



Platinum group elements in impactites of the ICDP Chicxulub drill core Yaxcopoil-1: Are there traces of the projectile?

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Abstract—This study presents results of platinum group element (PGE) analyses of impactites from the Yaxcopoil-1 (Yax-1) and Yucatán 6 drill cores of the 180 km-diameter Chicxulub crater. These are the main elements used for projectile identification. They were determined by nickel sulfide fire assay combined with inductively coupled plasma mass spectrometry. The concentration of PGE in the samples are low. The concentration patterns of the suevite samples resemble the pattern of the continental crust. We conclude that any meteoritic fraction in these samples is below 0.05%. A syn- and post-impact modification of the PGE pattern from meteoritic toward a continental crust pattern is very unlikely. The globally distributed fallout at the Cretaceous-Tertiary (K/T) boundary, however, has high PGE concentrations. Therefore, the lack of a significant meteoritic PGE signature in the crater is not an argument for a PGE-poor impactor. Taking the results of three-dimensional numerical simulations of the Chicxulub event into account, the following conclusions are drawn: 1) The main fraction of the impactor was ejected into and beyond the stratosphere, distributed globally, and deposited in the K/T boundary clay; and 2) the low amount of projectile contamination in the Yax-1 lithologies may reflect an oblique impact. However, the role of volatiles in the mixing process between projectile and target is not well-understood and may also have played a fundamental role.

INTRODUCTION

The hypothesis of a large impact at the Cretaceous-Tertiary (K/T) boundary was suggested for the first time by Alvarez et al. (1980) after the identification of an Ir-rich layer in the boundary clay at Gubbio, Italy, and almost simultaneously by Smit and Hertogen (1980) at Caravaca, Spain. Ten years later, the Chicxulub structure (Penfield and Camargo 1981; Hildebrand and Penfield 1990), Yucatán Peninsula, Mexico, with an age of 65.0 Ma (Swisher et al. 1992), was identified as the long-sought K/T crater (Hildebrand et al. 1991). The K/T boundary layer not only contains Ir as a detectable extraterrestrial component, it is also enriched in the other platinum group elements (PGE): Os, Ru, Rh, Pd, and Pt. The relevance of PGE for the quantification and identification of extraterrestrial components was claimed by various authors (e.g., Morgan et al. 1975, 1979; Palme et al. 1978, 1979; Palme 1980; and Koeberl 1998).

A major problem in quantifying the degree of mixing between impactor and target is that, for most of the craters, the

impactor type itself is not known. The projectile types are mostly described as chondrites or iron meteorites (Koeberl 1998). A projectile quantification in wt% based on Ir concentration alone can result in erroneous estimations because of the compositional variations between different meteorite types. The PGE amount in chondrites varies, for example, for Ir between 760 ng/g for CV chondrites and 360 ng/g for L chondrites (Wasson and Kallemeyn 1988). CH chondrites (metal-rich) can contain over 1000 ng/g (Bischoff et al. 1993). The variations in iron meteorites are even higher (e.g. Koeberl 1998). This clearly shows that the type of projectile needs to be identified for a clear quantification of the projectile proportion admixed into the impactites.

Two different approaches have mainly been used to identify the Chicxulub projectile. The first approach focused on the extraterrestrial signature of the worldwide distributed Chicxulub ejecta at the K/T boundary, while the second one involved geochemical studies of the impactites within the crater.

The distal ejecta layer related to the Chicxulub impact

crater may contain extremely high amounts of projectile material (nominal CI chondrites) of several wt% (Kyte et al. 1980). The studies of PGE at the K/T boundary revealed that the element patterns vary between different localities. These variations were interpreted as the result of fractionation processes resulting from the depositional environment or as a product of ballistic fractionation (Evans et al. 1993, 1994, 1995). PGE studies led to the conclusion that the Chicxulub projectile was a chondrite (e.g. Kyte et al. 1985). Chondrites are responsible for most of the craters larger than 1.5 km in diameter (Koeberl 1998). A more precise identification was based on a fossil meteorite reported from a Pacific marine K/T boundary section drilled at DSDP site 576. This piece of meteorite was interpreted as a fragment of the Chicxulub projectile and shows a texture that resembles a carbonaceous chondrite (Kyte 1998). Studies based on Cr isotopes of the K/T clay from Stevns Klint and Caravaca by Shukolyukov and Lugmair (1998) also indicated a carbonaceous chondrite for the Chicxulub projectile and as the source for the Cr enrichment.

The identification of the extraterrestrial signature in the impactites inside the crater was not as clear as the results from the distal ejecta. The amount of sample material available for analysis from the Chicxulub crater was extremely small. Samples from the Chicxulub 1 (C-1) and Yucatán 6 (Y-6) drill cores were analyzed by different groups. Ir measurements of samples from C-1 and Y-6 performed by Hildebrand et al. (1993), Koeberl et al. (1994), and Claeys et al. (1995, 1998) show that the concentrations were, in most cases, below the analytical detection limit. The Ir concentrations were similar to the average continental crust (0.03 ng/g) proposed by Peucker-Ehrenbrink and Jahn (2001). Contrary to those results, Sharpton et al. (1992) and Koeberl et al. (1994) reported Ir concentrations between 2.5 and 15 ng/g in samples from C-1 and Y-6, indicating strongly heterogeneous Ir contents, probably due to nugget effects. Schuraytz et al. (1996, 1997) described PGE nuggets from the Chicxulub impact melt in Y-6.

Koeberl and Shirey (1997) recognized the possibility of determining the PGE source based on Os isotopes. Os

analyses of Chicxulub samples from the C-1 drill core (Koeberl et al. 1994) revealed Os concentrations of 25.2 ng/g in one sample, which were in agreement with higher Ir values found in the same sample. The observed $^{187}\text{Os}/^{188}\text{Os}$ ratios of 0.113 and 0.505 were interpreted to reflect heterogeneous contamination of the Chicxulub impactites with a meteorite component (Koeberl et al. 1994). This was generally confirmed by a recent Os isotope study on the Yaxcopoil-1 (Yax-1) impactites (Gelinas et al. 2004).

The aim of our study is to determine the amount of meteoritic contamination and to characterize the projectile by analyzing PGE, the siderophile elements Ni and Co, and the lithophile element Cr in impactites of the Chicxulub structure. Suevite-type polymict breccias from the Yax-1 drill core, supplied by the International Scientific Drilling Program (ICDP), and one sample of impact melt from the Yucatán 6 (Y-6) drill core were analyzed.

SAMPLING OF THE CHIXULUB IMPACTITES FROM THE YAX-1 DRILL CORE

Samples from the Yax-1 drill core expose a complex layered sequence of suevite-type polymict breccias (Stöffler et al. 2004). Fragments of silicate and carbonate melt, lithic clasts of the crystalline basement, and the sedimentary cover (mainly carbonate rocks) are mixed in various proportions. Compared to typical suevite from smaller craters, the sequence is extremely rich in (silicate) melt particles and rather poor in fine-grained matrix. The modal composition, the grain size of the components, and the matrix characteristics of the impactites are distinctly variable with depth and allow recognition of six different layers of suevitic rocks (Table 1). From bottom to top, the following main depositional stages were established (Stöffler et al. 2004): a) ground surging and mixing of impact melt and lithic clasts at the base of the ejecta curtain (unit 6); b) deposition of a thin veneer of melt that was laterally transported and brecciated (unit 5); c) collapse of the ejecta plume and deposition of fallback material from the lower part of the plume (unit 4); d) continued collapse of the ejecta plume and deposition of the

Table 1. Position of the analyzed samples within the suevitic unit of the ICDP drill core Yax-1, Chicxulub, Yucatán, Mexico, adapted from Stöffler et al. (2003).

Analyzed samples	Depth ^a (m)	Log name ^b (unit)	Proposed name
Yax-1 800.25 m	794.63–807.75	Redeposited suevite (1)	Upper sorted suevite (USS)
Yax-1 824.01 m	807.75–823.25	Suevite (2)	Lower sorted suevite (LSS)
Yax-1 838.29 m	823.25–846.09	Chocolate-brown “melt” breccia (3)	Upper suevite (US)
Yax-1 852.80 m	846.09–861.06	Suevitic breccia, variegated, glass-rich (4)	Middle suevite (MS)
Yax-1 865.01 m	861.06–884.96	Green monomict autogene melt breccia (5)	Brecciated impact melt rock (BMR)
	884.96–894.94	Variegated polymict allogenic clast melt breccia (6)	Lower suevite (LS)

^aNote that some values deviate slightly from the macroscopic division from Dressler et al. (2003).

^bLog name according to Dressler et al. (2003).

upper suevite (unit 3); and e) late phases of the collapse of the ejecta plume and settling of melt and solid particles through the atmosphere to form the lower and upper sorted suevite (units 2 and 1).

Multi-stage post-impact hydrothermal alteration has affected the whole sequence (Hecht et al. 2004). All glassy parts of silicate melt particles are altered to clay minerals (probably smectites). Plagioclase and clinopyroxene microphenocrysts in these melt particles are frequently overgrown by secondary K-feldspar. A more complete description of the suevitic units at Yax-1 is given by Stöffler et al. (2004).

Sampling was constrained by the availability of larger samples and the aim to cover most of the suevitic units (Table 1) that reflect different stages of deposition from the ejecta curtain and plume (as given above). No samples were taken from the lower suevite since this unit shows the strongest evidence for post-impact hydrothermal mass transfer (Hecht et al. 2004).

Sample Yax-1 800.25 m was taken from the upper sorted suevite, which is fine-grained (particle size generally less than 0.5 cm). Most melt particles are poor in microphenocrysts, but some dark aphanitic melt particles also occur. The matrix consists of a very fine-grained mixture of calcite grains and silicate melt or rock fragments altered to clay minerals (smectites).

Samples Yax-1 824.01 m and Yax-1 838.29 m are from the upper suevite, which is characterized by a serial grain size distribution and abundant matrix. Greenish to gray melt particles with irregular twisted shapes are up to a cm in size and contain plagioclase microphenocrysts displaying flow textures. Smaller melt particles may have shard-like shapes. Additional rare dark aphanitic melt particles occur. The matrix is enriched in calcite compared to the upper and lower sorted suevite.

Sample Yax-1 852.80 m from the middle suevite is similar to the samples from the upper suevite, however, the silicate melt particles exhibit a higher proportion of primary plagioclase microphenocrysts.

Sample Yax-1 865.01 m from the brecciated impact melt rock (unit 5) is composed of well-crystallized melt fragments with abundant clinopyroxene (augite) apart from plagioclase. Although secondary K-feldspar and clay minerals (Mg-rich saponites) occur, the melt particles of this sample are among the least altered of the whole suevitic sequence (Hecht et al. 2004).

ANALYTICAL METHODS

Major and some trace elements were determined by X-ray fluorescence spectroscopy (XRF) with a SIEMENS SRS 3000 on glass tablets (Schmitt et al. 2004). The PGE concentrations were measured at the GeoForschungsZentrum (GFZ) Potsdam using an inductively coupled plasma mass spectrometer (ICP-MS) following nickel sulfide fire assay pre-concentration and separation steps (Plessen and Erzinger 1998). This fire assay method allows extraction of 99% of the PGE from a silicate sample. It combines good analytical precision with low detection limits and is ideal for determining even minor proportions of meteoritic contamination. Table 2 shows the reagent blanks as well as detection and determination limits, respectively, calculated from the blank values.

The precision and accuracy of the combined fire assay and ICP-MS method was tested by analyzing international reference materials from the Canadian Certified Reference Material Project (CCRMP). The results are shown in Table 3. Three different reference samples were analyzed: TDB-1 and WGB-1 with low, and WMG-1 with high PGE concentrations. The results are in good agreement with certified values. Note that those reference values, which are given without standard deviation are only proposed or information values.

It has been well-documented that PGEs occur heterogeneously in many geological samples (Hall and Pelchat 1994; Plessen and Erzinger 1998). PGEs tend to form alloy nuggets, which may collect most of the PGEs within the sample. Therefore, great care has to be taken in the sampling protocol so that the obtained PGE abundances are representative of the whole rock composition (Ely and Neal 2002). Representative analyses are obtained by processing large amounts of sample (10–100 g) (Hall and Bonham-Carter 1988). It has also been shown that the distribution of PGE carrier phases in the rock results in some samples being more homogeneous than others in terms of PGE concentration (McDonald 1998; Plessen and Erzinger 1998). This may result in poor reproducibility of the data if sample aliquots in the mg range are used. The nickel sulfide fire assay procedure allows concentration of PGE from a relatively large mass of sample of up to 70 g, using up to 105 g of assay flux material. The size of the sample used in this study varied between 20 and 40 g (Table 4). The samples Yax-1 824.01 m and Yax-1 838.29 m were analyzed twice.

Table 2. PGE and Au concentrations of reagent blanks determined by substituting the silicate sample with pure quartz.

	Ir (pg/g)	Ru (pg/g)	Pt (pg/g)	Rh (pg/g)	Pd (pg/g)	Au (pg/g)
Blank	21	27	18	4	60	48
Blank + 3s (d.l.) ^a	38	62	43	13	127	89
Blank + 6s (det. l.) ^b	55	98	67	22	194	130

^ad.l. = detection limit.

^bdet. l. = determination limit.

Table 3. Results of the determination of PGE and Au concentration in international reference materials.^a

Standard	Ir (ng/g)	Ru (ng/g)	Pt (ng/g)	Rh (ng/g)	Pd (ng/g)	Au (ng/g)
TDB-1 Ref.	0.15	0.3	5.8 ± 1.1*	0.7	22.4	6.3 ± 1.0*
TDB-1 Lit. (n = 25)	0.12 ± 0.02	0.25 ± 0.08	3.8 ± 0.6	0.33 ± 0.04	20 ± 1.7	4.8 ± 1
This study						
TDB-1 (n = 3)	0.12 ± 0.004	0.24 ± 0.07	4.8 ± 1.0	0.42 ± 0.03	20 ± 1.0	4.0 ± 0.8
WGB-1 Ref.	0.33	0.3	6.1 ± 1.6*	0.32	13.9 ± 2.1*	2.9 ± 1.1*
WGB-1 Lit. (n = 30)	0.20 ± 0.04	0.2 ± 0.04	3.8 ± 1.0	0.14 ± 0.01	13 ± 1.1	2.0 ± 0.9
This study						
WGB-1 (n = 8)	0.18 ± 0.06	0.16 ± 0.01	3.7 ± 1.1	0.15 ± 0.04	10 ± 2.9	0.5 ± 0.2
WMG-1 Ref.	46 ± 4*	35 ± 5*	731 ± 35*	26 ± 2*	382 ± 13*	110 ± 11*
WMG-1 Lit. (n = 6)	47 ± 2.3	26 ± 1.3	705 ± 25	26 ± 0.5	380 ± 20	105 ± 5
This study						
WMG-1 (n = 3)	45 ± 2.4	27 ± 2.5	688 ± 33	25 ± 1	338 ± 32	85 ± 13

^aRef. = certified* and proposed values (Govindaraju 1994); Lit. = data from Plessen and Erzinger (1998); n = number of analyses; TDB = diabase; WGB and WMG = gabbros.

RESULTS AND DISCUSSION

The results of the analyses are shown in Table 4. The Ir concentrations are extremely low in many of the samples and, in some cases, are even below the detection limit of the analytical method (Table 2). The obtained Ir values are, thus, similar to the results from Claeys et al. (1998). The results are also plotted in Fig. 1. The PGE pattern for all samples (Yax-1 and Y-6) are similar and resemble those of the continental crust. The Ni/Cr ratios of impactites, ranging from 0.33 to 0.38, are also similar to averaged continental crust, with a ratio of approximately 0.44. In contrast, the Ni/Cr ratios of chondrites vary between 3 and 6 (Wasson and Kallemeyn 1988).

The PGE signature resulting from various proportions of the projectile can be estimated by model mixing of small amounts of average carbonaceous chondrite material to average continental crust material (Fig. 1). Admixture of 0.05% and 0.1% carbonaceous chondrite CV Ir = 760 ng/g (Wasson and Kallemeyn 1988) to the continental crust both produce distinct “chondritic” patterns. The model sample with 0.05 wt% of a carbonaceous chondrite raises the Ir concentration by about one order of magnitude (Fig. 1). The extremely low PGE concentrations in the Chicxulub impactites indicate that if there is an admixture of PGE-rich extraterrestrial material, its fraction is much less than 0.05 wt%. These results are also supported by the Os isotope data from Yax-1 samples (Gelinás et al. 2004), which indicate a contamination with a meteorite component below 0.01% for most samples and below 0.1% for all samples.

PGEs in impact melts from different craters generally show little or no fractionation from the projectile pattern (Koeberl et al. 1997; McDonald et al. 2001; McDonald 2002; Tagle and Claeys 2002). Although evidence for some selective mobility of PGE exist (e.g., Wallace et al. 1990; Colodner et al. 1992), a relative depletion of the more refractory PGE, like Ir and Ru, by hydrothermal alteration is unlikely, since these elements are less mobile than Pd and Pt

(Fuchs and Rose 1974; Varajão et al. 2000). Therefore, a syn- and post-impact modification of the PGE patterns from a meteoritic toward a continental crust pattern is improbable.

The present results, together with the results of Hildebrand et al. (1993), Claeys et al. (1995, 1998), and Gelinás et al. (2004), indicate that allochthonous impactites (suevitic breccias and melt rocks) from the drill cores Yax-1, Y-6, and C-1, located within the central basin of the Chicxulub impact structure, reflect only very minor contamination with projectile material. However, the globally distributed fallout at the K/T boundary has high PGE concentrations, indicating that the Chicxulub projectile was most likely an asteroid with a chondritic composition, as noted before.

The Chicxulub structure is not the only impact crater on earth where no significant amount of projectile material was found (Table 5). If the unlikely assumption that the K/T boundary is not related to the Chicxulub impact event is excluded, the data support a non-homogeneous spatial distribution of the projectile material between the proximal and distal impact formations. This means that the scarcity of a meteoritic signal in crater impactites does not necessarily imply a PGE-poor impactor. The reason for the low amount of a meteoritic component in the impactites may be explained by the mechanics of the impact processes, which affect the proportion of the projectile that becomes incorporated into the melt and remains in the crater after the impact. This process is not well-understood. The mixture between the target material and the projectile takes place at the contact interface between target and projectile. During the first seconds of impact, the molten and vaporized impactor material expands, and some proportion of it intrudes the melt or even the target rocks that will melt after pressure releases. This process can be influenced by different parameters:

- The results of three-dimensional numerical simulations of the Chicxulub event (Pierazzo and Melosh 1999,

Table 4. Composition of the Chicxulub Yax-1 suevite samples and the Y6-N19 melt rock sample; data for the continental crust (Wedepohl 1995); Rh values from Peucker-Ehrenbrink and Jahn (2001).

	Yax-1 800.25 m Whole rock	Yax-1 824.01 m Whole rock	Yax-1 838.29 m Whole rock	Yax-1 852.05 m Whole rock	Yax-1 865.01 m Whole rock	Y6-N19 Whole rock	Continental crust (CC)
Mass (g)	40	20/34 ^a	20/40 ^a	30	20	31	
Wt%							
SiO ₂	45.80	46.10	46.80	54.50	53.90	60.50	61.50
TiO ₂	0.53	0.52	0.51	0.66	0.60	0.39	0.68
Al ₂ O ₃	12.50	12.60	12.70	15.20	16.30	13.40	15.10
Fe ₂ O ₃ ^b	5.73	5.24	5.30	3.57	6.50	4.29	6.28
MnO	0.04	0.03	0.04	0.03	0.03	0.10	0.10
MgO	5.49	5.27	4.61	5.55	6.58	2.56	3.70
CaO	10.40	12.30	10.80	6.43	6.47	9.37	5.50
Na ₂ O	1.92	2.54	2.63	4.34	3.46	3.26	3.20
K ₂ O	2.17	3.16	4.12	3.80	2.79	2.30	2.40
P ₂ O ₅	0.02	0.10	0.09	0.13	0.12	0.09	0.18
SO ₃ ^c	<0.10	<0.10	<0.10	<0.10	<0.10	1.60	n.r. ^d
LOI	14.8	11.90	11.90	5.40	3.30	2.50	n.r.
Total	99.40	99.76	99.50	99.61	100.05	100.36	98.64
μg/g							
Ba	76	193	217	312	177	649	584
Co	<15	<15	<15	<15	<15	<15	24
Cr	46	50	45	80	55	42	126
Ni	17	19	17	<15	18	<15	56
Rb	71	57	67	45	41	65	78
Sr	278	515	534	458	500	577	333
V	21	48	36	79	65	84	98
Y	<10	14	15	12	<10	15	24
Zn	068	53	42	51	46	42	65
Zr	122	119	124	144	127	109	203
ng/g							
Ir	0.06	<0.04	<0.04	0.10	<0.04	0.06	0.02
		<0.04	<0.04				
Ru	0.26	<0.06	<0.06	0.68	0.66	<0.06	0.21
		<0.06	<0.06				
Pt	0.38	0.34	0.57	0.84	0.47	0.45	0.51
		0.42	0.53				
Rh	0.05	0.02	0.02	0.06	0.03	0.02	0.06
		0.04	0.03				
Pd	0.54	1.10	1.94	1.70	1.01	0.26	0.52
		1.04	1.84				
Au	0.54	1.19	2.64	1.82	2.33	0.57	2.50
		0.85	2.16				

^aAnalyzed twice for PGE.^bTotal Fe as Fe₂O₃.^cTotal S as SO₃.^dn.r. = not reported.

2000) show that there is a clear relationship between the impact angle, the velocity, and the amount of projectile that gets incorporated into the melt. With increasing speed and decreasing impact angle, the amount of projectile that remains in the crater or in its near vicinity decreases. These results foster the assumption of an oblique impact for the Chicxulub crater, first proposed by Schultz and D'Hondt (1996).

- The impact melt volume increases exponentially with increasing size of the projectile (Grieve and Cintala 1992). This results in a higher dilution of the impactor material in the molten target rocks. The amount of ejected rock also increases with the size of the impactor. The results from the Morokweng crater and the Popigai crater do not support the assumption of a significant role of impactor size on the degree of projectile admixture. The

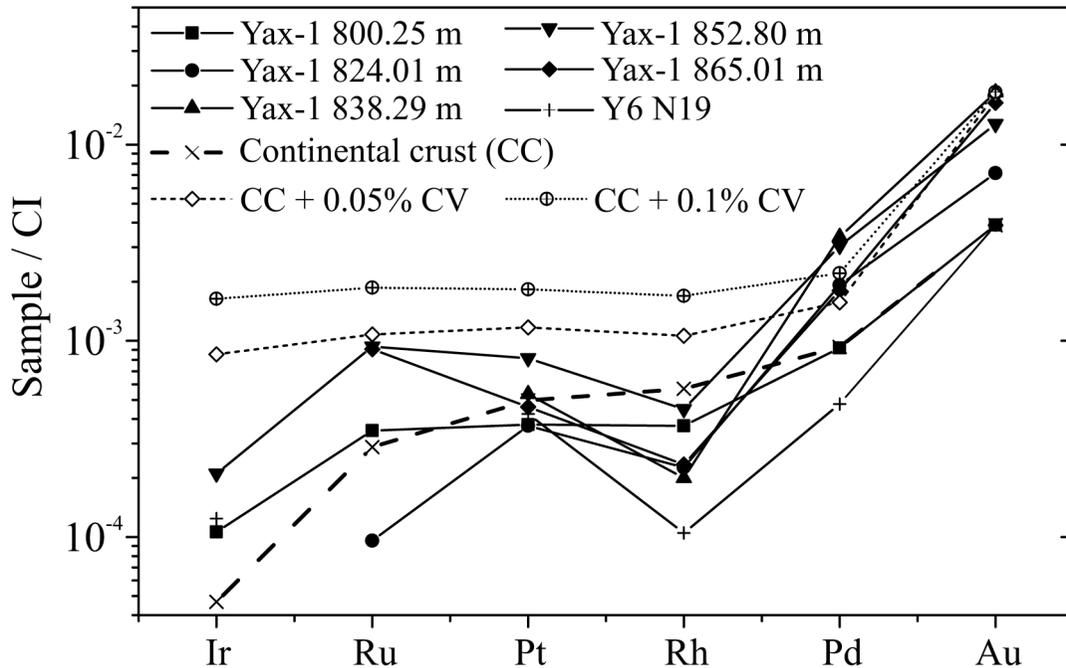


Fig. 1. CI-normalized PGE and Au concentrations of the Chicxulub Yax-1-suevites and Y6-N19 impact melt rock compared to the composition of the continental crust (CC) (Wedepohl 1995; Rh values from Peucker-Ehrenbrink and Jahn [2001]) and CC with 0.05% and 0.1% contamination of a CV carbonaceous chondrite (data from Wasson and Kallemeyn 1988). See text for explanation.

Table 5. Meteorite impact craters with low or no detectable projectile contamination (Earth Impact Database 2003). For some of these craters, an achondritic projectile is proposed; for others no clear enrichment of the impactites is found, and the impactor type could not be determined.

Crater	Diameter (km)	Age (Ma)	Impactor type	Reference
Gow Lake	5	<250	?	Wolf et al. (1980)
La Moinerie	8	400 ± 50	?	Grieve and Shoemaker (1994)
Nicholson Lake	13	<400	Achondrite?	Wolf et al. (1980)
El'gygytgyn	18	3.5 ± 0.5	Achondrite?	Grieve and Shoemaker (1994)
Ries	24	15 ± 1	Achondrite?	Morgan et al. (1979); Schmidt and Pernicka (1994)
Strangways	25	<470	Achondrite?	Morgan and Wandless (1983)
Mistatin	28	36.4 ± 4	?	Wolf et al. (1980)
Clearwater West	36	290 ± 20	?	Palme et al. (1978)
Lake Saint Martin	40	220 ± 32	?	Palme (1982)
Manicouagan	100	214 ± 1	?	Palme et al. (1978)

Morokweng crater, with a diameter of 80 km, has contamination of the impact melt between 1 and 7 wt%. The projectile was identified as an ordinary L or LL chondrite (McDonald et al. 2001). Compared to the Popigai crater with a diameter of 100 km, a similar type of projectile (L chondrite), and with a contamination of the impact melt of around 0.25 wt% (Tagle and Claeys 2002), it seems likely that the size of the impactor is not among the main factors influencing the admixture process.

- The properties of the interface between impactor and target may play the primary role in the admixture process. If the target is covered by a volatile-rich layer, as in case of Chicxulub, the mixing process will be hindered by the high amount of volatiles ejecting against

the intruding projectile material. A possible correlation can be expected, where the projectile contamination of the impact melt is a function of the thickness of the sediment layer (volatile-rich) and the diameter of the impactor.

The fate of the projectile in impact events plays a very important role for understanding impact processes (Pierazzo and Melosh 2000). Therefore, the Chicxulub impact with its low amount of projectile contamination within the crater and its relation to the worldwide K/T boundary layer may provide key information on this process.

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