

Geochemical identification of projectiles in impact rocks

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Abstract—The three major geochemical methods for impactor identification are evaluated with respect to their potential and limitations with regards to the precise detection and identification of meteoritic material in impactites. The identification of a projectile component in impactites can be achieved by determining certain isotopic and elemental ratios in contaminated impactites. The isotopic methods are based on Os and Cr isotopic ratios. Osmium isotopes are highly sensitive for the detection of minute amounts of extraterrestrial components of even $<<0.05$ wt% in impactites. However, this only holds true for target lithologies with almost no chemical signature of mantle material or young mantle-derived mafic rocks. Furthermore, this method is not currently suitable for the precise identification of the projectile type. The Cr-isotopic method requires the relatively highest projectile contamination (several wt%) in order to detect an extraterrestrial component, but may allow the identification of three different groups of extraterrestrial materials, ordinary chondrites, an enstatite chondrites, and differentiated achondrites. A significant advantage of this method is its independence of the target lithology and post-impact alteration. The use of elemental ratios, including platinum group elements (PGE: Os, Ir, Ru, Pt, Rh, Pd), in combination with Ni and Cr represents a very powerful method for the detection and identification of projectiles in terrestrial and lunar impactites. For most projectile types, this method is almost independent of the target composition, especially if PGE ratios are considered. This holds true even in cases of terrestrial target lithologies with a high component of upper mantle material. The identification of the projectile is achieved by comparison of the “projectile elemental ratio” derived from the slope of the mixing line (target-projectile) with the elemental ratio in the different types of possible projectiles (e.g., chondrites). However, this requires a set of impactite samples of various degree of projectile contamination.

INTRODUCTION

Impact structures occur on the surface of all solid bodies in the solar system and attest to the importance of impacts not only in the formation of planets but also in later surface-shaping and modifying processes (e.g., Grieve 1991; Grieve and Shoemaker 1994). The temporal correlation between one of the largest mass extinctions at the Cretaceous-Paleogene (K/Pg) boundary and the Chicxulub impact also exemplifies the significance of such an event for the biosphere of the Earth (e.g., Hildebrand 1993; Claeys et al. 2002). The precise identification of the crater-forming projectile allows the documentation of origin and frequency of the types of bodies that have impacted Earth. The identification of impacting asteroids also plays a major role in understanding impact processes and their relation to the dynamics of asteroids in the Main Belt. First attempts to identify the nature of the

projectiles responsible for impact craters were carried out on lunar samples (Anders et al. 1973; Ganapathy et al. 1970; Morgan et al. 1974). Abundance patterns and ratios of certain elements were used for identification. The selected elements mainly shared two characteristics: 1) it was possible to accurately analyze them at low concentration levels with radiochemical neutron activation analysis, and 2) they were found in much higher concentrations in meteorites than in lunar crustal rocks. The elements used for such studies were mainly Ir, Re, Ni, Au, Ge, Sb, and Bi. Based on these first results for the Moon, Morgan et al. (1975) attempted to characterize for the first time the nature of projectiles in terrestrial impactites. These authors pointed out that the elements Ir and Ni were the most sensitive ones, as they exhibited the highest meteorite/crustal ratios. However, Ni concentrations in terrestrial and lunar rocks are much higher than those of the remaining platinum group elements (PGE)

and, therefore, the latter are more appropriate. The use of the complete suite of PGE for impactor characterizations has steadily increased with improvements in the analytical techniques. Whereas initial studies only used some PGE (e.g., Morgan et al. 1975; Grieve 1978; Palme et al. 1978), more recent work includes almost the complete set of PGE for the impactor characterization (e.g., Schmidt et al. 1997; McDonald et al. 2001; Norman et al. 2002; Tagle and Claeys 2004). Among the elements used for impactor identification are PGE (Os, Ir, Ru, Pt, Rh, Pd), Ni, and Cr. These elements are referred here as impactor relevant elements (IRE). The introduction of the osmium and chromium isotope methods (Turekian 1982; Shukolyukov and Lugmair 1998) have significantly improved the detection and identification of extraterrestrial material. This paper discusses the potential and limitations of methods for projectile identification with special emphasis on the application of elemental ratios.

POSSIBLE IMPACTOR TYPES

Interplanetary bodies, such as comets and asteroids, are responsible for the formation of impact structures. The main sources of comets are believed to be the Oort Cloud and the Kuiper Belt. However, cometary impactors likely play a minor role (~1%) in the total impactor population for the Earth-Moon system (e.g., Ivanov et al. 2002; Morbidelli et al. 2002; Chapman 2004). The identification of a cometary impactor is problematic, mainly because the composition of comets is essentially unknown with respect to their small proportion of nonvolatile elements, which are the most relevant ones for the identification of the impactor. Therefore, it is currently not possible to unequivocally identify a cometary impactor by geochemical or isotopic methods.

The main source of asteroids is the asteroid belt located between the orbits of Mars and Jupiter. So far, no asteroid has been sampled directly. Nevertheless, meteorites (with the exception of those from Moon and Mars) are fragments of asteroids. Hence, it is possible to infer the composition of asteroids from the composition of meteorites. Asteroids are divided into two groups. The first group is undifferentiated asteroids, which are the parent bodies of chondritic meteorites. These bodies underwent some metamorphism, but not melting (e.g., Brearley and Jones 1998; Burbine et al. 2002). The second group is differentiated asteroids, which underwent melting and complete or partial differentiation, and are the parent bodies of achondrites, stony-iron meteorites, and iron meteorites (Mittlefehldt et al. 1998). In order to identify and characterize the extraterrestrial components of impactites, it is essential to understand the composition of these interplanetary bodies.

Undifferentiated asteroidal material represents the most common extraterrestrial material reaching Earth, given that 85% of all observed meteorite falls are chondrites (Grady 2000). Chondrites are generally subdivided into various

groups that mostly contain five or more members. In fact, 13 groups of chondrites have been identified and, in addition, ~14 grouplets or unique meteorites have been proposed (e.g., Weisberg 2001; Mittlefehldt 2002). No major element fractionation appears to have affected the composition of the chondrite parent bodies after their formation. Therefore, it is possible to retrace the composition of the entire parent body based on the composition of single meteorites (e.g., Palme 1988; Wasson and Kallemeyn 1988; Burbine et al. 2002). Some meteorites exhibit significant degrees of shock and are depleted in volatile elements (Wasson and Kallemeyn 1988), however, the ratios of refractory and moderately volatile elements are constant (e.g., Friedrich et al. 2003; Horan et al. 2003; Tagle 2004). This permits the definition of characteristic elemental ratios ("fingerprints") for different chondrites.

Most differentiated meteorites are believed to be samples from the crust (e.g., HEDs or angrites), core-mantle boundary (pallasites), and the cores (iron) of differentiated asteroids. The significant degrees of melting and differentiation experienced by their parent bodies have managed to erase most of the evidence of their chondritic precursors. The composition of a single differentiated meteorite is primarily the result of magmatic processes, such as crystal-liquid fractionation, and does not represent the bulk composition of its parent body. This is one of the main difficulties in resolving precise chemical characteristics for the identification of such impactors. Differentiated achondrites such as HEDs have compositions similar to the Earth's mantle or other mafic to ultramafic terrestrial rocks. Therefore, the detection or identification of a differentiated achondrite projectile is relatively difficult and probably possible only under special conditions. For example, in the case of a large degree of projectile contamination (a few wt%) identification could potentially be based on the Cr-isotope method (see the "Cr Isotopes" section).

Finally, the number of asteroidal parent bodies sampled through meteorite collections is estimated at 100 to 150 (Burbine et al. 2002). These numbers are, however, relatively low compared to the ~670,000 asteroids larger than 1 km in the Main Belt (Ivezic et al. 2001). Even if meteorite collections provide a good sample of asteroid belt compositions, the possibility that some percentage of asteroid types is still missing from meteorite collections cannot be discounted. For most of the estimated 50 to 70 parent bodies of iron meteorites (Wasson 1995), the silicate counterpart is unknown. Therefore, the existence of as-yet unknown asteroids among potential terrestrial impactors need to be taken into consideration when identifying projectile types.

Table 1 summarizes the results of identification of projectiles at terrestrial impact structures and also includes spherule layers and data for a large lunar impact basin (Table 1). Spherule layers are distal ejecta layers of ancient impacts where the associated crater structure is often

Table 1. Impactor types at impact craters.

Crater name	Location	Age (Myr)	Diameter (km)	Impactor type ^a	Evidence ^b	Reference ^c
Morasko	Poland	<0.01	0.10	IIIC	M	1, 2, 3
Kaalijärvi	Estonia	0.004 ± 0.001	0.11	IA	M	1, 2
Wabar	Saudi Arabia	0.006 ± 0.002	0.12	IIIA	M, S	1, 2
Henbury	Australia	<0.005	0.16	IIIA	M, S	1, 2
Odessa	USA	<0.05	0.17	IA	M	1, 2
Boxhole	Australia	0.0300 ± 0.0005	0.17	IIIA	M	1, 2
Macha	Russia	<0.007	0.30	Iron	M, S	1
Aouelloul	Mauritania	3.1 ± 0.3	0.39	Iron	S, Os*	1
Monturaqui	Chile	<1	0.46	IA?	M, S	1
Wolfe Creek	Australia	<0.3	0.88	IIIB	M, S	1, 2
Barringer	USA	0.049 ± 0.003	1.19	IA	M, S	1, 2
New Quebec	Canada	1.4 ± 0.1	3.4	OC; type L?	S	1
Brent	Canada	450 ± 30	3.8	OC; type L or LL	S	1
Sääksjärvi	Finland	~560	6.0	Stony-iron?	S	1
Wanapitei	Canada	37.2 ± 1.2	7.5	OC; type L, LL	S	18
Bosumtwi	Ghana	1.03 ± 0.02	11	Iron / non CC?	S, Os*, Cr*	1, 4
Lappajärvi	Finland	77.3 ± 0.4	23	Non CC	S, Cr*	1
Rochechouart	France	214 ± 8	23	Stony-iron	S, Cr*	1, 5
Ries	Germany	15 ± 1	24	No contamination	S	1, 6
Clearwater East	Canada	290 ± 20	26	OC; type LL	S	7
Clearwater West	Canada	290 ± 20	36	No contamination	S	8
Saint Martin	Canada	220 ± 32	40	No contamination	S	9
Morokweng	South Africa	145.0 ± 0.8	70	OC; type LL	M, S, Cr*	10, 19
Popigai	Russia	35 ± 5	100	OC; type L	S, Cr*	11
Manicouagan	Canada	214 ± 1	100	No contamination	S	8
Chicxulub ^d	Mexico	64.98 ± 0.05	170	CC	M, S, Os*, Cr*	12, 13
Eltanin	South Pacific	2.15	— ^e	Mesosiderite	S	14
Serenitatis Basin	Moon	3.9 Gyr	740	OC; type LL	S, Cr	15
Spherule beds						
Hammersley Basin	Australia	2.49 Gyr	No crater	EC, type EL?	S, Cr*	16
Barberton (S3, S4)	South Africa	3.1–3.5 Gyr	No crater	CC	S, Cr*	17

^aOC = ordinary chondrites; EC = enstatite chondrite; CC = carbonaceous chondrite; ? = questionable.

^bS = siderophile elements (PGE, Ni, Au); Cr* = chromium isotopes; Os* = Os isotopes; M = projectile fragment.

^c1 = Koeberl 1998 and references therein; 2 = Koblitz 2000; 3 = Tagle et al. 2004; 4 = Koeberl 2004; 5 = Tagle et al. 2003; 6 = Morgan et al. 1979; 7 = McDonald 2002; 8 = Palme et al. 1978; 9 = Palme 1982; 10 = McDonald et al. 2001; 11 = Tagle and Claeys 2005; 12 = Shukolyukov and Lugmair 1998; 13 = Kyte 1998; 14 = Kyte 2002; 15 = Tagle 2005; 16 = McDonald and Simonson 2002; 17 = Kyte et al. 2003; 18 = Wolf et al. 1980; 19 = Maier et al. 2006.

^dEnrichment in ejecta layer.

^eDeep water impact, no crater structure.

unknown. All impact craters smaller than 1.5 km in diameter were caused by iron meteorites (Table 1) as a result of the pronounced atmospheric disruption of stony projectiles of similar size (Bland and Artemieva 2003).

Iron meteorites are classified based on their Ir, Ga, and Ge composition (Wasson and Kallemeyn 2002 and references therein). It has been proposed that some iron meteorite groups are co-genetically related, even if they have a distinct composition (Wasson and Kallemeyn 2002). For example, the former groups IA and IB are combined to IAB, and the same holds true for the IIIAB irons. Even if these meteorites are

genetically related, we believe that projectile identification should be as precise as possible. Therefore, we use the classification of meteorite fragments that are clearly associated with a specific impact crater (Koblitz 2000 and references therein). In the case of the Morasko craters, the differences in the PGE patterns between IIIC and IIID iron meteorites, according to Tagle (2004 and references therein), were used for classification of the Morasko meteorite as a IIIC (Table 1).

The majority of the remaining craters were produced by ordinary chondrites. Carbonaceous chondrites are rare

impactors and enstatite chondrite are only represented by one proposed impactor. The nonchondritic projectiles are dominated by stony-irons, including the mesosiderite projectile fragments found at the Eltanin impact site (Kyte 2002). A relatively large number of terrestrial craters, where the projectile type has been investigated, do not contain any clear projectile signature. This is interpreted usually as the result of differentiated PGE-poor projectiles. Some caution, however, must be exercised, since to date no unambiguous projectile signature has been found in the impactites occurring within the Chicxulub impact structure (see later discussion).

METHODS OF PROJECTILE IDENTIFICATION

Identification of Impactor Fragments

Impactor fragments are rarely found associated with terrestrial impact craters, hampering a direct identification of the impactor type. Although there is a widespread belief that the impactor is completely vaporized in large-scale impacts, this is not supported by numerical modeling. For impact angles of $<45^\circ$ and impact velocities of 20 km s^{-1} , less than 50% of the impactor's masses vaporized and the remaining fraction "survives" the impact as melt or in solid form and is deposited within, or down range of, the crater (Pierazzo and Melosh 2000). Any exposed remnants of the impactor, however, are strongly affected by weathering processes and are destroyed after a few thousand years, as it is for meteorites. Therefore, virtually all impactor fragments are found in the vicinity of very young terrestrial impact structures. Due to the size-frequency relation for impacts, these young craters are also relatively small ($<1.5 \text{ km}$) and were produced by iron meteorites, as this is the only type of relatively small body that can survive atmospheric passage relatively intact and impact with enough remaining kinetic energy to create a hypervelocity impact structure (Melosh 1989). Nevertheless, under conditions of rapid protection from weathering processes, it may be possible to find other types of impactor remnants associated with larger and older impact structures. This may be the case for a carbonaceous chondrite discovered at the K/Pg boundary in a sedimentary core from the Pacific Ocean, inferred to be a fragment of the impactor responsible for the Chicxulub structure (Kyte 1998). The use of projectile fragments is not worthwhile for most old impact structures. Even if a fossil meteorite is found at certain distances of a crater, a clear link of the fragment and the crater may still be difficult to establish.

Geochemical Tracing of the Projectile

The high energies released during a hypervelocity impact result in melting and vaporization of some or all of the projectile (Pierazzo and Melosh 2000) during the early stages

of impact. The vertical velocity component is higher for the projectile material than for the shocked downward-moving target rocks resulting in mixing of both components. Fractions of the molten/vaporized projectile material incorporated in the target rocks will ultimately form a component of the impact melt rocks. The detection of this extraterrestrial component can be achieved by determination of IRE.

Although distal ejecta may contain significant amounts of IRE, as was discovered by Alvarez et al. (1980) and Smit and Hertogen (1980) at the K/Pg boundary, within a crater impact-melt rocks generally contain the highest concentrations of projectile material. Impact-melt rocks commonly reflect a rather homogeneous average of the composition of the target lithologies, which are similar to the average continental crust for large impact structures (e.g., Dressler and Reimold 2001). Most terrestrial crustal rocks are strongly depleted in IRE, compared to most meteorite types. However, in mafic and ultramafic rocks certain IRE are less depleted than in average continental crust.

Cr-Ir Ratios

The IRE can be divided into two groups: PGE and Ni, which has siderophile behavior, and Cr, which has a partially lithophile character (Lodders 2003). As a result of differentiation of the Earth into metallic core, mantle, and crust, most of the terrestrial PGE partitioned into the core, whereas Cr remained mostly in the mantle. Due to a late veneer of $\sim 0.8\%$ chondritic material, the composition of the Earth's mantle is slightly enriched in PGE compared to the concentrations expected from the metal/silicate melt partition coefficients, and exhibit relatively high Cr concentrations resulting from primary differentiation (O'Neill 1991). Therefore, Cr/PGE ratios in the Earth's mantle and crust are significantly higher than in most extraterrestrial materials.

Figure 1 shows the Cr and Ir contents of extraterrestrial materials and common terrestrial rocks. The diagonal lines that cross the diagram represent constant elemental ratios in the log/log plot. The terrestrial rocks plotted include averages of the upper continental crust (UCC), total continental crust (CC), primitive upper mantle (PUM), and various basalts, gabbros, dunites, peridotites, as well as greywacke. A brief description and the references of these data are summarized in Table 2. Apart from mantle lithologies, most PGE data for crustal rocks are for rather PGE-rich, mafic rocks, such as some basalts and gabbros. These mafic crustal rocks vary in Cr and Ir abundances over two orders of magnitude between the Earth's mantle at high element concentration and the average continental crust at low element concentration (Fig. 1). With only a few exceptions, terrestrial crustal rocks vary in Cr and Ir over a rather limited Cr/Ir ratio. The average of the upper continental crust also follows this trend towards low Cr and Ir concentration (Fig. 1). This general Cr/Ir correlation has been shown previously by Righter et al.

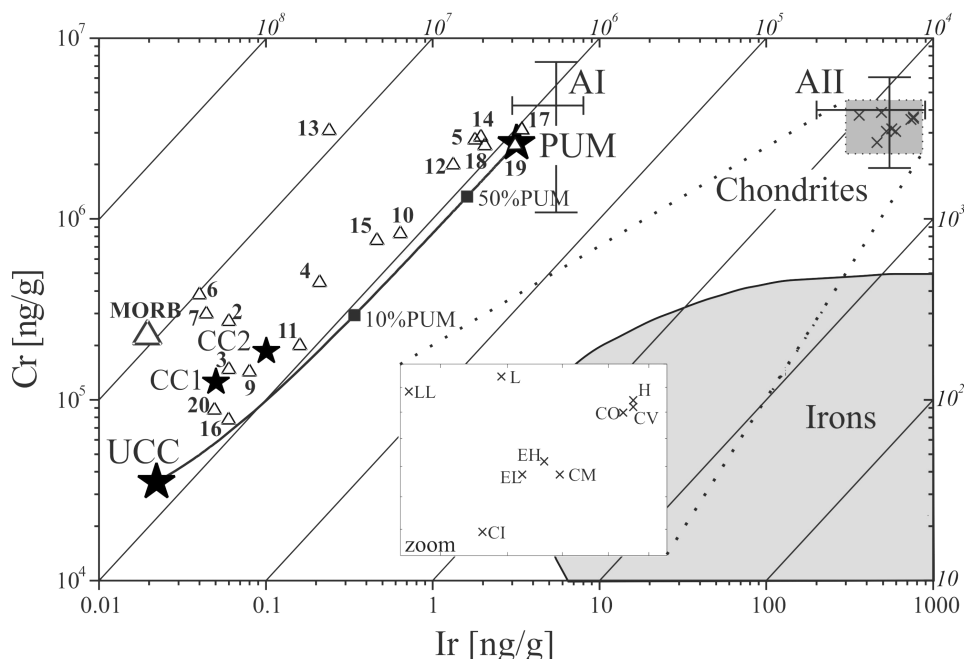


Fig. 1. Cr versus Ir concentrations for terrestrial and extraterrestrial material. AI = PGE-poor achondrites (HED, angrites, and aubrites), AII = PGE-rich achondrites (brachinites, ureilites, lodranites, acapulcoites, and winonaites). Source of data: chondrites (Wasson and Kallemeyn 1988); iron meteorites, achondrites I (AI), and achondrites II (AII) error represent the range of published concentrations (Koblitiz 2000); numbers 1 to 20 represent terrestrial rocks, concentrations and references are given in Table 2. PUM = primitive upper mantle; MORB = mid-ocean ridge basalt; UCC = continental crust; CC = continental crust; values above and right of the diagram represent the Cr/Ir ratio of the respective line; note that for higher resolution of the chondrite a field has been “zoomed” within the middle of the diagram.

(2000), and also by Becker et al. (2001) who used Os, which is generally equivalent in concentration to Ir. This suggests that Cr and Ir exhibit a similarly compatible behavior during the major differentiation processes involved in formation and modification of the Earth's crust. From our compilation of data, it follows that most terrestrial crustal rocks display Cr/Ir ratios above 10^6 . Exceptions occur when fractionation processes are dominated by Fe oxides or Fe sulfides that preferentially incorporate Ir over Cr. Iron- or sulfide-rich rocks, especially with some mineralization, may have Cr/Ir ratios below 10^6 . However, such cases, for example PGE-rich ore mineralization, are very local phenomena, which only rarely influence the composition of impactites.

As mentioned previously, most extraterrestrial materials impacting Earth have much lower Cr/Ir ratios than terrestrial rocks. This compositional difference is even more pronounced between impactors and the Moon, which has a higher Cr/Ir ratio than the Earth (Richter et al. 2000). The composition of chondrites exhibits only minor variations with respect to Cr and Ir, with Cr/Ir ratios from two to more than three orders of magnitude lower than terrestrial and lunar rocks, respectively. The compositional mixing resulting in an impact melt formed from the Earth's crust by a chondritic projectile would result in a decrease of the terrestrial Cr/Ir ratio towards the chondritic ratio, depending on the degree of projectile contamination.

However, chondrites are not the only possible impactors. The compositions of other potential projectiles are also plotted in the Cr/Ir diagram (Fig. 1). Values for iron meteorites, as well as differentiated and primitive achondrites, represent the range (minimum and maximum) in Ir and Cr concentration of meteorites taken from the database MetBase 5.0 (Koblitiz 2000). Iron meteorites are strongly depleted in Cr but usually enriched in siderophile elements such as Ni and PGE. Iron meteoritic projectiles should be easily identified by the PGE enrichment of the impactites and low Cr/PGE or Cr/Ni ratios. The values for iron meteorites plot in a range of 4 to 65,000 ng/g for Ir and 320 to 500,000 ng/g for Cr (only 5 meteorites from the almost 500 analyzed and listed in MetBase 5.0, including Cr, have higher concentrations). Instead of subdividing the achondrites into primitive and differentiated, we separated them based on PGE content. The ranges of achondrites with low PGE concentrations are shown on Fig. 1 and are labelled as achondrite type I (AI), including HED and angrites, and those with higher PGE concentrations, achondrites type II (AII), include brachinites, ureilites, lodranites, acapulcoites, and winonaites. Differentiated achondrites (AI) are the counterparts of iron meteorites with respect to their parent bodies and are therefore depleted in PGE and enriched in Cr. The Ir concentrations in AII achondrites are similar to chondrites but are usually slightly (acapulcoite and

Table 2. Cr and Ir concentrations in terrestrial rocks.

	Ir (ng/g)	Cr (μ g/g)	Rock type ^a (n)	Reference ^b
1	0.02	226	MORB (6)	1
2	0.06	271	Alkali basalt, low Cr and Ir (6)	1
3	0.06	147	Olivine tholeiitic basalt, low Cr and Ir (2)	1
4	0.21	444	Olivine tholeiitic basalt, high Cr and Ir (2)	1
5	1.8	2737	Komatiite (5)	1
6	0.04	380	Alkali basalt (8)	2
7	0.044	298	Transitional basalt (7)	2
8	0.006	226	Tholeiitic basalt (7)	2
9	0.08	142	CFB, low Ti (2)	3
10	0.64	827	CFB, low Ti and high Cr (6)	3
11	0.16	199	CFB, high Ti (16)	3
12	1.33	1991	CFB, high Ti and Cr (4)	3
13	0.24	3087	Dunite, low Ir (4)	4
14	1.93	2850	Dunite, high Ir (15)	4
15	0.46	770	Gabbro + gabbro-norite (12)	4
16	0.06	78	Diorite (2)	4
17	3.41	3127	Dunite (4)	5
18	3.11	2569	Harzburgite (10)	5
19	2.04	2543	Lherzolite (4)	5
20	0.05	88	Greywacke	6
CC 1	0.05	126	Continental crust	6
CC 2	0.1	185	Continental crust	7
UCC	0.02	35	Upper continental crust	7

^aMORB = middle ocean ridge basalts; CFB = continental flood basalt; (n) = number of average analyses.

^b1 = Rehkämper et al. 1999b; 2 = Vogel and Keays 1996; 3 = Momme et al. 2002; 4 = Vatin-Perignon et al. 2000; 5 = Rehkämper et al. 1999a; 6 = Wedepohl 1995; 7 = Taylor and McLennan 1985.

lodranite), or even strongly (ureilite), enriched in Cr compared to chondrites (Tagle 2004 and references therein). Nevertheless, even if they have nearly chondritic PGE concentrations, the element ratios are “disturbed” by partial melting processes in their parent body, and therefore nonchondritic PGE elemental ratios should be found. Since chondrites are the most common extraterrestrial material impacting Earth, we will focus on them in this paper.

Impact-melt rocks form in considerable volume during impact cratering on Earth (Grieve and Cintala 1992). The composition of the impact melt averages a few hundreds of cubic meters of target rocks at small craters and up to essentially the thickness of the continental crust for very large structures, such as Sudbury or Chicxulub. The composition of impact-melt rocks formed in medium to large structures in the continental crust most probably lie between the average upper and total continental crust, reflecting the lower and higher average Cr and Ir concentrations in the target, respectively (Fig. 2). Using the average upper continental crust and total continental crust of Taylor and McLennan (1985) as two very probable average end-member compositions, we have calculated two theoretical mixing trajectories between these indigenous end-members and two corresponding extreme compositions of the chondrites

(Fig. 2). The numbers along the mixing trajectories indicate the amount of projectile contamination, within the model impact melt, in wt%. The two model mixing lines span a field that covers the most likely mixing trajectory of contaminated impactites produced by the impact of chondrites (the most common projectile) into the continental crust. Impact melt rocks that are heterogeneously contaminated with a chondritic projectile will define such a mixing trajectory. The contamination of an impact melt rock, derived from the UCC or the CC, with an even small amount of extraterrestrial material, between 0.05 and 0.1 wt%, may significantly change the Cr/Ir composition of the impact melt rock (Fig. 2).

The Cr-Ir composition of impactites from four terrestrial impact structures, Morokweng (McDonald et al. 2001), Popigai (Tagle and Claeys 2004), Lappajärvi (Reimold et al. 1980) and Chicxulub (Tagle et al. 2004), plot in the proposed field along mixing trajectories between estimates for the continental crust and an extraterrestrial component (Fig. 2). It is possible to approximate the amount of projectile material incorporated into the melt, almost independent from the variations on the composition of the different end members (chondrites and Earth crust). The proposed amount of chondritic projectile for the impactites displayed in Fig. 2 is in the range of 0.1 to 6 wt%, which is in good agreement with previous estimations (McDonald et al. 2001; Tagle and Claeys 2005). The Morokweng impactites present the highest degree of impactor contamination. On the other hand, the Cr/Ir ratios of the Chicxulub impactites (Tagle et al. 2004) do not differ significantly from the terrestrial range (Fig. 2). Furthermore, the Cr and Ir values do not define a typical mixing trajectory between a homogeneous impactite and a projectile at Chicxulub. The chemical and Os-isotope compositions of the impactites from Chicxulub are generally similar to the range of terrestrial rocks and do not allow an unambiguous detection of an extraterrestrial component (Tagle et al. 2004); however Os-isotope studies suggested a small extraterrestrial input of <0.1% (Gelinis et al. 2004). The PGE concentrations in the co-genetic K/Pg-boundary clay, however, suggested a PGE-rich impactor for the Chicxulub event, most likely a carbonaceous chondrite, according to Cr isotope and fossil meteorite analysis (Kyte 1998; Shukolyukov and Lugmair 1998; Trinquier et al. 2006). The apparent lack of a projectile signature in impactites within a crater structure is, therefore, not a general argument for a differentiated achondrite, as proposed for example, for the Ries crater, Germany (Morgan et al. 1979).

In addition to the data for terrestrial structures, we have plotted the composition of poikilitic impact melts collected at the Apollo 17 landing site and the distribution of lunar crustal rocks (Fig. 2) (original PGE data by Norman et al. 2002). These impact melts are interpreted as the product of the Serenitatis basin formation (Norman et al. 2002 and references therein). The mixing line for the lunar impact melts defines a trajectory between a chondritic projectile and the

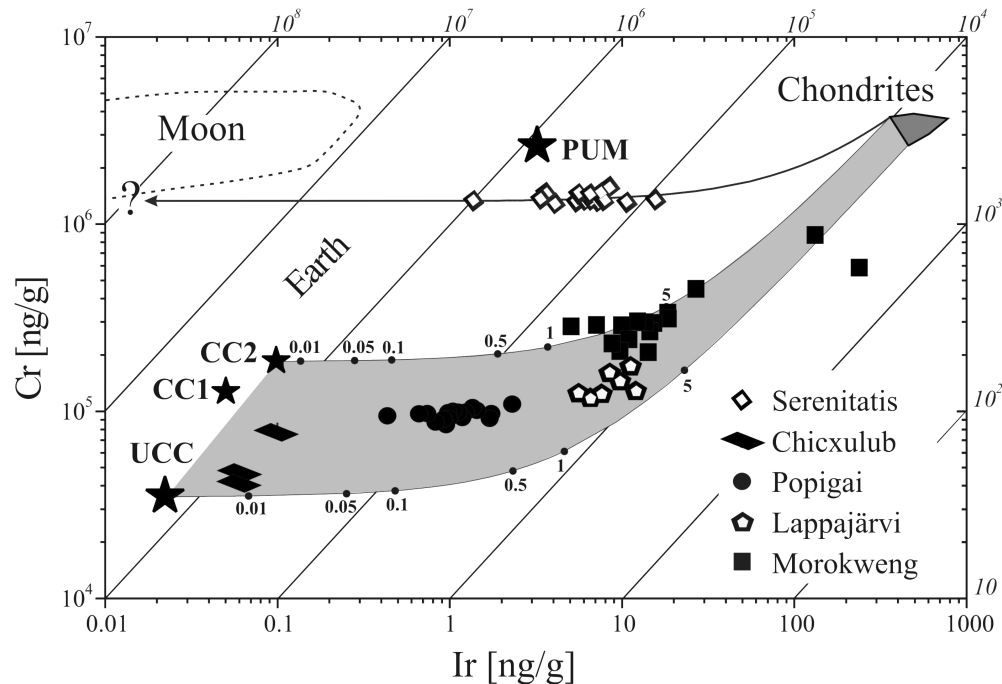


Fig. 2. Cr versus Ir concentrations of terrestrial and lunar target rocks compared to the composition of impact melts of five case studies. The grey field indicates the most likely mixing trajectories between chondritic projectiles and common terrestrial targets. Source of data: terrestrial rocks and chondrites (Fig. 1), Moon = lunar crust, values extracted from Fig. 5b in Richter et al. (2000). Numbers represent wt% chondritic material in the mixing trajectories. Some references of data are also given in the text.

compositional field appropriated for lunar crust (Fig. 2), supporting the assumption that these lunar impactites are clearly contaminated by projectile material. The more Cr-rich composition of the lunar target is in accordance with the occurrence of Cr-rich low-Ti lunar basalts at the impact site. Furthermore, a Cr-rich target composition is clearly supported by the data set on the composition of the Moon (see the “Moon” field in Fig. 4 given by Richter et al. 2000). These examples demonstrate clearly that the Cr/Ir ratios of impactites can be used to detect an extraterrestrial component.

Re-Os Isotopes

Turekian (1982) suggested that the differences between Os-isotopic ratios of crustal rocks and meteorites could be used to distinguish between a cosmic and a terrestrial component. Meteorites including chondrites and iron meteorites have generally high concentrations of both Re and Os. The concentration of Os is, with the exception of differentiated achondritic meteorites, higher than Re. Therefore, only small changes in the primary Os isotopic ratio have taken place during time. Studies of Os isotopes in chondrites by Walker et al. (2002) showed that $^{187}\text{Os}/^{188}\text{Os}$ ratios display relatively small variations among chondrites; the values are 0.12596 for carbonaceous chondrite, 0.12815 for enstatite, and 0.12833 for ordinary chondrite. For iron meteorites, Os-isotopic ratios vary between 0.11 and 0.18 (e.g., Morgan et al. 1995; Smoliar et al. 1996; Chen et al.

1998). Case studies have shown that Os-isotope ratios can be a sensitive tool for the recognition of an extraterrestrial component in impactites (Koeberl 1998; Koeberl and Shirey 1997; Koeberl et al. 2002). Since there is no significant difference between the Os isotopic composition of the Earth’s mantle and meteorites, the presence of a mantle component, such as ultramafic rocks, needs to be ruled out in order to ascribe the measured ratios to an extraterrestrial source (Koeberl and Shirey 1997). Some examples of Os-isotope studies of impactites illustrate this problem. Impactites of the Morokweng structure (Koeberl et al. 2002) lie on, or close to, a mixing line between a hypothetical impactor (CI chondrite) and the UCC (Fig. 3). The inferred target composition of Morokweng is average continental crust, with no apparent contribution from mantle material or young, mantle-derived mafic rocks. Therefore, the high Os and low $^{187}\text{Os}/^{188}\text{Os}$ ratios of the Morokweng impactites can be attributed to an extraterrestrial component. The case of Chicxulub impactites is more complicated; they showed much lower Os values and higher $^{187}\text{Os}/^{188}\text{Os}$ ratios (Gelinas et al. 2004) (Fig. 3). According to Gelinas et al. (2004) the Chicxulub samples reflect a mixing trend between the continental crust and a meteorite component. Several of the samples have values that do not differ substantially from those of the continental crust (Fig. 3). Those samples with higher Os and lower $^{187}\text{Os}/^{188}\text{Os}$ ratios could also reflect mafic rock inclusions in the impactites. A contribution of mafic rocks from the Chicxulub

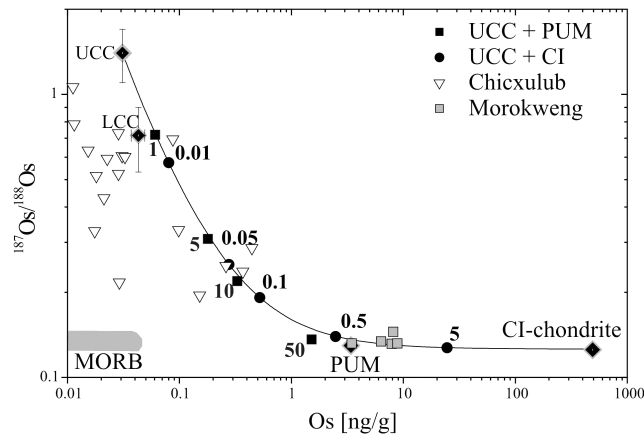


Fig. 3. $^{187}\text{Os}/^{188}\text{Os}$ ratios versus Os concentrations (ng/g) of some terrestrial rocks, CI chondrites (Wasson and Kallemeyn 1988), and impactites from Morokweng (Koeberl et al. 2002) and Chicxulub (Gelinas et al. 2004). The curve represents the calculated mixing line between CI chondrite values and the upper continental crust (UCC, Os = 0.031 ng/g and $^{187}\text{Os}/^{188}\text{Os}$ = 1.4, Peucker-Ehrenbrink and Jahn 2001). Percentages of projectile material mixed into hypothetical impact melt are shown as a line with black dots (0.01 to 5 wt%). The mixing trajectory between UCC and primitive upper mantle (PUM, Os = 3 ng/g and $^{187}\text{Os}/^{188}\text{Os}$ = 0.125, McDonough and Sun 1995; Meisel et al. 2001) is indicated only by solid squares (1 to 50 wt%). Lower continental crust (LCC, Os = 0.043 ± 0.006 ng/g and $^{187}\text{Os}/^{188}\text{Os}$ = 0.72 ± 0.18 was calculated as the range from the values given by (Esperanca et al. 1997; Saal et al. 1998; Peucker-Ehrenbrink and Jahn 2001); MORB = mid-ocean ridge basalt (Schiano et al. 1997).

target to the impactites was proposed by Kettrup et al. (2000). However, if we accept that the low $^{187}\text{Os}/^{188}\text{Os}$ samples reflect an extraterrestrial component, the contamination of the impactites is below 0.1 wt% (Gelinas et al. 2004). The Os-isotopic method is highly sensitive for the detection of a projectile component, under specific conditions. However, it is currently not possible to obtain any specific information about the projectile type with this method.

Cr Isotopes

Studies of Cr isotope ratios have significantly contributed to the recognition and identification of extraterrestrial components in impactites (Table 1). Detailed discussion of the method is given by Kyte et al. (2003) and Shukolyukov and Lugmair (1998). The variations in the Cr isotopic ratios are measured as deviations from the terrestrial standard $^{53}\text{Cr}/^{52}\text{Cr}$ ratio and are expressed as $\epsilon(53)$ (Lugmair and Shukolyukov 1998). Terrestrial rocks do not show much variation in the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio, supporting the assumption that the Earth was homogenized long after most ^{53}Mn decayed. Similar Cr isotopic ratios of lunar (anorthosite) and terrestrial rocks also advocate their genetic relation. The $^{53}\text{Cr}/^{52}\text{Cr}$ ratios for meteorites vary between +0.1 and +1.3 ϵ . Only carbonaceous chondrites appear to have a ^{53}Cr deficit (−0.4 ϵ). This is an artifact of the $^{54}\text{Cr}/^{52}\text{Cr}$ second-order fractionation correction used, as carbonaceous chondrites

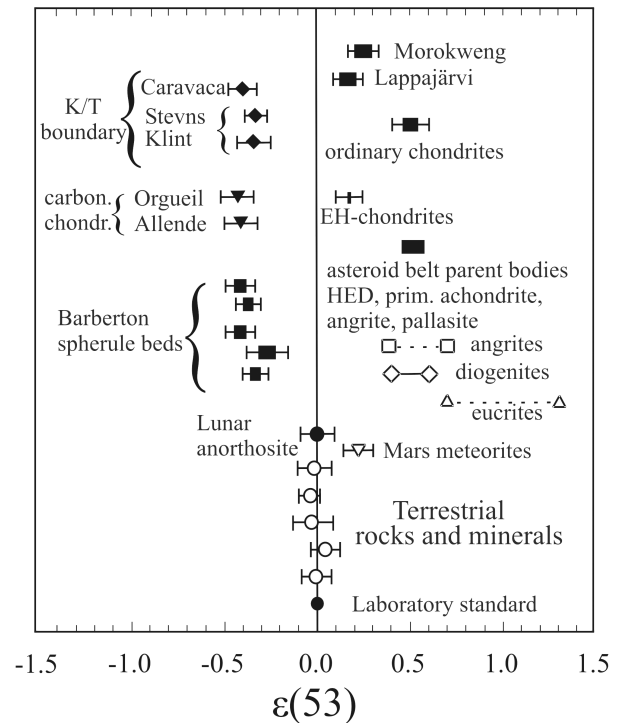


Fig. 4. $\epsilon(53)$ values in terrestrial rocks and impactites, compared to lunar anorthosite, Martian rocks, and different types of meteorites. The figure was redrawn from Shukolyukov and Lugmair (1998), including additional data from Shukolyukov and Lugmair (2000).

contain a presolar, ^{54}Cr -rich component (Lugmair and Shukolyukov 1998). The excess of ^{54}Cr allowed an identification of carbonaceous chondrite material in samples from the K/Pg-boundary at Caravaca and Stevns Klint, and in Barberton spherule layers, South Africa (Shukolyukov and Lugmair 1998; Kyte et al. 2003) (Fig. 4). The projectile component in these K/Pg boundary sites and in the S3 and S4 Barberton spherule layers are in the range of several wt% and up to almost 100%, therefore very large amounts of Cr of extraterrestrial origin have been inferred. Naturally a 100% extraterrestrial component in such spherule samples has remained controversial (e.g., Hofmann et al. 2006).

So far, only carbonaceous chondrites and enstatite chondrites show characteristic Cr-isotopic ratios, allowing a discrimination from other types of chondrites and differentiated meteorites that share a similar isotopic composition (Kyte et al. 2003). The effect of terrestrial Cr in the isotopic ratios may influence the results, as discussed by Kyte et al. (2003) for the S4 Barberton spherule layer in South Africa.

The Cr isotopes enable the detection of an extraterrestrial component in impactites and, in ideal cases, to distinguish between three groups of meteorites: a) carbonaceous chondrites, b) enstatite chondrites, and c) all other types of meteorites. The use of “raw” Cr-isotopic ratios could allow a

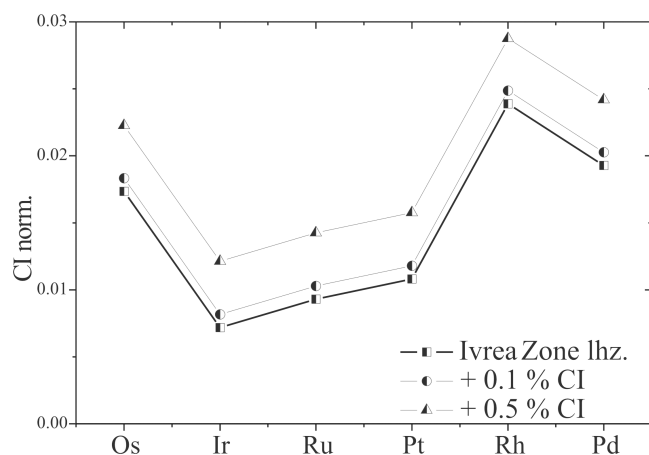


Fig. 5. Model impact melt rock composition resulting from an impact of a CI chondrite on a hypothetical lherzolite target. The PGE-patterns are strongly disturbed by the composition of the target. Therefore, no identification of the projectile is possible. Source of data: CI chondrite (Wasson and Kallemeyn 1988); Ivrea Zone lherzolite (Lorand 1989). Note PGE are plotted in order of decreasing condensation temperatures from solar nebula (after Lodders 2003).

better discrimination among carbonaceous chondrites; however, the effects of the indigenous Cr appear significant. The relatively high background of Cr in terrestrial and especially in lunar rocks does, however, restrict the detection of an extraterrestrial component in impactites and distal ejecta layers. The limit of detection of an extraterrestrial component is proportional to the indigenous Cr concentrations and the proportion of extraterrestrial material in the impactites (Koeberl et al. 2002; Frei and Rosing 2005). The identification of the impactor generally needs a high proportion of projectile contamination in impactites of at least several wt%, which is not very common in terrestrial craters.

PGE Ratios

The identification of the projectile component is usually accomplished by determining the CI-normalized PGE patterns of “contaminated” rocks. For flat PGE patterns, a chondritic impactor is generally proposed (Koeberl 1998; Palme 1982; Schmidt et al. 1997). However, the application of PGE patterns can be strongly influenced by the composition of the target which can mask small differences between various types of chondrites, and in the worst case (high indigenous PGE concentrations), hamper the recognition of a chondritic pattern for the projectile (e.g., Fig. 5).

Element patterns can only be used for the general identification of the projectile type in cases of low indigenous PGE concentration, but are generally not appropriate for a projectile identification down to the level of specific chondrite types, where a precise indigenous correction is required. Constraining the indigenous component, which is obtained by the determination of the total amount of PGE incorporated into impact melt from the

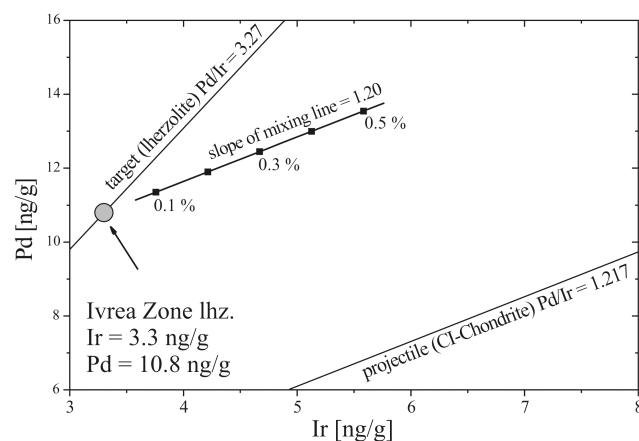


Fig. 6. The mixing trajectory of a model impact melt formed by a lherzolite target and a CI chondrite projectile (same as in Fig. 3). The amount of admixed projectile is given in numbers (0.1–0.5 wt% projectile). The projectile elemental ratio (PER) is determined by linear regression of the slope of the mixing line. Note that the slope of the regression for the impact melt rock is essentially equivalent to the Pd/Ir ratio in a chondritic projectile.

different target rocks is a difficult, and often impossible, task, and has been one of the major obstacles in precise projectile identification.

A new approach for the identification of the projectile type, without specifically accounting for the target component, is based on determination of projectile elemental ratios (PER). The impact melt rock composition is a mixture of the different target rocks with a projectile component, as shown in Fig. 2. Whereas impact melt rocks are relatively homogeneous in terms of major and trace element composition (e.g., Dressler and Reimold 2001; Grieve et al. 1977), the projectile component is usually unevenly distributed within the impact melt rocks with respect to impact relevant elements (IRE) concentration, which results in the equivalent of a mixing trajectory defined by individual impact melt rock compositions with variable amounts of the projectile component (Fig. 2). The PER can be determined by a linear regression of such mixing trajectories, even in case of a PGE-rich target. Although the chondritic projectile cannot be recognized in the normalized PGE pattern (Fig. 5), the slope obtained from the linear regression of the mixing trajectory is clearly dominated by the PGE ratio of the projectile (Fig. 6). This slope is termed the “projectile elemental ratio” (PER), as it is almost identical to the elemental ratio in the projectile. The deviation of the slope from the ratio in the projectile is inversely proportional to the projectile/target ratio of the selected elements. The illustrated Pd/Ir correlation in Fig. 6 is among the least precise cases for the determination of a PER, as the Pd concentration in the lherzolite target is relatively high compared to that of the projectile. Nevertheless, for Pd/Ir (Fig. 6) the deviation of the PER from the ideal projectile ratio is relatively small (~1%)

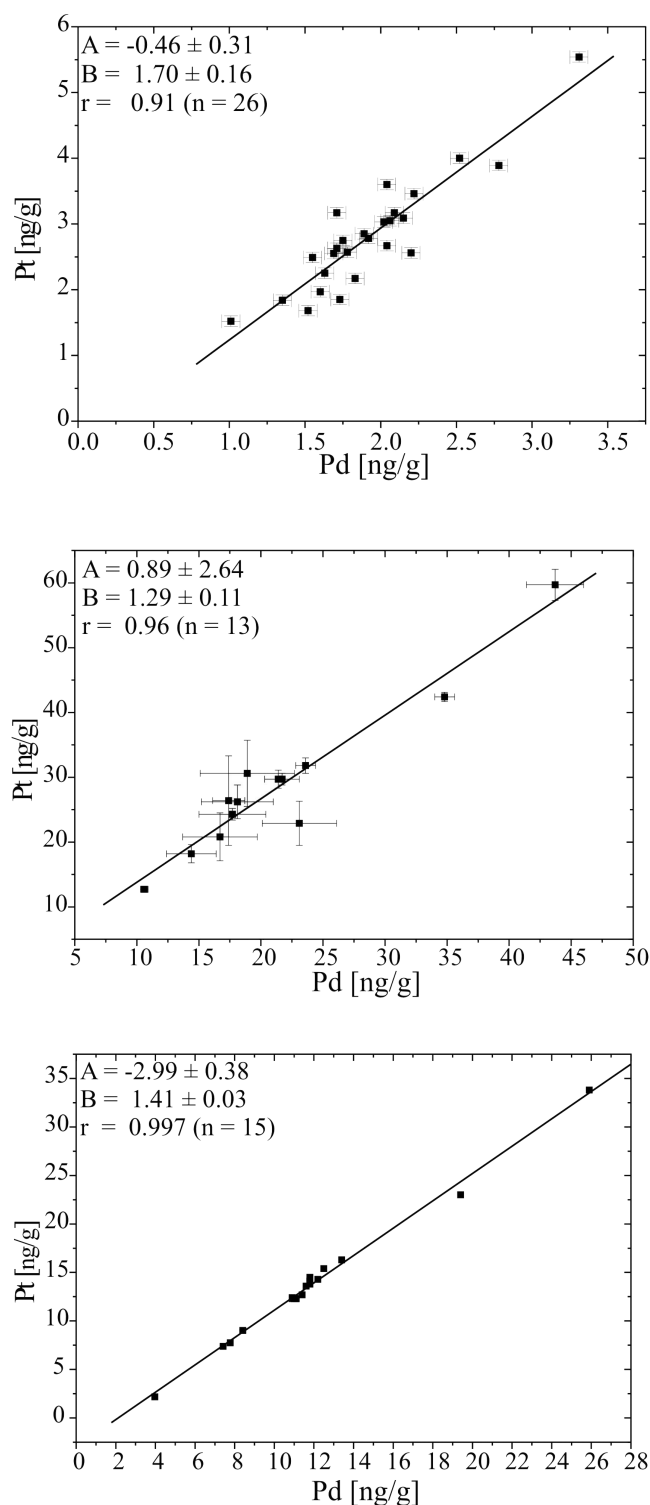


Fig. 7. Regression analysis of Pt versus Pd (linear regressions $Y = A + B * X$) in the impact melt rock of (a) Popigai (Tagle and Claeys 2005), (b) Morokweng (McDonald et al. 2001), and (c) Serenitatis basin (Tagle 2005). The slope (B) represents the projectile elemental ratio. The error bars reflect the analytical error given by the respective authors.

and probably below analytical resolution. The effects of the target composition on Cr/Ir or Ni/Ir ratios in impactites can be significant, due to the generally higher Cr and Ni background of the target rocks in comparison to the PGE. Consequently, the application of Cr/Ir or Ni/Ir ratios for precise impactor identification should be avoided.

The use of the slope of the mixing line for determination of the PER defines the composition of the projectile without correction for the indigenous PGE. This approach has been successfully used recently for the identification of projectiles in different impact structures, such as Morokweng, Clearwater East, Popigai, and the Serenitatis basin on the Moon (McDonald 2002; McDonald et al. 2001; Tagle 2005; Tagle and Claeys 2004). The determination of the PER for three different structures is illustrated for Pt/Pd ratios in Fig. 7.

In order to show possible effects on the pristine element ratios, due to fractionation we have chosen a PER (Pt/Pd), which generally involves less well-defined correlations among all possible PGE/PGE combinations, as shown for Morokweng and Popigai examples (Fig. 7). The good linear correlations ($r > 0.9$) (Fig. 7) between these PGE, however, supports the assumption that no major fractionation process or postimpact alteration has taken place in these cases. Nevertheless, some scatter can be recognized for Pt/Pd ratios (Figs. 7a and 7b) of Morokweng and Popigai impactites. It is interesting to note that no effect can be seen for these two elements on the Moon impactites (Fig. 7c), where all PGE ratios show almost ideal correlation. The disturbance of Pt/Pd ratios for these terrestrial examples is probably related to hydrothermal processes, as Pt and Pd represent the most mobile of all PGE. The other PGE appear to be relatively unaffected by secondary mobilization.

The PER obtained by combination of the different IRE can be calculated from the slope of the mixing line of two elements. The PER can then be compared to the elemental ratios in the different types of chondrite, firstly developed by Tagle (2004). At this time, the database includes 775 analyses for 275 chondrites that have been published over the past 40 years. Data reduction is based on the assumption that IRE ratios calculated for every analysis vary around a "true" ratio for each specific meteorite group. The collected data were carefully evaluated and filtered, not only to take possible analytical errors into account, but also problems due to sample inhomogeneity, as a result of small sample masses analyzed, and element loss as a consequence of weathering. In a first step, element/Ir ratios were calculated from each data set. Iridium was chosen because it is the most commonly determined element among the IRE. Aberrant element/Ir ratios occur in a few cases and were excluded from further calculations. In a second step, mean and standard deviation (1) of the element ratios were calculated for each chondrite group. Thereafter, a 2σ filter (which includes 95.5% of all analyses) was applied and only values

Table 3. Comparison of PGE element ratios of our database with published values.

	Wasson and Kallemeyn (1988)		McDonald et al. (2001)		Database used	
	Rh/Ir	Pd/Ir	Rh/Ir	Pd/Ir	Rh/Ir	Pd/Ir
H	0.29	1.14	0.30 ± 0.01	1.11 ± 0.03	0.31 ± 0.004	1.10 ± 0.10
L	No data	1.14	0.33 ± 0.01	1.35 ± 0.05	0.33 ± 0.007	1.23 ± 0.14
LL	No data	1.47	0.34 ± 0.01	1.64 ± 0.10	0.34 ± 0.006	1.47 ± 0.21

between the mean and $\pm 2\sigma$ were used for further computation. Values above or below the mean $\pm 2\sigma$ were excluded. Finally, the characteristic ratios for each chondrite group were calculated from the ratios passing the 2σ -filter. The uncertainty on these final ratios were calculated as 1σ of all values that passed the filter. The element ratios Rh/Ir and Pd/Ir are considered to be the most instructive ratios for projectile identification. A comparison of published data of ordinary chondrites (Wasson and Kallemeyn 1988; McDonald et al. 2001) with those of our comprehensive database that went through the process of data reduction, demonstrates that our database is consistent with already approved and published data sets (Table 3). A detailed presentation of our database is actually being prepared for publication (Tagle and Berlin, Forthcoming).

The results of the database show that not all possible element combinations are useful for an identification of the projectile type. For a precise identification of the projectile type, it is important to choose elemental ratios that allow the best discrimination between the different projectile types (chondrites). Condensation processes in the solar nebula mainly control fractionation of PGE in chondrites (e.g., Horan et al. 2003). Therefore, elements with large differences in the condensation temperature present the strongest variations in the elemental ratios. The lowest condensation temperatures among PGE are found for Rh and Pd (Lodders 2003). Element ratios including one of these elements and one of those with higher condensation temperatures allow the best discrimination between different chondrite types. As a consequence, Rh and Pd combined with Os, Ir, Ru, or Pt are the most relevant ratios for the identification of chondritic projectiles (Figs. 8a and 8b). Other ratios, such as those shown in Fig. 9, are not adequate for projectile identification, as they present almost no resolution among chondrite types. The identification of the projectiles for the Serenitatis basin and the Popigai and the Morokweng structures are shown in Figs. 8a and 8b. The elemental ratios include all PGE (except Os) and follow the principle of high/low condensation temperature or vice-versa. The fields defined by the slope of the different PGE overlap with the fields of discrete ordinary chondrites, allowing a precise identification of the projectile e.g., L or, most likely, LL chondrite for the Morokweng structure, (South Africa) (McDonald et al. 2001) an L chondrite for the Popigai crater (Siberia) (Tagle and Claeys 2005) and a LL chondrite for Serenitatis basin (Apollo 17 samples from the Moon) (Tagle 2005).

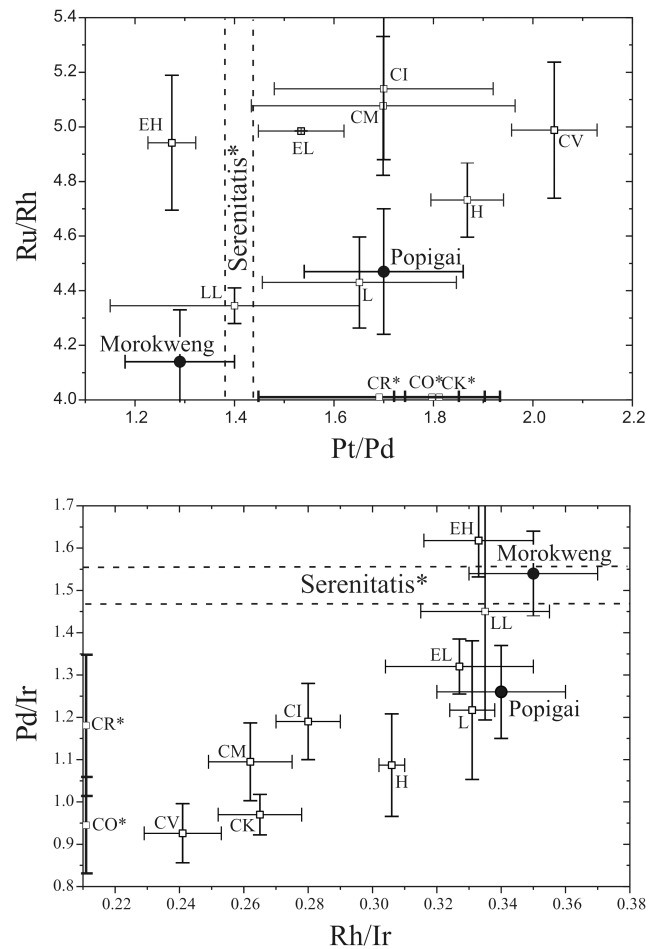


Fig. 8. Comparison of the PGE “projectile elemental ratios” of the impact melt rocks of Popigai, Morokweng, and Serenitatis to the elemental ratios of chondrites calculated from the database of Tagle (2004) for different types of chondrites. The uncertainty bars for the meteorites represent 1σ standard deviations. * = only one ratio known.

PGE combined with PER calculated from the slope of mixing trajectories of a suite of contaminated impactites from an individual impact structure and comparison with the composition of chondrites, permit a precise determination of the projectile type. Nevertheless, this method requires a larger number of samples than the Os- and Cr-isotopic method as well as inhomogeneous distribution of the projectile component in order to generate a well-defined linear regression. However, this has not been a limitation for any of the structures studied so far. Some additional problems may result from inhomogeneous distribution of the indigenous

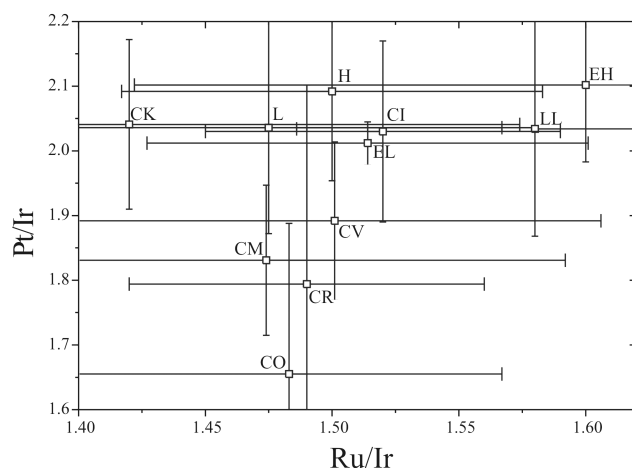


Fig. 9. PGE elemental ratios of chondrites, including only refractory PGE. In contrast to Fig. 8 there is no discrimination between the different chondrite types (database of Tagle 2004).

PGE within the analyzed samples, or due to a too small, <0.05%, meteoritic component; in such cases it would be almost impossible to determine any useful linear trend for impactites.

CONCLUDING REMARKS

Among the methods discussed, the Os isotope method is most sensitive for the detection of small amounts (<0.5%) of extraterrestrial components in impactites. However, this only holds true for target lithologies with no pronounced chemical signature of mantle or young mantle-derived mafic rocks. Furthermore, this method is not suitable for the characterization of the projectile type. The Cr isotope method requires the highest amount of projectile contamination in order to detect an extraterrestrial component. At high levels of projectile contamination of several wt% or more, the Cr isotope method allows the identification of at least three different groups of extraterrestrial material, including PGE-poor differentiated achondrites. In addition, this method is almost independent of the target composition and postimpact alteration, as has been shown in the 3.2 Gyr impact layers from Barberton (South Africa) (Kyte et al. 2003). This method, however, cannot be applied to lunar impact melt rocks, because of the high indigenous Cr on the Moon. In the case of PGE-poor achondrites, the Cr isotope method may be the only possible method for the identification of a projectile.

The application of IRE ratios (Cr/Ir, Ni/Ir, PGE/PGE) represents a powerful method for the detection and identification of a projectile in terrestrial and lunar impactites, as it does not require correction for an indigenous component. This also applies in the case of terrestrial target lithologies with a high component of upper mantle material. In addition, for the most common extraterrestrial material impacting Earth, chondrites, it has been shown that it is even possible to

identify the specific chondrite type. However, an identification of the projectile cannot be achieved on single samples. The regression method is only applicable to a set of samples with different degrees of projectile contamination of rather homogeneous impactite (generally impact melt). Future improvements in analytical techniques, as well as a growing amount of PGE data on chondrites, will probably enhance the precision of projectile identification further.

The identification of a ~25 cm LL chondrite fragment in the impact melt of the Morokweng impact structure by Maier et al. (2006) supports the results obtained by the PER as the same type of projectile was previously suggested by McDonald et al. (2001) based on PGE ratios. For the first time a projectile fragment supplies a direct test validating the chemical identification of projectile traces in impact crater rocks.

About one-third of the over 170 impact craters known on Earth contain preserved impact melt rocks, and are, therefore, potential candidates for projectile identification. Even if only a fraction of all projectiles that have impacted the Earth could be properly identified, it would be an important step in the understanding of the impactor sources. Nevertheless, there is a long way to go in order to link the dynamics of the asteroid belt, the formation of near-Earth asteroids, and compositional results obtained from spectral studies of asteroids with impact cratering rates and projectile types. Further studies of terrestrial craters and future lunar samples with a more complete lunar crater record, may help identify the projectiles from ancient impacts, such as those from the late heavy bombardment.

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