

# Main Geochemical Signatures Related to Meteoritic Impacts in Terrestrial Rocks: A Review

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**Abstract.** The chemical composition of impact melt rocks, breccias and ejecta layers is dominated mainly by the proportions and composition of target rocks. However, small quantities of vaporized and molten meteorite material mixed with them significantly alter the concentrations and ratios of certain elements and isotopes. The identification of this meteoritic signature is used to propose an impact formation for structures of uncertain origin, as well as a possible criterion for inferring the impactor type. The most common criteria applied to these studies are the detection of a positive siderophile element anomaly, the Re-Os isotopic system, and the Mn-Cr isotopic system. An enrichment in Cr, Ni and Co, at the ppm level, and Os, Re, Ir, Ru, Rh, Pd and Au, at the ppb level, usually indicates the presence of a component containing high abundances of those elements. These ratios help identify the projectile as either a chondrite or an iron meteorite, but do not detect an achondritic projectile. The application of the Re-Os system method is based in the low  $^{187}\text{Os}/^{188}\text{Os}$  ratio of chondritic and iron meteorites, in comparison with present day higher ratio of normal upper crust, and the high Os contents in meteorites compared to crustal rocks. The admixture of a meteoritic component to crustal rocks produces a  $^{187}\text{Os}/^{188}\text{Os}$  anomaly. The Mn-Cr system considers the deviations of the  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios from the standard terrestrial  $^{53}\text{Cr}/^{52}\text{Cr}$  ratio as a result of the addition of an extraterrestrial component. This isotopic study often allows an accurate determination of the impactor type, especially when combined with PGE ratios. The applications and limitations of each method are reviewed.

# 1

## Introduction

The presence of a meteoritic component in impact-derived rocks, either in the crater or in distal ejecta, can be decisive in assigning an impact origin for a certain structure or ejecta layer (Koeberl and Shirey 1997). Some projectiles can be identified from the presence of physical remnants of the meteorite (e.g., Meteor Crater, Arizona). However, the high temperatures during impact usually vaporize impactors larger than around 40 m in diameter (which hardly undergo atmospheric retardation, and encounter the target with relatively undiminished force) (Grieve 1997; Montanari and Koeberl 2000). Also, meteorites are not very resistant towards erosion, and last only a few thousand years (in the case of stony meteorites) or a few tens to hundreds of thousand years (in the case of iron meteorites) on the surface of the Earth. Thus, meteorite fragments usually only survive in young (~0.1 Ma) craters smaller than 1.5 km in diameter. There are some rare exceptions; for example, abundant meteorite fragments have been found on the ocean floor in deposits from the Eltanin impact event, which hit the South Pacific Ocean about 2.1 million years ago (Kyte and Brownlee 1985), believed to be from a 1-4 km-sized projectile (Gersonde et al. 1997; Flores et al. 2002). Probable meteorite material (severely altered and replaced) has also been found in K-T boundary sediments (Kyte 1998; Robin et al. 1993).

A number of recent hydrocode simulations of impacts at various angles indicate that the shock pressure and the amounts of solid, molten and vaporized projectile can vary considerably with the angle of impact (e.g., Pierazzo et al. 1997; Pierazzo and Melosh 1999, 2000; Schnabel et al. 1999). A downrange focusing of projectile material was observed in oblique impacts, especially in low impact angles ( $\leq 30^\circ$ ), accompanied by the ejection of most of the projectile from the opening crater in the early stages of the impact. Shock melting and vaporization occur inside the projectile, mainly in its leading part, for all impacts except for the most oblique considered, a  $15^\circ$  impact, decreasing with angle of impact. The shock is weakest in the trailing half of the projectile, where any component surviving the impact in the solid state has its origin. According to Pierazzo and Melosh (1999), over 50% of the projectile is entrained in the expansion plume in the early phases of the  $15^\circ$  impact (these authors regret that their simulations do not continue long enough to see how this early entrainment could influence the distribution of the projectile material worldwide).

Schnabel et al. 1999 considered velocity, but not angle of fall, in their simulations of an hydrocode for the Canyon Diablo impact. Their choice of a 15 m radius and an impact velocity of  $20 \text{ km s}^{-1}$  for the impactor yields an estimation of ~15% solid material as a 1.5 to 2 m thick shell, covering the trailing hemisphere and about one third of the leading hemisphere. If an impact velocity of  $15 \text{ km s}^{-1}$  is assumed, the solid shell thickens to ~5 m and constitutes ~63% of the mass. In both cases the rest of the projectile melts, but does not vaporize. Vaporization would require higher but atypical velocities for Earth-crossing asteroids.

The quantity of the recondensed meteoritic vapor that may be mixed with the vaporized, molten, or shocked and brecciated target rocks is generally  $\leq 1\%$ . Schmidt et al. (1997) determined a meteoritic component of 0.5% of a nominal CI component for Sääksjärvi crater, and about 0.1% for Mien and Dellen. French et al. (1997) detected a minor extraterrestrial component ( $\leq 0.15\%$ ) in the melt-bearing breccias of the Gardnos impact structure. Nevertheless, the abundance of a meteoritic component is sometimes found to be much higher than these values. The amounts found in samples from the Clearwater East impact structure, Canada, corresponds to 4 to 7% of a nominal CI component, according to Palme et al. 1979 and Schmidt 1997. Recently, McDonald (2002), after re-evaluating the existing PGE data, proposed that up to 8% ordinary (possibly type-L) chondrite component is present in the impact melt. For the Morokweng impact melt rocks, McDonald et al. (2001) calculated an ordinary chondrite component at levels of up to 7.5%, in agreement with the earlier assessment by Koeberl et al. (1997). Such high abundances of meteoritic contamination may be explained by a higher impact angle, or lower impact velocity. In some cases it is possible to differentiate the chemical signature of the usually minute meteoritic contamination from the compositional signature of the normal terrestrial target rocks (Grieve 1991; Koeberl and Shirey 1997). For this purpose, detailed trace element and/or isotopic studies are necessary, as reviewed in the following chapters.

## 2

### Siderophile Trace Element Analysis

Some siderophile and related elements are more abundant in meteorites than in terrestrial crustal rocks (Table 1). Therefore, melt rock siderophile and highly siderophile element (HSE) abundances and their interelement ratios in the impact rocks are compared to the average continental crust composition of these elements (Tables 1 and 2). An enrichment in Cr, Ni and Co, at ppm level, and Os, Re, Ir, Ru, Rh, Pd and Au, at ppb level, usually indicates the presence of either a chondritic or an iron meteoritic component. An achondritic signature is more difficult to discern, because these meteorites have significantly lower contents of the key siderophile elements (Koeberl and Shirey 1997; Schmidt 1997; Koeberl 1997, 1998; Table 1). Chondrites have high abundances of Cr (typically about 0.26 wt%; Anders and Grevesse 1989), whereas iron meteorites have more variable Cr contents that are typically around 100 times lower than in chondrites (Buchwald 1975). Enrichments in Cr and low Ni/Cr or Co/Cr ratios can be used to distinguish between chondritic and iron (Ni/Cr  $\sim 40000$  and Co/Cr  $\sim 100$  in the latter) projectiles (Evans et al. 1993). However, as the Co, Cr, and Ni contents are common on the upper crust (average 8, 37, and 45 ppm respectively; Schmidt et al. 1997), their elemental enrichments may be ambiguous.

Platinum group elements (PGE) are better suited for identifying a meteoritic component. The abundances of the PGE (Ru, Rh, Pd, Os, Ir, Pt) and Au in chondrites and iron meteorites are several orders of magnitude higher than those

detected in terrestrial crustal rocks (e.g., Morgan et al. 1975; Palme et al. 1978, 1979; Morgan and Wandless 1983; Evans et al. 1993). Chondrites typically contain about 400-800 ppb Ir and Os (depending on the chondrite type), whereas the concentration of Ir and Os in the continental crust is approximately 0.02 ppb, according to Taylor and McLennan (1985). A more recent determination by Peucker-Ehrenbrink and Jahn (2001) sets a similar proxy for the values of Ir and Os in the upper continental crust: 22 and 31 pg/g, respectively. This means that the signal to background ratio is very high for PGE in impact rocks. The abundance of platinum-group elements and their interelemental ratios have been used to determine the type or class of meteorite. However, it has to be considered that some PGE enrichment is normal in certain terrestrial rocks; for example, gold mineralizations near the Bosumtwi crater were suggested to be responsible for the Ir enrichment in Ivory Coast tektites (Jones, 1985). Although the degree of PGE fractionation in various types of mantle rocks has been recognized to be quite large (McDonald et al. 1994; Gueddari et al. 1999; Rehkämper et al. 1999; Schmidt et al. 2000) the PGE patterns of the mantle and in some mantle-derived rocks may be similar to those of chondrites (Table 1; Koeberl and Shirey 1997).

**Table 1.** Siderophile elements composition of several terrestrial (basalt, granite, peridotite and Earth's upper crust) meteoritic (CI, eucrite), and impact (Clearwater East structure) materials.

	Basalt JB-1A (1)	Granite G-1 (2)	Peridotite JP (1)	Upper continental crust (3)	CI (4)	Eucrite (Juvinas) (5)	Clearwater East Impact melt rocks (6)
ppm							
Co	38.6	2.3	116	8 <sup>#</sup>	508 <sup>a</sup>	3.3	-
Cr	392	20	2807	37 <sup>#</sup>	2650 <sup>a</sup>	2330	-
Ni	139	3.4	2458	45 <sup>#</sup>	10700 <sup>a</sup>	1.1	-
ppb							
Au	0.71	3.2	2300	0.40	148	7.1	4.90
Ir	0.023	2	20	0.03	480	0.028	25.19
Os	0.018	0.11	79	0.03	492	0.018	26.94
Pd	0.6	1.9	13	2.00	560 <sup>a</sup>	4	32.20
Pt	1.6	8.2	49	-	982	-	153*
Re	0.18	0.63	0.15	0.08	39	0.01	0.58
Rh	-	< 5	-	0.38	140	-	9.58
Ru	-	< 400	65	1.06	683	-	38.12

Data sources: (1) Terashima et al. (1994). (2) Gladney et al. (1991). (3) Schmidt (1997) except # Schmidt et al. (1997). (4) Jochum (1996), except a Wasson and Kallemeyn (1988), average. (5) Morgan et al. (1978). (6) Average of 5 samples by Schmidt (1997), except \*Evans et al. (1993), one sample.

It would, therefore, be difficult to distinguish a meteoritic component if the entire target was – for example – an ophiolite mantle section. However, impact melt rocks are silica normative when a CIPW norm is calculated, because of the

normally high volume of siliceous crustal rocks they incorporate. Mantle rocks are generally not silica saturated, and conventional geochemistry would reveal this (McDonald, personal communication, 2002).

Knowledge of the amount of siderophile elements that are provided by the basement rocks is a prerequisite for the identification of extraterrestrial material in impact melts. This indigenous component has to be subtracted from the melt content of the siderophile elements in the impact melt or breccia to obtain the net meteoritic contribution (e.g., Palme 1980). Mixing calculations can be carried out to determine the relative proportion of the various target rocks types that are known or suspected to contribute to breccias or melt rocks (e.g., French et al. 1997; Koeberl et al. 1998b), for example, rock components found included in a suevite. The harmonic least-squares (HMX) mixing calculation program (Stöckelmann and Reimold 1989) can be employed for this purpose. Unfortunately, mixing calculations are sometimes complicated by the uncertainties surrounding the exact type and composition of target rocks. Erosion or partial burial by younger rock sequences may make it difficult to confidently estimate the proportions of different target rocks, especially if they are large or more than a few million years old (McDonald, personal communication, 2001), or the indigenous PGE concentrations very low or highly variable (e.g., Schmidt and Pernicka 1994). The analytical procedure is also difficult and time consuming, and this method only gives reliable results if the target stratigraphy is simple.

Before making calculations, the average compositions are scrutinized to determine which parameters show variations between the target rock groups large enough to be useful for distinguishing the resulting mixtures. Element concentrations likely to have undergone post-impact changes, such as alkalis, are of little use in calculating target rock proportions, as they may give unreliable results. Once a model of the bulk composition of the impact rocks has been built up, the siderophile element composition of this model is compared to the siderophile element abundances observed in the impactites. Schmidt (1997) used only one analysis (a quartz monzonite from the basement) to infer the entire target suite PGE contribution to the Clearwater East impact melt rocks, which is not very representative of the target area petrology. The composition of that quartz monzonite was then subtracted from the average PGE concentrations of the melt rocks to produce a series of "net PGE ratios". Schmidt's results appeared to match corresponding ratios in CI chondrites. However, PGE-bearing particles in the Clearwater East melt are heterogeneously distributed, yielding a broad range of Ir concentration in the melt rocks (e.g., Palme et al. 1981; Evans et al. 1993). As a result, the geochemical significance of the average concentrations used by Schmidt (1997) is questionable.

The correlation method is a better alternative. PGE-Ir regressions are frequently used for this purpose (e.g., Morgan and Petrie 1979; Palme 1980; McDonald et al. 2001). Among the HSE, Ir and Os have the lowest CI-normalized abundance in crustal rocks ( $6.5$  and  $6.2 \times 10^{-5}$ , respectively; Evans et al. 1993). Consequently, their contribution to a melt rock contaminated by a meteoritic component is lower than for other elements. If the meteoritic component is homogeneously distributed and indigenous Ir is negligible, then correlations and their slopes (controlled by

the PGE/Ir ratios of the dominant PGE component) can be determined. The y-axis intercepts at Ir equals zero is used to constrain the indigenous PGE contribution (Fig. 1). The correlation method is limited by the fact that small variations in the absolute concentrations of HSE in impact melt rock samples with high concentrations of strongly siderophile elements have a large influence on the y-intercept (at Ir = 0) (Schmidt 1997). Fitting a tightly constrained regression line, through many samples of impact melt from a crater, averages out deviations for individual samples and permits extrapolation back to a y-axis intercept that is independent of assumptions over the target rock composition (McDonald et al. 2001). McDonald (2002) reviewed and re-interpreted the available PGE data from samples from the Clearwater East impact melt with this approach and concluded that the most consistent projectile was an ordinary (possibly type-L) chondrite. This agrees with Cr isotope data of Shukolyukov and Lugmair (2000b).

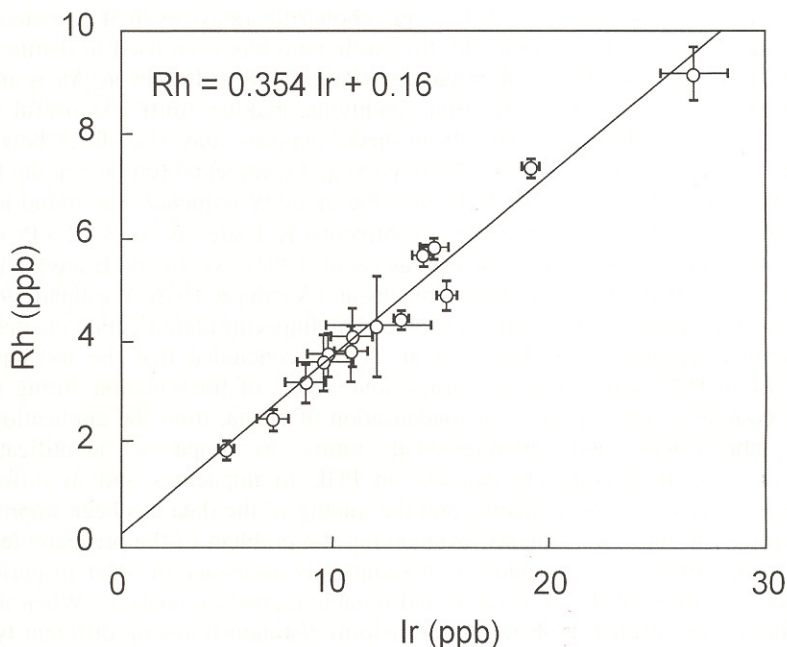
**Table 2.** Comparison of element ratios of different meteorites and impact melt rocks

	Meteorites						Impact Melt Rocks	
	CI	H	L	LL	IIIAB	IAB	ClearwaterEast	Morokweng
Os/Ir	1.06 <sup>#</sup>	-	-	-	-	-	0.98	-
Ru/Ir	1.42	1.42	1.47	1.49	1.38	2.04	1.53	1.50
Rh/Ir	0.29	0.30	0.33	0.34	-	-	0.36	0.53
Pd/Ir	1.21 <sup>#</sup>	1.11	1.35	1.64	0.29	1.01	1.31 <sup>#</sup>	1.54
Pt/Ir	1.97	2.08	2.17	2.22	1.9	2.2	8.6*	2.10
Ni/Ir	23000*	-	-	-	1900	7800	-	13400
Cr/Ir	5.5*	-	-	-	0.02	-	-	8020
Ir/Au	3.22	3.45	3.03	2.70	5.55	1.05	5.48 <sup>#</sup>	3.22
Pt/Au	7.07*	-	-	-	10.7	2.3	2.95*	-
Pd/Au	4.0*	-	-	-	6.6	1.2	1.97*	-
Ru/Rh	4.95	4.63	4.40	4.33	-	-	3.04	4.14
Ir/Re	12 <sup>#</sup>	-	-	-	-	-	57 <sup>#</sup>	-
Pt/Pd	-	1.88	1.16	1.35	-	-	-	1.29
Pt/Ru	1.39*	-	-	-	1.4	1.1	8.6*	-
Pd/Ru	0.79*	-	-	-	0.12	3.55	2.95*	1.09

Data sources: Averages: CI: Jochum (1996), 2 analyses, except <sup>#</sup>Schmidt (1997) and \*Evans et al. (1993) and references therein. H, L and LL: McDonald (2002) Number of analyses: H, 2; L, 3; LL, 2. IIIAB and IAB: Evans et al. (1993) and references therein. Clearwater East: Impact melt rocks, McDonald (2002), except <sup>#</sup>Schmidt (1997), 5 analyses, and \*Evans et al. (1993), 2 analyses. Morokweng: Impact melt rocks, McDonald et al. (2001), 16-18 analyses, depending on ratio.

Different processes occurring during the formation of impact glasses and melts cause problems with meteoritic component identification. The main factors controlling the incorporation of a meteoritic component into impact rocks are impact angle and projectile velocity (see introduction). However, this energy

scaling relationship does not explain the fractionation detected within a single crater (e.g., Meteor Crater, Wabar, and some Australian craters). Locations at different radial distances from the impact site have been found to show different siderophile element and PGE signatures, which do not coincide exactly with the interelement ratios of the impactor when it is partly preserved. Differences in vaporization and/or condensation temperatures could cause the PGE to fractionate among themselves, but no obvious correlation with any physical or chemical properties has yet been detected (Attrep et al. 1991; Mittlefehldt et al. 1992 a, b; Koeberl and Shirey 1997). Fractionation effects have also been detected for distal ejecta from the K-T boundary impact in different localities (Evans et al. 1993; Evans and Chai 1997).



**Fig. 1.** Regression between contents of Ir and Rh in impact melt rocks from the Morokweng structure, South Africa. Error bars show one standard deviation of the mean concentration. From McDonald et al. (2001).

Siderophile element fractionation in the impact melt while still molten is also possible. In large craters, where the melt can remain hot for several thousand years, different mineral phases, such as pyroxenes, magnetite and chromite, may take up various proportions of the siderophile elements (Ni, Co, and Cr, but not PGE), leading to an irregular distribution of these elements and, possibly, fractionated interelement ratios and patterns (Palme et al. 1979; Koeberl et al. 1994a, Koeberl 1998). This can render ratios such as Cr/Ni, Ni/Ir and Cr/Ir of

limited use. The fractionation of PGE observed in Clearwater East and Morokweng was attributed to a small-scale redistribution in sulphide and oxide phases (e.g., magnetite, chromite; Koeberl 1997). However, other authors (McDonald, personal communication, 2001) consider that the evidence for vaporization or condensation fractionation of the PGEs in thick melt sheets or global ejecta is not strong, and possibly explained by the small sizes of the sample taken for analysis. When larger samples are considered, the PGEs appear less fractionated.

Hydrothermal processes associated with the hot impact melt may also change the PGE concentrations in impact rocks (Gostin et al. 1989; Wallace et al. 1990), although distant ejecta deposits are not affected by this process. The relative mobility of these elements has to be considered before interpreting the ratios involving PGE, as this may lead to non-chondritic ratios even if a meteoritic component is present. For example, the Au/Ir ratio has been used to distinguish between cosmic and terrestrial signatures (Palme 1982). However, Au is much more mobile than Ir under terrestrial conditions, making Au/Ir less useful than other PGE ratios. Remobilization from ejecta deposits may also differ between marine (underwater at the time of the impact) and continental (on land at the time of the impact) sites. In marine K-T sites, the mobility sequence was found to be  $Rh > Au > Pd > Pt > Ru > Ir$ , while in continental K-T sites an  $Au > Pd > Pt \approx Rh > Ru > Ir$  sequence was determined (Evans et al. 1993). As Ru and Ir are the least mobile of the PGE (Cousins 1973; Cousins and Vermaak 1976; Westland 1981), the use of the Ru/Ir ratio minimizes problems in impactor identification created by differential remobilization. Evans et al. (1993) concluded that the incomplete database of PGE contents in meteorites, and effects of fractionation during melt sheet cooling or the vaporization/condensation of ejecta, limit the application of PGE abundances and interelemental ratios to impactor identification. Nevertheless, more complete datasets on PGE in impactites and in different meteorite types are now available, and the quality of the data has been improved by appropriate replicate analysis, overcoming the problem of the precision levels (McDonald 1998). A large number of samples is necessary in order to perform statistical analysis of the PGE ratios and reliable regression analysis. When these conditions are fulfilled, PGE ratios can help to distinguish among different types of projectiles (McDonald et al. 2001; McDonald 2002).

### 3

## The Re-Os Isotopic System

The abundance of Re and Os and the  $^{188}\text{Os}/^{187}\text{Os}$  isotopic ratios may allow a confirmation of the presence of a cosmic component in terrestrial rocks, although they do not permit the determination of the meteorite type. This was first shown for the K-T boundary by Turekian (1982) and Luck and Turekian (1983), and for rocks at impact craters by Fehn et al. (1986). The Re-Os isotopic system is based on the  $^{187}\text{Re}$  decay via  $\beta$ -decay into  $^{187}\text{Os}$ , with a half-life of  $42.3 \pm 1.3$  Ga (Lindner



et al. 1989). All seven naturally occurring osmium isotopes are stable. Regarding the geochemical behavior of Re and Os, the former is moderately incompatible and is, therefore, enriched in the melt, whereas the latter is strongly retained in the mantle during partial melting of mantle rocks and remains in the residue. This behavior results in high Re, but low Os, concentrations in most crustal rocks, and their Re/Os ratio is usually no less than 10 (Koeberl 1998). The Earth's mantle has Re and Os concentrations, which are much lower than those of meteorites. However its Re/Os ratio is indistinguishable from that of meteorites (Faure 1986), especially chondrites and irons, which have relatively high Re and Os contents, with Os more abundant than Re (ca. 600 and 50 ppb, respectively, in chondrites), resulting in Re/Os ratios  $\leq 0.1$ . Moreover, achondrites are an exception, as they have low Re and Os concentrations (contents of 0.06 and 0.44 ppb, respectively, have been measured in Moore County eucrite; Mason 1979; Table 3). Consequently, meteoritic and mantle rock  $^{187}\text{Os}/^{188}\text{Os}$  ratios experience only small changes with time, in contrast to crustal rocks (Fig. 2). Present-day mantle has a low  $^{187}\text{Os}/^{188}\text{Os}$  ratio of 0.12-0.13 (e.g., Smoliar et al. 1996, Meisel et al. 1996). Meteorites also have low  $^{187}\text{Os}/^{188}\text{Os}$  ratios. For example, a suite of data for 12 ordinary chondrites define a narrow range of present day  $^{187}\text{Os}/^{186}\text{Os}$  of  $0.1289 \pm 0.0011$ . Data for 10 enstatite chondrites define a similar average – present day  $^{187}\text{Os}/^{186}\text{Os}$  of  $0.1283 \pm 0.0005$ . In contrast, a suite of four carbonaceous chondrites define a 1-2% lower  $^{187}\text{Os}/^{186}\text{Os}$  of  $0.1259 \pm 0.0005$  (Meisel et al. 1996).  $^{187}\text{Os}/^{188}\text{Os}$  ratios of about 0.67-1.61 are representative of upper continental crust (Koeberl and Shirey 1997; Koeberl et al. 1998a).

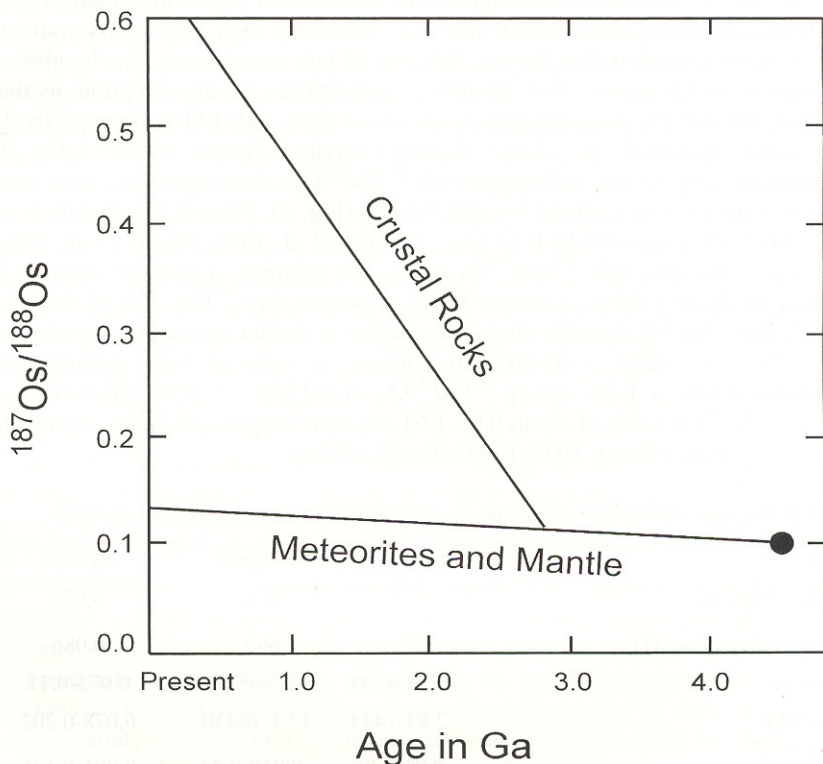
**Table 3.** Average abundances of Re and Os in terrestrial and extraterrestrial materials.

Rock	Re (ppb)	Os (ppb)	Re/Os
CI chondrites (1)	36.5	486	0.075
Ordinary chondrites (1)	57	660	0.086
IIAB (1)	1.39-4799	12.7-65270	0.073-0.11
IIIAB (1)	2.83-1444	17.1-18430	0.078-0.202
Eucrites (1)	0.01-0.06	0.018-0.44	0.081-0.136
Basalt JB-1A (2)	0.18	0.018	10
Granite G-1 (3)	0.63	0.11	5.727
Peridotite JP (2)	0.15	79	0.002
Average Upper Continental Crust (4)	0.8	0.03	2.66
Average Upper Continental Crust (5)	0.198	0.031	6.387

Data sources: (1) Koeberl and Shirey (1997) and references therein; (2) Terashima et al. (1994); (3) Gladney et al. (1991); (4) Schmidt (1997); (5) Peucker-Ehrenbrink and Jahn (2001).

Due to the high Os and Re abundances in chondrites, the admixture of a small meteoritic component to crustal target material significantly alters the Os isotopic

characteristics of the resulting impact melt or breccias (Table 4, Fig. 3). While a high abundance of Os could be due to crustal enrichment processes and incorporation of ore minerals, non-crustal Os isotopic compositions clearly indicate the presence of a meteoritic or mantle component. To distinguish between mantle and meteoritic signals, the differences in total abundance of Os in both materials is considered (Koeberl and Shirey 1997).



**Fig. 2.** Schematic evolution of the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of meteorites and the Earth's mantle and crust. From Faure (1986).

Mantle rocks have about 1-4 ppb Os, and typical chondrites have about 400-800 ppb Os. Thus, about 100 times more mantle material than meteoritic material would need to be added to normal crustal rocks to give the same Os isotopic ratio as the bulk rock. Ultramafic precursor rocks may be discerned by detailed geological field investigation, petrographic study of the rocks, trace element and, if necessary, supplementary Rb-Sr and/or Sm-Nd isotopic analysis (Koeberl and Shirey 1997).

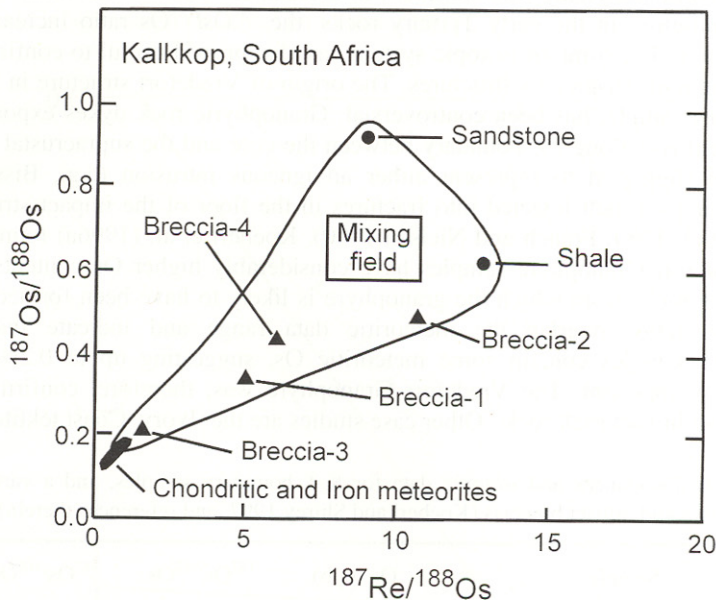
The method has been applied to the K-T boundary clay in various locations, in order to test its impact versus volcanic origin, e.g., Stevns Klint, Denmark (Luck

and Turekian, 1983), Woodside Creek, New Zealand (Lichte et al. 1986), and Sumbar, Turkmenistan (Meisel et al. 1995). In the latter study, the variation of the  $^{187}\text{Os}/^{188}\text{Os}$  ratio was measured across a complete boundary section. A significant sudden decrease of the  $^{187}\text{Os}/^{188}\text{Os}$  ratio from the end-Cretaceous rock layers to the actual K-T boundary clay was observed, in correlation with the maximum Ir and Os concentration; in the early Tertiary rocks, the  $^{187}\text{Os}/^{188}\text{Os}$  ratio increases to higher values. The osmium isotopic system has also proved useful to confirm the impact origin of suspicious structures. The origin of Vredefort structure in South Africa, for example, has been controversial. Granophyric rock dykes exposed in its basement and along the boundary between the core and the supracrustal rocks have been suggested to represent either an igneous intrusion (e.g., Bisschoff 1972), or impact melt injected into fractures in the floor of the impact structure (French et al. 1989; French and Nielsen 1990). Koeberl et al. (1996a) found that most Vredefort Granophyre samples have considerably higher Os contents than the country rocks from which the granophyre is likely to have been formed. The  $^{187}\text{Os}/^{188}\text{Os}$  ratios overlap the meteoritic data range and indicate that the granophyre samples contain some meteoritic Os, suggesting up to 0.2% of a chondritic component. The Vredefort Granophyre was, therefore, confirmed to represent an impact melt rock. Other case studies are the Ivory Coast tektites and

**Table 4.** Os abundances and isotopic data for K-T boundary samples, and a variety of impact glasses and impact breccias (Koeberl and Shirey 1997, and references therein).

Sample	Os (ppb)	$^{187}\text{Os}/^{188}\text{Os}$	$^{187}\text{Os}/^{186}\text{Os}$
<i>K-T boundary localities</i>			
Starkville South, CO, U.S.A.	25	0.14	1.2
Madrid, CO, U.S.A.	12.2	0.140	1.167
Woodside Creek, New Zealand	60	0.135	1.12
Stevns Klint, Denmark	110	0.1668	1.386
<i>Ivory Coast tektites</i>			
IVC 8902	0.0889	0.2087	1.734
IVC 2069	0.129	0.1528	1.270
<i>Bosumtwi crater impact glasses</i>			
BI 9201	0.125	0.9009	7.49
<i>Kalkkop crater impact breccias</i>			
Br-2 (100.4)	0.0354	0.487	4.049
Br-3 (112.7)	0.1886	0.2149	1.790
<i>Chicxulub impact melt rocks</i>			
CI-N10-1A	25.2	0.113	0.941
CI-N10-2	0.056	0.505	4.200

Morokweng crater (Koeberl and Shirey 1993a, b; Koeberl et al. 2002), Chicxulub, Mexico (Koeberl et al. 1994a), Saltpan crater, South Africa (Koeberl et al. 1994b), Kalkkop crater, South Africa (Koeberl et al. 1994c), or the Manson structure, Iowa, U.S.A. (Koeberl and Shirey 1996; Koeberl et al. 1996b).



**Fig. 3.** Ratios of  $^{187}\text{Os}/^{188}\text{Os}$  versus  $^{187}\text{Re}/^{188}\text{Os}$  for target rocks (shale and sandstone) of the Kalkkop impact crater, South Africa, in comparison with data for four impact breccias and the data array for chondritic and iron meteorites (small solid dots). From Koeberl and Shirey (1997).

#### 4

### The Cr-Mn Isotopic System

The chromium isotope systematics were recently explored for impact studies. The radioactive nuclide  $^{53}\text{Mn}$  decays to stable  $^{53}\text{Cr}$  with a half-life of 3.7 Ma.  $^{53}\text{Mn}$  is now extinct in the Solar System, but was present when the early planetesimals were forming, as indicated by variations in the relative abundance of the radiogenic daughter  $^{53}\text{Cr}$  in various ancient objects in the Solar System (Birck and Allègre 1988; Hutcheon et al. 1992; Nyquist et al. 1997). Lugmair and Shukolyukov (1998) performed high-precision mass spectrometric analysis of chromium, and developed a technique that allows to measure small  $^{53}\text{Cr}/^{52}\text{Cr}$  variations of less than 1  $\epsilon$  with an uncertainty of 0.05 to 0.10  $\epsilon$  units (1  $\epsilon$  is one part in  $10^4$ ). These isotopic variations are measured as the deviations of the

$^{53}\text{Cr}/^{52}\text{Cr}$  ratios from the standard terrestrial  $^{53}\text{Cr}/^{52}\text{Cr}$  ratio. Terrestrial samples exhibit  $^{53}\text{Cr}/^{52}\text{Cr} \sim 0 \text{ } \epsilon$  regardless of their origin, because the Earth homogenized after  $^{53}\text{Mn}$  had fully decayed (Table 5). Samples from the Moon give the same result as the Earth, because of their close genetic relationship (e.g., Hartmann and Davis 1975; Hartmann 1986; Stevenson 1987; Melosh 1989). Most classes of meteorite have excess  $^{53}\text{Cr}$  relative to the terrestrial value. The ordinary chondrites show a characteristic  $^{53}\text{Cr}/^{52}\text{Cr}$  of  $\sim 0.48 \text{ } \epsilon$ . Although the  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios of individual eucrites and diogenites vary because of an early planet-wide Mn/Cr fractionation, their parent body (Vesta) is characterized by the close-to-chondritic  $^{53}\text{Cr}$  excess of  $\sim 0.57 \text{ } \epsilon$ . The Mn-Cr isotope systematics of the angrites, primitive achondrites, and pallasites are also consistent with  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios of  $\sim 0.5 \text{ } \epsilon$  in their bulk parent bodies. The  $^{53}\text{Cr}$  excess is  $\sim 0.22 \text{ } \epsilon$  for the Martian meteorites, and  $\sim 0.17 \text{ } \epsilon$  for the EH-chondrites (Fig. 4; Shukolyukov and Lugmair 1998). Carbonaceous chondrites, however, show an apparent deficit of  $^{53}\text{Cr}$  of  $\sim -0.40 \text{ } \epsilon$ . This results from the use of  $^{54}\text{Cr}/^{52}\text{Cr}$  ratio for a second order fractionation correction. They were found to contain Cr of presolar origin, characterized by mostly elevated but sometimes lower than normal  $^{54}\text{Cr}/^{52}\text{Cr}$  ratios (Podosek et al. 1997). The actual, unnormalized  $^{53}\text{Cr}/^{52}\text{Cr}$  ratio is similar to that of other undifferentiated meteorites, and the apparent  $^{53}\text{Cr}$  deficit in the carbonaceous chondrites is actually due to an excess of  $^{54}\text{Cr}$ .

Since the measured excesses of radiogenic  $^{53}\text{Cr}$  are very small for the samples with relatively low Cr concentrations, such as olivines and those with long exposure ages, a potential contribution from spallation reactions has to be taken into account. The use of the  $^{54}\text{Cr}/^{52}\text{Cr}$  ratio for a second order fractionation correction introduces an additional uncertainty due to the presence of spallogenic  $^{54}\text{Cr}$ . Birck and Allègre (1985) determined production rates for Cr in the iron meteorite Grant. The production rates for  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$  turned out to be approximately the same:  $\sim 2.9 \times 10^{11}$  atoms/g per Ma. These values agree reasonably well with the less precise values for the production rate of  $^{53}\text{Cr}$  in Grant of  $\sim 2.3 \times 10^{11}$  atoms/g per Ma by Shima and Honda (1966). Thus, with known exposure age and Cr and Fe concentrations (Fe is the main target for Cr production), a spallation correction can be performed (Lugmair and Shukolyukov 1998).

The observed distribution of radiogenic  $^{53}\text{Cr}$  may not be due to differences in the bulk Mn/Cr ratios of the parent bodies. Instead, this distribution may reflect an original spatial heterogeneity of  $^{53}\text{Mn}$  in the early Solar System, which is now evident as a radial gradient in the radiogenic  $^{53}\text{Cr}$  abundances (Lugmair and Shukolyukov 1998; Shukolyukov and Lugmair 2000a). Regardless of the scenario, this observed difference allows us to distinguish extraterrestrial material on the basis of high-precision measurements of the Cr isotopic composition.

This method was successfully applied by Shukolyukov et al. (1999) and Koeberl et al. (2002) for the Morokweng structure impact melt. A substantial portion of the Cr in their samples was found to be of cosmic origin ( $^{53}\text{Cr}/^{52}\text{Cr} = 0.24\text{--}0.27 \text{ } \epsilon$ ), and the isotopic ratio was clearly different from those of the carbonaceous and enstatitic chondrites. Thus, they concluded that the most probable projectile is an ordinary chondrite type material. The authors

**Table 5.**  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios and Cr concentrations in terrestrial and extraterrestrial samples (from Shukolyukov and Lugmair 1998).

Sample	Cr (ppm)	$^{53}\text{Cr}/^{52}\text{Cr}$ ( $\epsilon^*$ )
	Terrestrial minerals, rock, and sediment	
Laboratory standard - terrestrial normal	-	$\equiv 0$
KH-1 Px, Kilbourne Hole, USA (px)	2500	$-0.01 \pm 0.08$
JAG 89-9, Jagersfontein, S. Africa (gte)	-	$0.04 \pm 0.08$
SC Ol, San Carlos Volcanic Field, USA (ol)	202	$-0.03 \pm 0.11$
MB 81-14, Deccan Traps, India (basalt)	112	$-0.04 \pm 0.06$
ODP 31-302-5-5, Western Pacific (clay)	34	$-0.02 \pm 0.09$
	Bulk meteorites and their parent bodies	
Allende (CV3)	3540	$-0.38 \pm 0.11$
Orgueil (CI)	2530	$-0.46 \pm 0.07$
OC (H, L) and their parent bodies	$\sim 3900$	$\sim 0.48$
Eucrites	1600-3200	0.7 - 1.3
Diogenites	6000-12700	0.4 - 0.6
HED parent body (Vesta)	-	$\sim 0.57^\dagger$
Primitive achondrites and their parent bodies	-	$\sim 0.53$
Angrites	800-1800	0.4 - 0.7
Angrite parent body	-	$\sim 0.48^\dagger$
Pallasite parent body	-	$\sim 0.52^\dagger$
SNC-meteorites (Mars)	-	$\sim 0.22$
EC (EH) and their parent body	2900-3900	$\sim 0.17$
Lunar anorthosite 60025	24	$0.00 \pm 0.09$

\*1  $\epsilon$  unit is 1 part in  $10^4$ .  $^\dagger$ Calculation based on Mn-Cr isotope systematics. px = pyroxene, gte = garnet, ol = olivine.

complemented the Cr isotope study with the PGE ratios (Cr/Ir) to focus their result to a L chondrite. Shukolyukov and Lugmair (1998) measured chromium concentrations in K-T boundary sediments commonly 20 to 30 times higher than those in background sediments (e.g., Kyte et al. 1980, 1985). In samples from Caravaca, Spain, Shukolyukov and Lugmair (1998) measured Cr isotopic

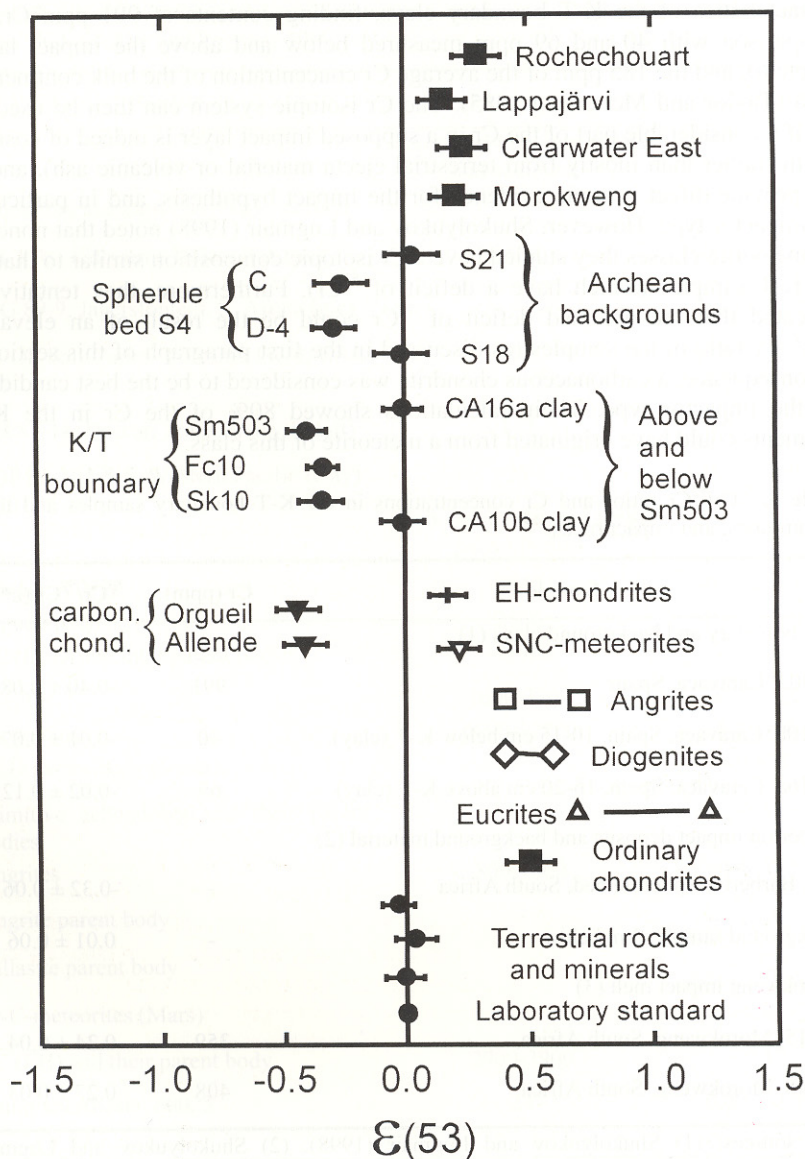
characteristics of the K-T boundary clays, finding contents of 991 ppm Cr, in comparison with 40 and 69 ppm measured below and above the impact layer (Table 6), and the 185 ppm of the average Cr concentration of the bulk continental crust (Taylor and McLennan 1985). The Cr isotopic system can then be used to test if a considerable part of the Cr in a supposed impact layer is indeed of cosmic origin (rather than mostly from terrestrial ejecta material or volcanic ash), and it can provide direct isotopic evidence for the impact hypothesis, and in particular the impactor type. However, Shukolyukov and Lugmair (1998) noted that none of the meteorite classes they studied have a Cr isotopic composition similar to that of the K-T samples (which have a deficit of  $^{53}\text{Cr}$ ). Furthermore, they tentatively indicated that the obtained deficit of  $^{53}\text{Cr}$  could be the result of an elevated  $^{54}\text{Cr}/^{52}\text{Cr}$  ratio in the samples (as discussed in the first paragraph of this section). In consequence, a carbonaceous chondrite was considered to be the best candidate for the impactor type. Their calculations showed 80% of the Cr in the K/T sediments could have originated from a meteorite of this class.

**Table 6.**  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios and Cr concentrations in the K-T boundary samples and their backgrounds, and impact rocks.

Sample	Cr (ppm)	$^{53}\text{Cr}/^{52}\text{Cr}$ ( $\epsilon^*$ )
K-T boundary and background clays (1)		
SK503, Caravaca, Spain	991	$-0.40 \pm 0.08$
CA10b, Caravaca, Spain, 10-15 cm below K-T (clay)	40	$-0.01 \pm 0.07$
CA16a, Caravaca, Spain, 16-20 cm above K-T (clay)	69	$-0.02 \pm 0.12$
Barberton impact deposits and background material (2)		
D-4, Barberton spherule bed, South Africa	-	$-0.32 \pm 0.06$
Background sample, 3 m below	-	$0.01 \pm 0.06$
Morokweng impact melt (3)		
MO15, Morokweng, South Africa	359	$0.24 \pm 0.04$
MO48, Morokweng, South Africa	408	$0.27 \pm 0.03$

Data sources: (1) Shukolyukov and Lugmair (1998). (2) Shukolyukov and Lugmair (2000b). (3) Shukolyukov et al. (1999). \* $\epsilon$  unit is 1 part in  $10^4$ .

Chromium isotopic studies were necessary to confirm the presence of an extraterrestrial component in the spherule bed (S4) from the Barberton Greenstone Belt, South Africa, supporting the hypothesis of an impact origin, and making this the oldest impact deposit on Earth (Shukolyukov et al. 2000). Previous PGE analyses showing relative abundances of Ir, Pt, and Os nearly similar to those in chondritic meteorites (Kyte et al. 1992) were not considered conclusive by some



**Fig. 4.**  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios in various terrestrial, impactite, K-T boundary and meteoritic samples. After Shukolyukov and Lugmair (2000b) and Shukolyukov et al. (2000). K-T boundary samples: SM503: Caravaca, Spain; FC10 and SK10: Stevens Klint, Denmark. Archean samples: Spherule bed S4: Barberton Greenstone Belt, South Africa.



authors (Koeberl et al. 1993; Koeberl and Reimold 1995), who argued that the extreme enrichments of siderophile elements (up to 5 times the chondritic abundances), much higher than in any other known impact deposit (or even in meteorites), could be explained by secondary mineralization. However, samples from the spherule bed were found to have a  $^{53}\text{Cr}/^{54}\text{Cr}$  ratio between  $\sim 0.26 \pm 0.11 \epsilon$  and  $\sim 0.32 \pm 0.06 \epsilon$ , where as background sediments yielded normal terrestrial  $^{53}\text{Cr}/^{54}\text{Cr}$  ratio (Shukolyukov et al. 2000).

A drawback with the chromium isotopic method is that a substantial amount of the chromium has to be of extraterrestrial origin to show an effect in the Cr isotopic composition of terrestrial rocks. For example, in rocks with crustal Cr abundances, only meteoritic components  $<1.2\%$  can be detected (Koeberl et al. 2002). Therefore, the Cr isotopic method is much less sensitive than the Os isotopic method. Additionally, analytical procedure is complicated and requires extreme precision, thus limiting the number of samples that can be analyzed. Nevertheless, the Cr isotopic method, where applicable, can provide additional information regarding the nature of the impactor (Koeberl et al. 2002). Although this determination is not possible for iron meteorites, which do not carry significant amounts of Cr, it allows to discern different types of ordinary chondrites, and it is the only procedure that can discriminate achondritic impactors, which have low concentrations of Os, but higher abundances of Cr.

## 5

### Conclusions

Meteoritic components have been identified in about a quarter of the craters known on Earth (Table 7; Koeberl 1998). The estimates of impacting body types are dominated by chondrites (41% of the inferred impactors), probably because their geochemical signature is the most easily identifiable due to the relative high abundance of siderophile elements and Cr. Non-chondritic impacting bodies are often identified simply because the body was not chondritic, rather than through any firm indication that it was an achondritic or an iron body (Grieve 1991, 1997). Iron meteorites have been proposed for 34% of the impact structures, mainly on the basis of the presence of meteorite fragments, or metallic spherules, at the crater site. Conflicting identifications have been made for a number of impact structures. Both iron and chondritic projectiles have been proposed for Bosumtwi (Palme et al. 1978; Koeberl and Shirey 1993b), Zhamanshin (Palme et al. 1978; Glass et al. 1983), and Rochechouart (Wolf et al. 1980; Lambert 1982) impact structures. Many identifications based only on Ni, Co, and Cr studies are highly uncertain, as no PGE or isotopic data are available.

A search for siderophile anomalies at some impact structures may be unsuccessful due to a variety of reasons already mentioned above. This may include sampling problems, the impact of a differentiated projectile with little or no siderophile element enrichment with respect to terrestrial materials, or uncertainties in making corrections for indigenous siderophile elements because of

Table 7. (cont.)

Name	Location	Diameter	Impactor	Evidence
Chicxulub	Yucatan, Mexico	170	Chondrite	S, Os, Es
Vredefort	South Africa	300	Chondrite	S, Cr, Os

Diameters (in kilometers) from: Earth Impact Database (2002), except Morokweng (Reimold et al. 2000) \*Crater field; diameter corresponds to the largest dimension of largest structure. Evidence: S, siderophile element enrichment and/or pattern; Os, Os isotopic ratio; M, meteorite fragments; MS, metallic spherules; Es, siderophile element enrichment in ejecta. References in Koeberl (1998), and later works: Kalkkop (Reimold et al. 1998), S (PGE) in Morokweng (McDonald et al. 2001) and Clearwater Lake East (McDonald 2002), Cr in Lappajärvi, Rochechouart and Clearwater Lake East (Shukolyukov and Lugmair 2000b), S in Boltysh (Lorenz 1999) and Mjøltnir (Dypvik and Attrep 1999), M in Lappajärvi (Badjukov and Raitala 2000) and Cr and Os in Morokweng and Vredefort (Koeberl et al. 2001, 2002).

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