Os/^{188}Os$ ratio increases to higher values. These results provide clear evidence for an extraterrestrial component at the K–T boundary. Despite the potential of these analyses, no other K–T boundary sections, or any other boundary sections, have yet been studied.

3.2. Bosumtwi crater (Ghana) and Ivory Coast tektites

Tektites are natural glasses occurring on Earth in four distinct strewn fields: Australasian, Ivory Coast, Central European, and North American. Geochemical arguments have shown that tektites have been derived by hypervelocity impact melting from terrestrial upper-crustal rocks (see reviews by Koeberl, 1986, 1994b). Tektites occur in three different forms on land (Muong Nong-type, splash-form, and ablation shaped), and as microtektites predominantly in deep-sea cores. The occurrence of microtektites often helps to define the outline of a strewn field (Fig. 3). In contrast to impact glasses, which are found directly in or at the respective source crater, tektites are distal ejecta. This has made the identification of the source crater (and confirmation of an origin by impact) somewhat difficult (Koeberl, 1994b). However, the 11-km-diameter Bosumtwi crater in Ghana was inferred to be the Ivory Coast tektite source crater, based on geographical proximity (Fig. 3), and because the tektites and the crater have the same age (Gentner et al., 1969; Koeberl et al., 1989), similar chemical composition (Schnetzler et al., 1967; Jones, 1985), as well as Rb/Sr (Schnetzler et al., 1966; Kolbe et al., 1967), and oxygen isotopic characteristics (H.P. Taylor and Epstein, 1966; Chamberlain et al., 1993).

In an effort to detect possible meteoritic signatures in tektites, Palme et al. (1978, 1981) analyzed two Ivory Coast tektites by RNAA and found Ir and Os abundances of 0.24 and 0.33 ppb and 0.099 and 0.199 ppb, respectively. These values are higher than those of average crustal rocks, which prompted Palme et al. (1981) to suspect that an iron projectile might have been responsible for the Bosumtwi crater. This suggestion was rejected by Jones (1985), who concluded that the target rocks could supply the high Ir because the Bosumtwi crater is in an area of gold mineralization. Thus, the Ivory Coast tektites were a good candidate for trying out the potential of the Re–Os isotopic method to constrain the meteoritic component. Koeberl and Shirey (1993a,b) determined the

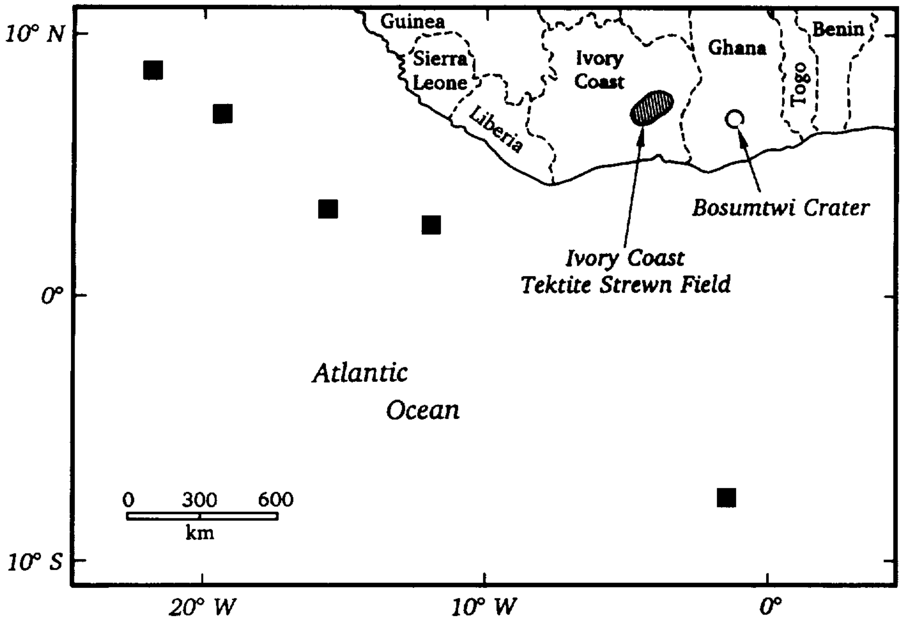

Fig. 3. Geographical location of the Bosumtwi impact crater (Ghana) in relation to the Ivory Coast tektite strewn field, which is generally thought to be derived from the Bosumtwi crater. The *solid squares* indicate locations where Ivory Coast microtektites have been found in deep-sea sediments, thus defining the extent of the strewn field.

abundances and isotopic ratios of Os and Re in four Ivory Cost tektites, two impact glass samples, and five different target rocks from the Bosumtwi crater. The high Os abundances in the target rocks (Fig. 4) seem to confirm the suspicion of Jones (1985) that the PGEs and Au in the tektites could very well be derived from the Bosumtwi country rocks, which have much higher Os contents than normal crustal rocks. No distinction of a cosmic component is possible from these abundance data.

However, the ^{187}Os/^{188}Os ratios of the tektites vary between 0.153 and 0.209 (Table 3). These values overlap the range for carbonaceous chondrites and iron meteorites (Fig. 5), but are inconsistent with the origin of the Os from crustal rocks, as any significant crustal Os contribution would result in elevated ^{187}Os/^{188}Os and ^{187}Re/^{188}Os ratios. Bosumtwi crater target rocks have ^{187}Os/^{188}Os ratios ranging from 1.48 to 4.98 (Koeberl and Shirey, 1993b; Table 3). These values are typical for old continental crust, and clearly different from those of the tektites (Fig. 6). The Bosumtwi impact glass falls between the target rock and tektite values. The variable and relatively high Os abundances in the target rocks indicate that some of the Os in the tektites is derived from the country rocks. The large difference in isotopic ratios, though, indicates that this fraction does not exceed 10–20% of the total Os in the tektites, because otherwise the isotopic values would not remain close to meteoritic ratios. Fig. 6 also provides an explanation for the initially somewhat puzzling observation that most tektites plot to the left of the meteorite data array, as the isotopic composition of the tektites results from mixing of Os from country rocks with Os from a meteorite. Some of the tektite compositions seem to indicate loss of Re. From the isotopic ratios, and based on chondritic abundances, Koeberl and Shirey (1993b) estimated a meteoritic contribution to the tektite composition not exceeding 0.05–0.1 wt%.

3.3. Kalkkop crater (South Africa)

The 640-m-diameter Kalkkop structure is located at 32°42′30″S and 24°26′E, about 48.3 km south-southwest of the town of Graaff-Reinet in the Eastern Cape Province of South Africa. The

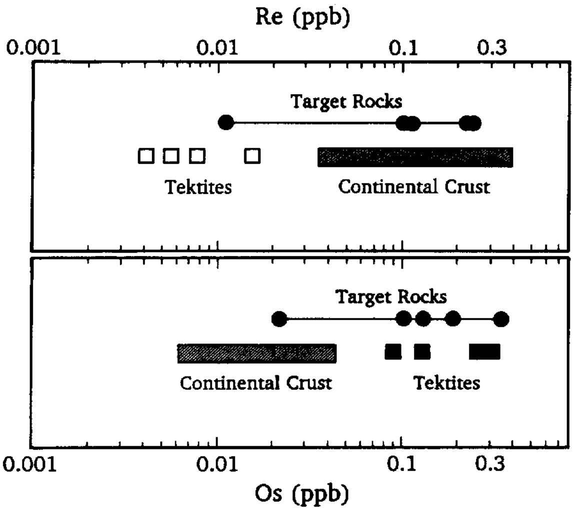

Fig. 4. Range of Re and Os contents in Ivory Coast tektites (*open squares*) and target rocks (*solid dots*) from the Bosumtwi impact crater (cf. Table 3) compared to the range commonly observed in typical upper continental crustal rocks (extreme values are omitted; for data sources see Table 1 and text). The Os contents of the tektites show significant overlap relative to those of the target rocks (which have unusually high Os abundances), making it difficult to determine the presence of an extraterrestrial component in the tektites from abundance data alone.

following description is based on Reimold et al. (1993) and Koeberl et al. (1994c). The basement of the structure consists of sandstone, mudstones, shales, and rare chert lenses. The basement rocks are part of the Beaufort Group of the Karoo Sequence with a stratigraphic age on the order of 225 Ma. The excellent preservation of the structure suggest a Quaternary formation age. In mid-1992, a new vertical bore-hole was drilled to 380-m depth. The stratigraphic record obtained consists of 89.3 m of post-impact crater sediment, which is underlain by a breccia. The breccia contains inclusions of clay minerals that were interpreted by Koeberl et al. (1994c) as altered glass fragments. Some small unaltered glass particles were also found during petrographic studies. Because of the small glass content, the Kalkkop breccia is a suevite. The clast population varies considerably with depth over a scale of meters. Below about 140 m, the clast size increases to larger than 1 m.

Koeberl et al. (1994c) analyzed four suevite samples, from 89.15-, 100.4-, 112.7-, and 130.15-m depth, and two sandstone and shale target rock samples, which were taken from large, unaltered rock clasts encountered in the drill-core. The abundances and isotopic ratios of Os in the target rocks are typical for old continental crust ($^{187}Os/^{188}Os = 0.920$ and 0.613 for sandstone and shale, respectively; Table 4). Two of the suevite samples have Os contents about 10 times higher than values obtained for the target rocks. These samples show low $^{187}Os/^{188}Os$ ratios of 0.215 and 0.333, respectively (Table 4). Such values are distinctly different from the target rock ratios and incompatible with old continental crustal values. Geologic and petrologic studies of the breccias have failed to provide any evidence for the existence of any mafic, ultramafic, or otherwise mantle-derived components. This is evident from the major-element composition, and especially from the Sm–Nd isotopic composition, which for all samples falls in the range of $\epsilon_{Nd} = -7$ to -6 (Koeberl et al., 1994c). This is a range expected for old crustal rocks. Thus, the elevated Os content, together with the near-meteoritic $^{187}Os/^{188}Os$ ratio, demonstrate that the suevite contains about up to 0.05% of an extraterrestrial component. Fig. 7 shows the mixing relationship between target rocks and a meteoritic component for the Kalkkop rocks.

3.4. Saltpan crater (South Africa)

The Saltpan crater is located at 25°24′30″S and 28°04′59″E, about 40 km north-northwest of Pretoria, South Africa. The origin of the crater, either by explosive volcanism or by meteorite impact, has been discussed by various authors earlier this century (e.g., Wagner, 1920; Rohleder, 1933; Milton and Naeser, 1971). The crater formed in 2.05-Ga-old Nebo granite of the Bushveld Complex, and at the crater rim, various intrusive rocks are exposed. These rocks were earlier interpreted as evidence of a volcanic origin of the crater, but are now known to be a feature of the regional geology and not related to the local cratering event (e.g., Reimold et al., 1992; Koeberl et al., 1994a,b; Brandt and Reimold, 1995). In 1988/1989, a drill core was obtained from the

Table 3
Re–Os isotopic data for Ivory Coast tektites and Bosumtwi crater (Ghana) impact glasses and target rocks

Sample	Re (ppb)	^{188}Os (10^{-15} mol/g)	Total Os (ppb)	^{187}Os (%)	^{187}Re/^{188}Os	^{187}Re/^{186}Os	^{187}Os/^{188}Os	^{187}Os/^{186}Os
Ivory Coast tektites:								
IVC 8901	0.0056	177	0.255	2.4	0.1063±22	0.884	0.1819±20	1.512
IVC 8902	0.0078	61.4	0.0889	2.7	0.4276±66	3.555	0.2087±30	1.734
IVC 2069	0.0155	89.4	0.129	2.0	0.5841±78	4.855	0.1528±24	1.270
IVC 2069(2)	0.0153	38.2	0.0551	2.1	1.344±11	11.17	0.1616±80	1.343
IVC 3395	0.0041	213	0.307	2.2	0.0640±9	0.532	0.1654±14	1.375
Bosumtwi crater impact glasses:								
BI 9201	0.0727	78.9	0.125	10.8	3.099±29	25.8	0.9009±49	7.49
BI 9202	0.112	14.2	0.049	57.1				
Bosumtwi crater target rocks:								
J 492 (graywacke)	0.214	178	0.327	24.0	4.03±33	33.5	2.338±38	19.43
J 494 (graywacke)	0.101	54.9	0.128	40.2	6.193±95	51.47	4.978±23	41.37
J 493 (microgranite)	0.01048	45.0	0.0969	35.0	1.104±56	9.180	3.983±67	33.11
J 505 (microgranite)	0.218	98.2	0.1873	26.5	7.45±18	61.92	2.665±15	22.15
J 508 (granodiorite)	0.111	12.3	0.0208	16.7	30.21±69	251.1	1.483±22	12.33

Data after Koeberl and Shirey (1993b). For details on the analyses, see text. Total Os includes radiogenic ^{187}Os, the percentage of which is given in the next column. Uncertainties quoted in the ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios refer to the last digits. Total uncertainties in the ^{187}Os/^{188}Os ratio can be up to ±3 rel.%, based mainly on the error propagation from the uncertainty in the spike calibrations; mass spectrometric uncertainties are usually <1 rel.%.

center of the crater, to a depth of 200 m. The drill core penetrated 90 m of lacustrine sediments that are underlain by 53 m of unconsolidated suevitic breccia. The discovery of shock metamorphic effects in various minerals from the suevitic breccia provided confirming evidence for an impact origin of the Saltpan crater (Reimold et al., 1992). The age of the crater-forming event was determined by fission-track measurements on impact glasses that were isolated from the suevite, showing that the crater was formed at about 220 ka (Koeberl et al., 1994b).

The Re–Os isotope characteristics of basement granites and suevitic breccias from the Saltpan crater were analyzed by Koeberl et al. (1994a) (see Table 4). The Os contents of the two granitic target rocks are 6.3 and 7.0 ppt, respectively, which is consistent with values expected for granite. The ^{187}Os/^{188}Os ratios of those granites are high, with values of 0.713 and 0.736, respectively. Such high values are within the range expected for old crustal rocks (Esser and Turekian, 1993; Koeberl and Shirey, 1993b). In contrast, the Os abundances in the bulk suevitic breccias are more than ten times higher, at 81.4 and 75.5 ppt, respectively. They have low ^{187}Os/^{188}Os ratios of 0.205 and 0.206, respectively. The ^{187}Os/^{188}Os vs. ^{187}Re/^{188}Os diagram (Fig. 8) shows that isotopic ratios of the breccias are consistent with derivation by mixing of a meteoritic component with basement granites.

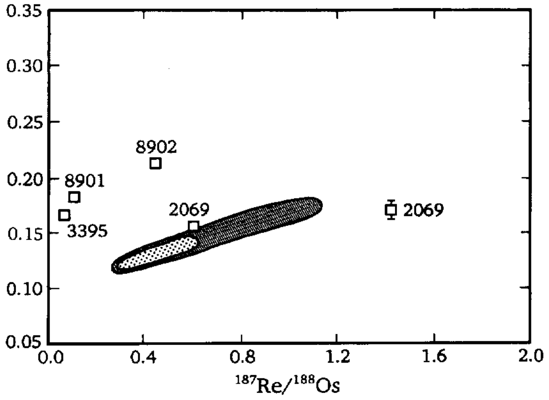

Fig. 5. Ratios of $^{187}Os/^{188}Os$ vs. $^{187}Re/^{188}Os$ for Ivory Coast tektites (*open squares*; sample numbers see Table 3; after Koeberl and Shirey, 1993a,b), plotted together with fields showing the data arrays for carbonaceous chondrites (*dotted area*) and iron meteorites (*shaded area*). Meteorite data after Walker and Morgan (1989), Horan et al. (1992), and Morgan et al. (1992). The tektite data are very close to the meteoritic values (see Fig. 6).

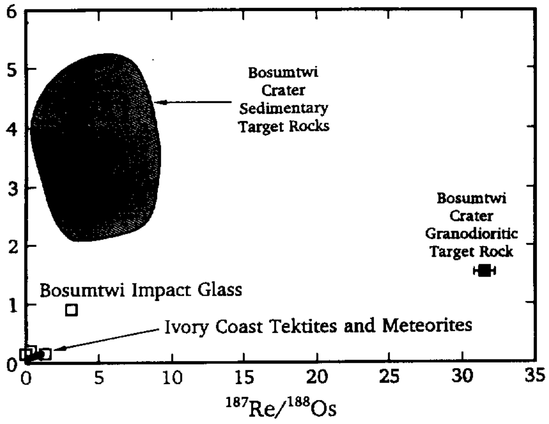

Fig. 6. Ratios of $^{187}Os/^{188}Os$ vs. $^{187}Re/^{188}Os$ for target rocks from the Bosumtwi (Ghana) impact crater and Ivory Coast tektites (*open squares*; sample numbers see Table 3; after Koeberl and Shirey, 1993a,b). The *solid bar* in the lower left-hand corner overlapping the tektite symbols marks the meteorite data array (see Fig. 5). The *hatched area* marks the field defined by the sedimentary Bosumtwi target rocks; a single granodioritic target rock is shown with a *solid square* on the right. Also included is an impact glass sample from the Bosumtwi crater (labelled *open square*).

There is no indication from the petrographical studies and the major- and trace-element chemical composition for the presence of any peridotitic, ultramafic, or any other mantle component in the breccias. After correction of the average Os abundance in the breccias for the indigenous Os content of the granites, an excess of about 0.072 ppb Os is obtained. Assuming an average chondritic Os abundance of 486 ppb (Anders and Grevesse, 1989) results in about 0.015 wt% of a chondritic component in the bulk breccia.

Koeberl et al. (1994a) found that the compositions of the suevites are indistinguishable from those of the granites. Impact glasses isolated from the suevites also show predominantly granitic compositions, with the exception of significant Mg and Fe enrichments. In addition, enrichments in Mn, Cr, Co, Ni, and Ir are obvious in the glasses, but less evident for the bulk suevite. Koeberl et al. (1994b) concluded that these enrichments are the result of a significant meteoritic contribution to the impact glass composition. About 10% of a chondritic component is necessary to explain the elevated abundances of these elements in the impact glasses. An iron meteorite is an unlikely alternative because it cannot explain the enrichments in Mg and Cr. The estimate of 10% chondritic component in the glass fragments can be compared with the result derived from the Re–Os studies for the bulk breccia. Impact glasses make up ≤1 vol% of the suevite, and the hand-picked glasses have been selected mainly because of their brown or green color and make up a subset of about one-tenth of the total number of impact glasses. This rough estimate yields about 0.01 wt% of a chondritic component in the bulk breccia, which agrees well with the 0.015 wt% obtained from the Re–Os studies. The determination of Re and Os concentrations and Os isotope ratios in hand-picked impact glasses was not possible, because only a few mg of the hand-picked glasses were available.

The meteoritic contribution found for the Saltpan impact glasses is rather high compared to glasses or melt rocks at other craters (e.g., Palme et al., 1978; Morgan, 1978; Palme, 1982). An exception is impact melt from the West Clearwater crater with up to about 10% meteoritic contribution (Palme et al., 1979). In addition, the Saltpan crater is the only small crater known to have been made by a chondritic meteorite, in contrast to

Table 4
Re–Os isotopic data for impact breccias and target rocks from the Kalkkop and Saltpan craters, South Africa

Sample	Re (ppb)	^{188}Os (10^{-15} mol/g)	Total Os (ppb)	^{187}Os (%)	^{187}Re/^{188}Os	^{187}Re/^{186}Os	^{187}Os/^{188}Os	^{187}Os/^{186}Os
Kalkkop crater impact breccias:								
Br-1 (89.15)	0.247	166.0	0.244	4.31	5.05±15	41.96	0.334±10	2.773
Br-2 (100.4)	0.076	23.59	0.0354	6.18	10.83±32	89.99	0.487±15	4.049
Br-3 (112.7)	0.062	129.9	0.1886	2.82	1.613±48	13.40	0.2154±64	1.790
Br-4 (130.15)	0.045	25.15	0.0375	5.62	6.04±18	50.17	0.441±13	3.668
Kalkkop crater target rocks:								
Sandstone-107.3	0.033	12.30	0.0194	11.0	8.94±27	74.30	0.920±28	7.645
Shale-131.05	0.053	13.98	0.0213	7.64	12.77±38	106.1	0.613±18	5.098
Saltpan crater impact breccias:								
Breccia-113	0.171	56.3	0.081	2.69	10.8±3	84.7	0.205±4	1.70
Breccia-116	0.110	52.3	0.076	2.71	7.05±21	58.6	0.206±8	1.71
Saltpan crater target granite:								
Basement-136	0.054	4.06	0.0063	8.73	44.9±1.3	373.3	0.713±19	5.92
Basement-154	0.0089	4.50	0.0070	9.00	6.68±20	55.6	0.736±13	6.12

Data after Koeberl et al. (1994a,c). Sample numbers are depths in the drill core in meters. See Table 3 for information on the individual columns.

other small craters (up to a few km in diameter), for which the projectile type is known, which were formed by iron meteorite projectiles (Grieve, 1991).

3.5. Manson crater (Iowa, U.S.A.)

The 36-km-diameter Manson impact structure in north-central Iowa (at 42°35'N, 94°31'W) is the largest well-preserved impact structure in the U.S.A. (Hartung and Anderson, 1988). At the center of the structure, which is covered by a thin veneer of glacial till, granitic basement rocks are present, which have been uplifted from a depth of up to about 4 km. The presence of shock metamorphic features in minerals (e.g., multiple sets of planar lamellae in quartz) provided conclusive evidence that Manson is of impact origin. Interest in Manson was intensified when a possible K–T boundary age was suggested (Kunk et al., 1989). A subsequent core drilling program led to the recovery of 12 cores (named M1 through M11 and M2A) totaling over 1200 m (see papers in Koeberl and Anderson, 1996). The study of some of this core material provided evidence that the Manson structure is not of K–T age, but is about 74 Ma old (Izett et al., 1993).

Koeberl and Shirey (1996) studied seven impact melt rock, breccia, and target rock samples from the M1, M8, and M10 drill cores. The samples consist of relatively complex mixtures of numerous different target rock types and, accordingly, a large variety of breccia types was found (Koeberl et al., 1996a). The Os and Re abundances show a wide range, with Re contents varying from about 0.009 to 0.85 ppb, and Os contents ranging from 0.005 to 2.69 ppb. The lowest Os contents occur in crystalline basement rocks, while the highest Os abundance (2.69 ppb) was found for the fine-grained impact melt rock M-1/429.0. This value would correspond to about 0.5% of a meteoritic (chondritic) component, assuming Cl abundances (Anders and Grevesse, 1989).

This result is confirmed by Re–Os isotopic data (Table 5; Fig. 9a), which show that the impact melt rock M-1/429.0 plots close to the meteoritic data array. Any contribution from mantle rocks to the impact melt rock can be excluded (see Koeberl and Shirey, 1996). The only other sample

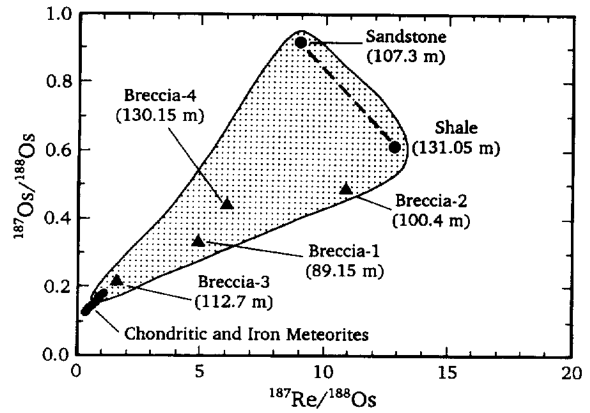

Fig. 7. Ratios of $^{187}Os/^{188}Os$ vs. $^{187}Re/^{188}Os$ for target rocks (shale and sandstone) of the Kalkkop impact crater, South Africa, in comparison with data for four impact breccias (*solid triangles*) and the data array for chondritic and iron meteorites (*small solid dots*; see caption to Fig. 5 for sources). The sample depths in the drill core are given as well (after Koeberl et al., 1994c). The *dotted area* marks the mixing field between target rocks and meteorites. All impact breccias fall within this mixing field; breccia-3 plots very close to the meteorite data array, indicating a larger meteoritic contamination than any other breccia, which is in perfect agreement with the fact that this sample has also the highest Os content of all breccias.

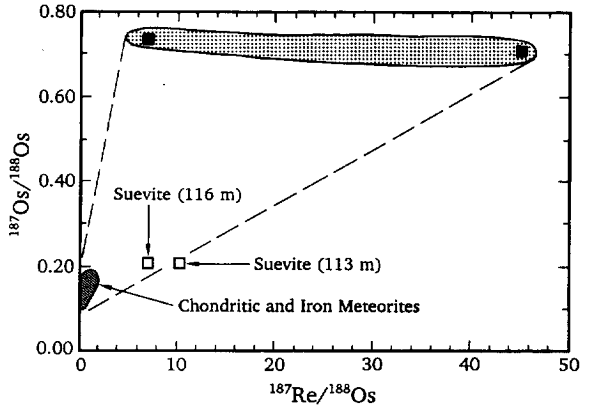

Fig. 8. Ratios of $^{187}Os/^{188}Os$ vs. $^{187}Re/^{188}Os$ for target rocks (Nebo granite, *solid squares*) and impact breccias (suevites, *open squares*) of the Saltpan impact crater, South Africa (after Koeberl et al., 1994a). The *hatched area* in the lower left indicates the data array for chondritic and iron meteorites (see caption to Fig. 5 for sources). The *dotted area* on top marks the isotopic compositions of the target rocks. The data for the suevite samples plot within the mixing field defined by the isotopic compositions of the target rocks and the meteorites, indicating admixture of a small cosmic component. This is also supported by elemental abundance data (see Table 4).

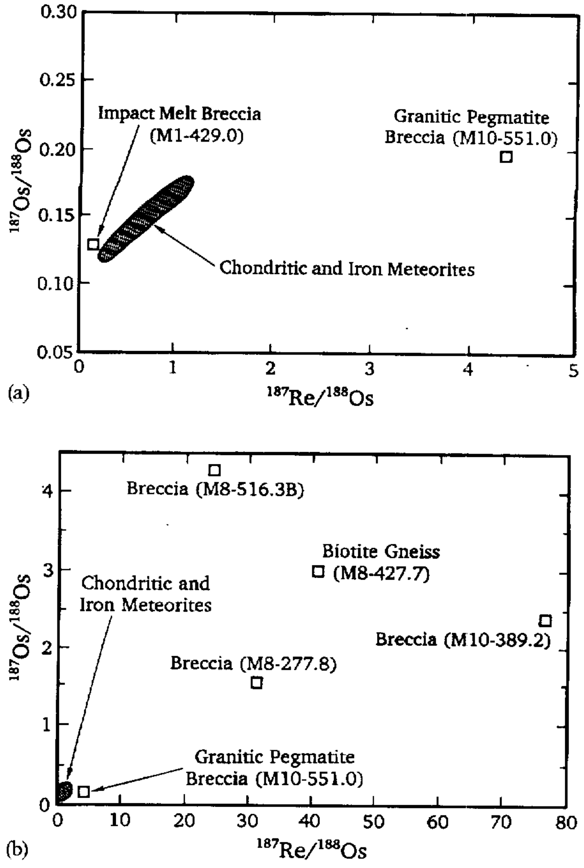

Fig. 9. Ratios of $^{187}Os/^{188}Os$ vs. $^{187}Re/^{188}Os$ for target rocks and impact breccias from the Manson impact crater, Iowa, U.S.A. (after Koeberl and Shirey, 1996).

a. Plot showing the proximity of the datum for the impact melt breccia M1-429.0 to the meteoritic data array (*hatched area*; see Fig. 5 for sources), indicating a significant meteoritic contribution in this sample, which is corroborated by a high Os content in this sample (see text). The granitic pegmatite sample M10-551.0 also has a low Os isotopic ratio.

b. The same diagram with a much more expanded scale, showing the data for several other breccias and target rocks; see text for discussion.

Table 5
Re–Os isotopic data for impactites and target rocks from the Manson (Iowa, U.S.A.) and Chicxulub (Mexico) craters

Sample	Re (ppb)	^{188}Os (10^{-15} mol/g)	Total Os (ppb)	^{187}Os (%)	^{187}Re/^{188}Os	^{187}Re/^{186}Os	^{187}Os/^{188}Os	^{187}Os/^{186}Os
Manson crater impact melt rocks, breccias, and target rocks:								
M-1/429.0 (impact melt rock)	0.0922	1879	2.69	1.69	0.165±4	1.371	0.1276±2	1.061
M-8/277.8 (impact melt breccia)	0.0877	9.51	0.016	17.1	31.0±8	257.6	1.537±5	12.78
M-8/427.7 (biotite-gneiss)	0.8487	70.1	0.139	28.6	40.7±9	338.3	3.000±1	24.93
M-8/516.3B (fragmental breccia)	0.4763	66.4	0.148	37.0	24.1±7	200.4	4.281±47	35.65
M-8/516.3G (granite)	0.1301	1.3	0.0051	58				
M-10/389.2 (impact melt breccia)	0.2657	11.7	0.022	23.8	76.4±1.9	635.4	2.384±64	19.82
M-10/551.0 (granitic pegmatite)	0.0087	6.77	0.0099	2.56	4.31±12	35.81	0.195±2	1.623
Chicxulub impact melt rocks:								
Cl-N10-1A	1.599	17600	25.2	1.5	0.305±6	2.54	0.113±3	0.941
Cl-N10-2	0.952	36.5	0.056	6.3	87.7±1.8	729.1	0.505±15	4.200
Impact glass from the Haitian K–T boundary:								
Beloc	0.107	65.2	0.095	3.3	5.50±16	45.75	0.251±7	2.089

Notes: Data from Koeberl et al. (1994d) and Koeberl and Shirey (1996). See Table 3 for information on the individual columns.

that has a low ^{187}Os/^{188}Os ratio is the brecciated pegmatite M-10/551.0 from the granitic basement, but the datum for this sample is different from the meteoritic data (Fig. 9a). It also has a very low Os content (0.01 ppb). However, as the sample shows minor evidence of impact melting, it is not impossible that its Os isotopic composition was altered by a meteoritic contribution. As this quartz-rich sample is unlikely to have a significant indigenous Os content, the addition of only a very minor meteoritic component (on the order of 0.002%) to this rock would already be enough to change the Os isotopic composition. The addition of a similar amount of meteoritic matter to another basement rock will go unnoticed because of much higher background values.

The breccias M-8/516.3B and M-10/389.2 and the basement biotite gneiss M-8/427.7 define the spread in the Re–Os isotopic composition of the target rocks (Fig. 9b). They all have high ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios (Table 5), which are typical for those of old continental crust (in agreement with Rb–Sr and Sm–Nd data that confirm the old continental crustal provenance of these samples; Blum et al., 1996). The impact melt breccia M-8/277.8 plots between the range of target rock values and the meteoritic data array, and may indicate a minor meteoritic contamination (Koeberl and Shirey, 1996).

3.6. *Sudbury structure (Ontario, Canada)*

The 1.85-Ga-old Sudbury structure is one of the largest impact structures on the Earth, with an original diameter that has been estimated at about 200 km (Grieve et al., 1991). The structure, which has been tectonically deformed and is now mainly exposed in the form of the Sudbury Igneous Complex, has provided one of the largest nickel source of the world. The "Igneous Complex" is exposed as a series of concentric, deformed, rings that dip towards the center of the basin-like structure. A melt rock body (consisting of norite, quartz gabbro, and granophyre) is overlain by brecciated rocks of the Onapping formation and underlain by a sublayer of mafic norite, a so-called Footwall breccia, and other brecciated rocks of the Sudbury breccia (e.g., Grieve et al., 1991; Stöffler et al., 1994). The sublayer contains abundant Fe–Ni–Cu–PGE sulfide mineralization. Over the past several decades, there has been a vigorous discussion regarding the origin of the Sudbury structure, either by volcanism or by meteorite impact (see, e.g., Pye et al., 1984; Deutsch, 1994; Stöffler et al., 1994).

One important question was how the Sudbury Igneous Complex formed in either model. Two alternatives had been proposed, one stating the Igneous Complex had formed from mantle-derived melt that was heavily contaminated by crustal rocks, and other model proposed that it is the result of complex crystallization of extensively remelted ancient crust. The latter model was favored by Faggart et al. (1985) and Grieve et al. (1991) on the basis of Sm–Nd isotope data. The Re–Os isotopic system allows to test these two models. Walker et al. (1991) and Dickin et al. (1992) studied the abundances of Re and Os and the Os isotopic composition of sulfide ore from the Levack West, Falconbridge, Strathcona, and Creighton mines. Walker et al. (1991) were able to obtain Re–Os isochron ages ranging between 1.77 and 1.84 Ga for ores from the different mines. Walker et al. (1991) and Dickin et al. (1992) also found high initial $^{187}Os/^{188}Os$ ratios ranging from 0.56 to 0.91. These high values indicate that the Os in the sulfide ores was derived from ancient crust, with only a minor possible contribution from mantle rocks. While there does not seem to be any evidence for a meteoritic component in the Sudbury ores studied so far, this result still favors the impact origin of the structure, as impact melting is the only mechanism that can fuse the large quantities of crustal rock necessary to form the Sudbury Igneous Complex.

3.7. Chicxulub crater (Mexico)

Geological, geophysical, and petrographic evidence was used to propose the Chicxulub structure in Yucatán, Mexico, as a large buried impact structure (e.g., Hildebrand et al., 1991). Crystalline fine-grained impact melt rocks and impact breccias have been identified in drill-cores from within the structure (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 and impact glasses found at the K–T boundary, mainly in Haiti (Sharpton et al., 1992; Swisher et al., 1992; Krogh et al., 1993). Blum et al. (1993) found that the Rb–Sr and Sm–Nd isotope systematics of Chicxulub impact melt rocks and Haitian impact glasses are identical, and, therefore, inferred that Chicxulub was the source crater for the impact debris found at the K–T boundary. This result was confirmed by studies of shocked zircons from the K–T boundary and rocks from the Chicxulub structure (Krogh et al., 1993). Geophysical studies indicate that Chicxulub may have a diameter of close to 300 km (Sharpton et al., 1993). Thus, there is overwhelming evidence that the Chicxulub impact structure represent the long-sought K–T boundary impact crater. It has remained unknown until now because the structure is presently covered beneath 300–1000 m of Tertiary carbonate rocks of the Northern Yucatán platform.

In some of the impact melt rocks from the Chicxulub 1 (C1) and Yucatán 6 (Y6) drill cores, Ir contents of up to 13.5 ppb were found (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. Koeberl et al. (1994d) studied the Re and Os abundances and Os isotopic compositions of melt rocks from the C1 core. One of the impact melt rock samples contained 25.2 ppb Os, and very low $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ ratios of 0.113 and 0.305, respectively (Table 5). Such values are inconsistent with those of old continental crust, but very close to the meteoritic data array (Fig. 10). Another impact melt rock has only 0.056 ppb Os and a high $^{187}Os/^{188}Os$ ratio of 0.51 (Table 5; Fig. 10), similar to continental crustal values. This result indicates the presence of a heterogeneously distributed meteoritic component in the melt rock, which is supported by the highly variable Ir contents in this rock (Sharpton et al., 1992; Koeberl et al., 1994d; Schuraytz et al., 1994). Recently, Schuraytz et al. (1996) found isolated Ir grains in Chicxulub melt rock, confirming the highly irregular PGE distribution in these rocks. The Os abundance and isotopic data suggest a maximum of 3 wt% chondritic component, which is within the range of meteoritic components reported for large craters (see, e.g., Palme, 1982).

In the case of Chicxulub, the large size of the structure may suggest that mantle material could have been excavated. However, cratering models indicate that the Chicxulub-forming impact event excavated to a depth of 17–20 km, which is within the upper part of the crust. 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, as the samples have depleted mantle Nd model ages of about 1040 Ma and ϵ_{Sr}^{65Ma} and ϵ_{Nd}^{65Ma} values of about +58 and −3, respectively (Blum et al., 1993). Such values are inconsistent 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 −30 to −10.

Thus, major contributions from basaltic, ultramafic, or other mantle-derived material are excluded. MORB and related basalts contain only sub-ppb Os abundances and $^{187}Os/^{188}Os$ ratios

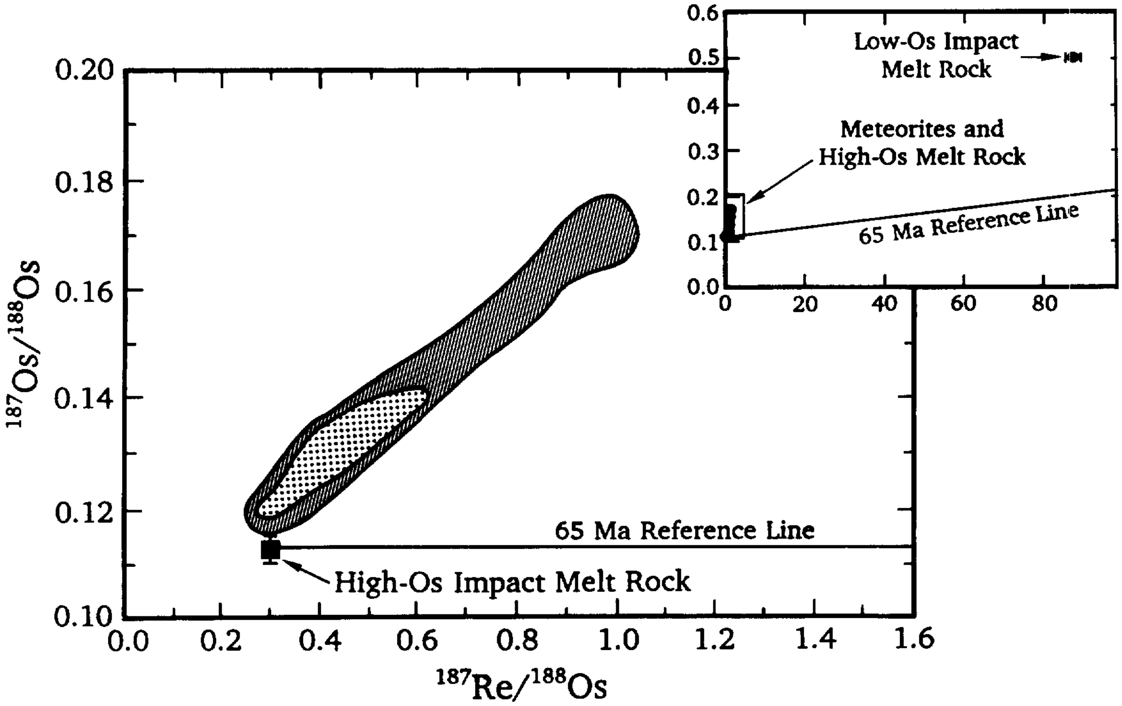

Fig. 10. Ratios of $^{187}Os/^{188}Os$ vs. $^{187}Re/^{188}Os$ for impact melt rock from the Chicxulub impact structure, Mexico (after Koeberl et al., 1994d). Also shown is the data array for meteorites (*hatched area*: iron meteorites, *dotted area*: carbonaceous chondrites; see Fig. 5 for data sources). This impact melt sample also has a very high Os content (25 ppb), clearly indicating a meteoritic contamination. The *inset* shows — at a much expanded scale — the data for another melt rock sample, which has a low Os content, crustal $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ values, and seems to lack an extraterrestrial component.

(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, but Os abundances in xenoliths are too low (2–3 ppb) to explain the high abundances observed in the Chicxulub melt rock. Consequently, the presence of a mantle component in the Chicxulub samples is unlikely.

Koeberl et al. (1994d) also reported Re–Os isotopic characteristics for impact glass from the Haitian K–T boundary (Table 5). The glass was found to contain 0.095 ppb Os, which is higher than the crustal average and the low-Os melt rock from Chicxulub. It has a $^{187}Os/^{188}Os$ ratio of 0.251, which is lower than the average crustal ratio and indicates admixture of meteoritic material (Fig. 10). The Re–Os study of K–T boundary impact glass closes the circle that started with studies of K–T boundary clay samples.

3.8. Vredefort structure (South Africa)

The Vredefort structure is located about 120 km southwest of Johannesburg, with a current diameter of about 100 km. The formation of the Vredefort structure has been dated at 2024 ± 5 Ma from U–Pb ages of zircons as well as (bulk) laser $^{40}Ar–^{39}Ar$ ages, both from pseudotachylitic breccia (Kamo et al., 1995, Spray et al., 1995). Thus, the Vredefort event occurred about 30 Myr after the formation of the Bushveld Complex. The origin of the structure, which may have initially been as large as 300 km in diameter, has been controversial (see, e.g., Reimold, 1993). Only recently, impact-characteristic shock metamorphic effects were found in the form of basal Brazil twins in quartz in Vredefort rocks (Leroux et al., 1994) and planar deformation features (PDFs) in zircon (Kamo et al., 1995).

Granophyric rock dikes with an age of 2 Ga are exposed in the basement core of the structure and along the boundary between the core and the supracrustal rocks of the so-called collar. In the internal model for the origin of Vredefort, it was suggested that the granophyre represents an igneous intrusion (e.g., Bisschoff, 1972). In contrast, in the impact model it was proposed that they represent impact melt that was injected into fractures in the floor of the impact structure (French et al., 1989; French and Nielsen, 1990). In a recent Re–Os isotopic study, Koeberl et al. (1996c) showed that most Vredefort Granophyre samples have considerably higher Os contents than the country rocks from which the granophyre is likely to have been formed by mixing. The $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ ratios of the Vredefort Granophyre scatter about a 2 Ga isochron, with the initial $^{187}Os/^{188}Os$ ratios (at 2 Ga) ranging (with one exception) from 0.13 to 0.22. These values overlap the meteoritic data range and indicate that all the granophyre samples contain some meteoritic Os. In addition, the Re–Os isotopic composition of the granophyre is significantly different from that any of the target rocks (Koeberl et al., 1996c). The presence of a meteoritic component is indicated because an ϵ_{Nd} of -13 for the granophyre, there is little chance that the initial value of 2.0 Ga would have been chondritic, unless it was overprinted by a meteoritic component. Isotopic composition and Os abundance suggests that the Vredefort Granophyre contains up to 0.2% of a chondritic component, confirming that the Vredefort Granophyre represents an impact melt rock.

4. Outlook

The Re–Os isotopic system has been used successfully for the determination and quantification of extraterrestrial components in impact-derived rocks and ejecta. The method may help to understand the mixing between bolide and target rocks and can provide confirming evidence for the impact origin of certain crater structures or sedimentary layers of unusual composition. If carefully and cautiously applied, Os isotope data may be used as a diagnostic tool for the establishment of an impact origin, similar to shock metamorphic effects. Currently, various glasses, melt rocks, and breccias from a number of other structures are being studied. Preliminary results show the existence of meteoritic components in rocks of the Gardnos (Norway; French et al., 1995, 1997) and the Aouelloul (Mauritania) crater structures. It is hoped that similar studies will be made in the future on rocks marking various geological boundaries, to help decide the causes of major extinction events.

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