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Clues to the nature of the impacting bodies from platinum-group elements (rhenium and gold) in borehole samples from the Clearwater East crater (Canada) and the Boltysh impact crater (Ukraine)

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(Dedicated to the memory of Paul Pellas)

Abstract–Seven large (10 g) impact melt rock samples from boreholes from the Boltysh impact crater (Ukraine) and six samples from the East Clearwater crater (Canada) were analyzed for Os, Ir, Ru, Rh, Pd, Re and Au by the nickel sulfide technique in combination with neutron activation. Earlier analyses of Clearwater East impact melt rocks have shown that they are strongly enriched in Ir, Os, Pd and Re. In this work, I confirm earlier findings and demonstrate similarly high enrichments of Rh and Ru. The average Os/Ir, Ru/Ir, Pd/Ir, Rh/Ir and Ru/Rh ratios of the melt rock samples from Clearwater East are CI-chondritic and yield an average Ir content of 25.2 ± 6.5 ng/g relative to an average upper crust concentration of 0.03 ± 0.02 ng/g Ir. The amount of meteoritic component corresponds to 4 to 7% of a nominal CI component for Clearwater East.

The impact melt rock samples from a bore hole from Boltysh are low in Ir with an average of 0.2 ± 0.1 ng/g. The CI-normalized abundances increase from the refractory to the more volatile siderophile elements (Os < Ir < Ru < Rh ~ Pd ~ Au ~ Ni ~ Co). Because of the low Ir anomaly and uncertainties in making corrections (correlations are weak) for indigenous siderophile elements, no clear projectile assignment can be made.

INTRODUCTION

In ~20 terrestrial impact structures, the type of the impacting projectile has been tentatively identified from abundances of siderophile and highly siderophile elements (HSEs) and their interelement ratios (Grieve and Shoemaker, 1994). The reliability of impacting body identification in many of the craters is generally based on relatively few HSEs and elemental ratios. For example, Janssens *et al.* (1977) proposed that the Rochechourt (France) meteorite was an IIA iron meteorite based on abundance ratios of Os, Ir, Ni and Pd.

In the East Clearwater impact structure, high concentrations of Os, Re, Ir, Pd, Ni, Co, Cr and Au have been detected in melt rocks by Palme *et al.* (1978, 1979), Grieve *et al.* (1980) and Evans *et al.* (1993). The flat chondrite-normalized pattern of all nonvolatile siderophile elements and a similar relative enrichment factor for Cr suggested the presence of ~7% of a chondritic component in the sampled portion of the impact melt layer of East Clearwater. This hypothesis required the addition of ~2% of ultramafic rocks to the East Clearwater impact melt (Palme *et al.*, 1979). An iron meteorite as projectile type was ruled out by Palme *et al.* (1978) because of the simultaneous enrichment of Cr. Iron meteorites have usually <50 μg/g Cr (Choi *et al.*, 1995). In comparison, the Cr content of CI chondrites is 2646 μg/g (Palme and Beer, 1993).

From Boltysh, so far only eight samples have been analyzed for Ir; three contain <1 ng/g Ir and five contain ~0.1 ng/g Ir (Gurov *et al.*, 1986; Grieve *et al.*, 1987). Grieve *et al.* (1987) concluded that the impactor could have been a stony projectile if the Ni (43 μg/g), Cr (56 μg/g) and Ir enrichments are meteoritic in origin.

The purpose of this study was to better characterize the meteoritic signatures of these two craters by additional analyses of highly siderophile elements (especially the less often analyzed elements, Os, Ru, Rh and Pd), which can be used in some cases to distinguish between magmatic iron meteorites, nonmagmatic iron meteorites and chondrites. The major compositional difference between magmatic and nonmagmatic groups is observed in log-log Ir-Ni trends, for which the slopes in magmatic groups range from –20 to –40, whereas those in the nonmagmatic groups are ~5 (Choi *et al.*, 1995). The trace-element fractionations in magmatic iron meteorites seem to be best modeled by fractional crystallization of an iron melt during solidification of iron cores in the parent bodies (Scott, 1972). Nonmagmatic iron meteorites have escaped the fractionation process and did not form a single molten core (Scott, 1972).

IMPACT STRUCTURES AND SAMPLES

The Clearwater samples are aliquots from rock samples from the same section of the melt sheet as analysed by Palme *et al.* (1979). The Boltysh samples, which were obtained from E. P. Gurov (Kiev), have been described previously by Grieve *et al.* (1987).

Clearwater Lake is situated in northern Quebec (Canada), which is some 150 km east of Hudson Bay (56°5'N, 74°7'W). The age of the cratering event is 290 ± 20 Ma. The topograhic diameter of the structure is ~22 km (Grieve, 1991, and references therein).

Samples examined in this study were obtained from drill holes 2-63 and 2-64 (see Palme *et al.*, 1979). I have included one basement rock (quartz-monzonite) in this study to infer the contribution to the siderophile element contents of the impact melt.

The Boltysh impact crater (Ukraine), located at (48°45'N, 32°10'E), which is some 850 km southwest of Moscow, is a circular depression in the Proterozoic Precambrian crystalline basement of the Ukrainian Shield, which is composed primarily of porphyritic, aplitic and Rapakivi granites with associated migmatites, along with a small amount of biotite gneiss. Boltysh was ascribed to impact origin on the basis of form and the occurrence of shock metamorphism (Masaitis, 1974; Yurk *et al.*, 1975). Bolthysh is a complex crater, ~24 km in diameter, with a 6 km diameter central uplift rising some 550 m above the autochthonous basement of the crater floor. Fission track dating of the impact melt rocks indicates ages ranging from 96 ± 10 to 105 ± 13 Ma (Komarov and Raykhlin, 1976). The samples for this study come from drill hole, B50, which is located 3.5 km from the crater center. Characterization of the Boltysh impact melt rocks is given by Grieve *et al.* (1987). Chemically, the melt rocks are relatively homogeneous (Hölker and Deutsch, 1996) and correspond to a mixture of granites and gneisses in the ratio of five to one (Grieve *et al.*, 1987). The impact melt rocks, which have an estimated volume of ~10 km^3, can be classified on the basis of matrix textures into two main types: microcrystalline and glassy matrix melt rocks. The sampled sequence of impact melt rocks lies between 574 to 734 m below the surface.

ANALYTICAL TECHNIQUES

Whole rock samples were cleaned with distilled water. No clasts were removed. After crushing with a hammer wrapped in polyethylene, samples were ground in an agate mill, and 10 g aliquots (<50 μm) of the homogenized samples were used for analysis. The highly siderophile elements were analysed by the fire assay neutron activation method using nickel sulphide as a collector, following the analytical procedures described by Schmidt *et al.* (1997a). The INAA procedure involved two irradiations: a short irradiation for Rh and a long irradiation for the other elements. Samples were first placed in a polycarbonate rabbit and irradiated for 5 min at a thermal neutron flux of 1.7 x 10^{12} neutrons cm^{-2} s^{-1} in the RP2 hydraulic rabbit facility of the Mainz TRIGA Reactor. For the short irradiation times, sample and standard were put together in one capsule. After a delay time of 2 min, samples were counted for 500 s. The ^{104m}Rh ($T_{1/2}$ = 4.41 min) γ-peak at 51 keV was used for the Rh-determination. A Rh standard was measured for 3 min in the same counting position as the actual sample. After completion of the first irradiation, samples were sealed together with chemical standards into a clean capsule and irradiated for 12 h in the core of the reactor at a flux of 4 x 10^{12} neutrons cm^{-2} s^{-1}. After a decay time of 16 h, γ-spectra of the samples and standards were taken to determine ^{109}Pd, ^{188}Re, Pt as ^{199}Au and ^{198}Au. After a second decay time of three weeks, the samples and standards were measured again to determine ^{192}Ir, ^{192}Os, and ^{103}Ru. Analyses were performed with two Ge(Li) detectors (efficiencies: 57.1% and 29.2%).

Concentrations of Os, Re, Ir, Ru, Rh, Pd and Au are given in Table 1. The values obtained for two replicates (2 g) of the international reference gabbro (WMG-1) are included in Table 1. Analytical uncertainties ($\pm 1\sigma$) reflect the propagation of errors due to counting statistics and uncertainties of elemental abundances in the reagents. Precisions estimated from counting statistics corresponding to one standard deviation for the analyzed elements are roughly: Os ± 1%, Re ± 10%, Ir ± 0.1%, Ru ± 1%, Rh ± 2%, Pd ± 2%, and Au ± 1%. Upper limits are shown for abundances below detection limits defined as background plus three standard deviations. Except for Pt, Au and Ir, reagent blanks of the Pt-group elements (PGEs) were below the detection limits. For Pt, we found unusually high blank values. Up to 500 ng/g Pt have been found in the flux material $Li_2B_4O_7$ obtained from the Merck Company. Therefore, the Pt values could not be used in this work. Iridium and Au concentrations have been corrected for blank values in Table 1.

CONTENTS OF SIDEROPHILE ELEMENTS IN BASEMENT ROCKS

A prerequisite for the identification of extraterrestrial material in impact melts is the knowledge of the amount of siderophile elements that is provided by basement rocks. Although only one basement rock (quartz-monzonite) from Clearwater East crater (see Table 1;

TABLE 1. Concentrations of Os, Re, Ir, Ru, Rh, Pd and Au of melt rocks and basement quartz-monzonite (DCW-1-64-472) from East Clearwater (Canada) and Boltysh (Ukraine) and from platinum group element reference material WMG-1, as determined by neutron activation analysis.

Clearwater East Impact melt rocks	Os ng/g	Re ng/g	Ir ng/g	Ru ng/g	Rh ng/g	Pd ng/g	Au ng/g
DCW-2-63-965	18.6 ± 0.1	0.55 ± 0.04	16.96 ± 0.01	25.4 ± 0.3	7.11 ± 0.12	27.1 ± 0.9	4.57 ± 0.20
DCW-2-63-972	34.0 ± 0.1	0.68 ± 0.05	32.12 ± 0.01	46.7 ± 0.3	12.33 ± 0.14	42.2 ± 1.2	7.68 ± 0.20
DCW-2-63-1005	30.6 ± 0.1	0.21 ± 0.03	28.69 ± 0.04	44.3 ± 0.4	9.24 ± 0.13	29.7 ± 0.6	3.62 ± 0.20
DCW-2-63-1039	30.3 ± 0.4	0.91 ± 0.05	28.39 ± 0.04	43.7 ± 1.0	11.23 ± 0.16	33.8 ± 1.2	3.82 ± 0.20
DCW-2-63-1110	21.2 ± 0.1	0.53 ± 0.01	19.80 ± 0.01	30.5 ± 0.3	8.01 ± 0.13	28.2 ± 0.4	4.79 ± 0.20
Average	26.94	0.58	25.19	38.12	9.58	32.20	4.90
Std. Dev. (σ)	6.65	0.25	6.47	9.52	2.18	6.14	1.63
DCW-1-64-472	0.03 ± 0.01	0.16 ± 0.01	0.03 ± 0.03	<0.1	1.71 ± 0.07	1.6 ± 0.1	0.20 ± 0.20
Boltysh Impact melt rocks							
50/580	<0.1	<0.02	0.07 ± 0.03	<0.2	1.48 ± 0.08	2.10 ± 0.12	0.54 ± 0.20
50/658.5	<0.1	0.06 ± 0.01	0.25 ± 0.03	0.53 ± 0.11	1.49 ± 0.07	2.59 ± 0.12	1.21 ± 0.20
50/574	<0.1	<0.07	0.26 ± 0.03	0.64 ± 0.07	1.74 ± 0.08	2.00 ± 0.18	0.69 ± 0.20
50/627.8	<0.1	0.05 ± 0.01	0.07 ± 0.03	<0.2	1.56 ± 0.08	2.41 ± 0.15	0.67 ± 0.20
50/600.3	<0.1	0.08 ± 0.01	0.24 ± 0.03	0.77 ± 0.08	1.97 ± 0.08	2.18 ± 0.16	0.78 ± 0.20
50/734	<0.1	<0.01	0.33 ± 0.03	0.83 ± 0.05	1.72 ± 0.08	2.64 ± 0.34	0.82 ± 0.20
50/696	<0.1	<0.01	0.15 ± 0.03	<0.3	1.00 ± 0.07	2.84 ± 0.21	0.45 ± 0.20
Average		0.06	0.20	0.61	1.57	2.39}	0.74
Std. Dev. (σ)		0.02	0.10	0.21	0.30	0.31	0.25
Gabbro standard							
WMG-1 (A)	27.8 ± 0.4	18.0 ± 0.3	49.82 ± 0.04	30.0 ± 1.4	27.36 ± 0.63	363 ± 7	31.7 ± 0.2
WMG-1 (B)	25.8 ± 0.4	18.0 ± 0.4	47.57 ± 0.04	31.3 ± 1.3	26.41 ± 0.53	370 ± 8	45.8 ± 0.2
WMG-1[#]	24[$]	n.d.	46 ± 4	35 ± 5	26 ± 2	382 ± 13	110 ± 11[@]
CI-chondrite[*]	486±24	38.3 ± 2.7	459±14	714±71	140±4	556±56	152±7
Continental Crust	0.05[†]	0.04–0.48[†,‡]	0.03[‡]	1.1[§]	0.38[§]	2.0[§]	0.1–2.5[‡]

Iridium and Au concentrations have been corrected for blank values; 0.19 ng/g for Ir and 0.4 ng/g for Au. All other values are below the detection limit of 0.2 ng/g for Ru, Rh and Pd, of 10 pg/g for Os and 20 pg/g for Re.

[*] Data from Palme and Beer (1993). The solar system abundance of Rh is from Jochum (1996).

[†] Turekian and Luck (1984); Walker *et al.* (1991) and Esser and Turekian (1993).

[‡] Schmidt and Pernicka (1994).

[§] Schmidt *et al.* (1997a); Schmidt and Palme (1997).

(A,B) Replicate analysis of certified reference material WMG-1 on 2 g samples from this work.

[#] Certified reference values from gabbro reference material (CANMET, 1994), [$] provisional value.

[@] Spettel (Max Planck Institute for Chemistry) determined on two 100 mg aliquots 71 ± 2 ng/g Au. Possibly, the certified Au value of the reference material WMG-1 is too high. It seems also that Au is inhomogeneously distributed in this reference material.

DCW-1-64-472) has been analysed in this study, it is sometimes possible to infer the contribution to siderophile element contents of the impact melt rocks by using correlations of HSEs (Schmidt *et al.*, 1997a). This indigenous component has to be subtracted from the melt content of siderophile elements to obtain the net meteoritic contribution. Among the HSEs, Ir and Os have the lowest CI-normalized abundance in crustal rocks (*i.e.*, their contribution to a melt rock contaminated with a meteoritic component is lower than for any other element). If the meteoritic component is homogeneously distributed, correlations such as, for example, Rh *vs.* Ir allow the determination of the indigenous contribution of Rh, given that indigenous Ir is negligible. The indigenous contents of Rh, Pd, Au and Ru were calculated from linear correlations with Ir (Fig. 1a–k). The excess siderophiles in Boltysh impact melt rock samples are very low, barely above background. This allows reasonably good estimates of the indigenous component, but the small difference between melt rock and basement makes a characterization of the projectile component practically impossible (see below). The indigenous contributions of HSEs calculated by this method may better represent the average siderophile element contribution of the basement than analyses of individual basement rocks. The latter method requires analyses of all types of basement rocks as well as the knowledge of their relative proportions in the melt. 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), as can be seen in the next sections.

CHARACTERIZATION OF METEORITIC COMPONENTS AND PROJECTILE IDENTIFICATION

Clearwater East

The major element composition of the analysed samples is rather constant (Table 3, in Palme *et al.*, 1979), which is in agreement with observations of a large number of terrestrial impact craters (*e.g.*, Grieve, 1987, and references therein). The five analyzed impact melt samples from Clearwater East are highly enriched in PGEs relative to average upper crust concentrations (Table 1). Palme *et al.* (1979) have found Ir and Au contents in five samples from the same core section as analysed in this work in the range of 23.8 to 45.0 ng/g and 5.0 to 8.6 ng/g, respectively. One basement sample (quartz-monzonite) has been analyzed to infer the PGE contribution to the siderophile element contents of the impact melt (Schmidt *et al.*, 1997b). We have found a high Rh (1.71 ± 0.07 ng/g) content in this sample in comparison with an average Rh content of ~0.4 ng/g in crustal rocks (Schmidt *et al.*, 1997a) and ~1 ng/g in mantle rocks. The Rh content in the basement sample agrees with estimates from the regression (1.8 ± 1.9 ng/g Rh). After subtraction of the indigenous component, the Rh/Ir ratio of East Clearwater is clearly chondritic (Fig. 1a). Other siderophiles in the basement sample are in the range of crustal abundances.

The y-intercept for Pd in Clearwater East is 9.0 ± 5.2 ng/g, which is much higher than the Pd content of the basement sample DCW-1-64-472 (1.6 ± 0.1 ng/g). In this sample, Palme *et al.* (1978) found 7.4 ng/g Pd, which is significantly higher than estimates of crustal rocks and the value obtained in this work. For Ru and Os, with excellent regressions (r^2 = 0.99), the y-intercepts are 1.55 ± 2.53 ng/g and 1.70 ± 1.03 ng/g, respectively. The content for Ru is at the upper range of estimates of the upper crust (Schmidt *et al.*, 1997a), but the Os y-intercept is much higher than the upper crustal content of ~0.05 ng/g (Turekian and Luck, 1984). From two melt rock samples, DCW-2-63-1039 and DCW-2-63-980.5, Palme *et al.* (1978) determined by radiochemical neutron activation analyses (RNAA) Os/Ir ratios of 1.03 and 1.10, respectively. The five different melt rock samples analysed in this study show an excellent correlation of Os and Ir (r^2 = 0.99) with Os/Ir of 1.07 ± 0.01 (Table 2), which is not distinguishable from Os/Ir determined by RNAA. Nevertheless, the indigenous component of Os, Ru and Pd is difficult to evaluate; as can be seen from Fig. 1b–d, a small change in the slope of the Os-Ir, Pd-Ir and Ru-Ir correlation has a large influence on the indigenous contribution. This demonstrates that the correlation method is too limited for melt rock samples with small (<1% of a nominal CI component) meteoritic contaminations to get reasonable indigenous Pt-group element estimations.

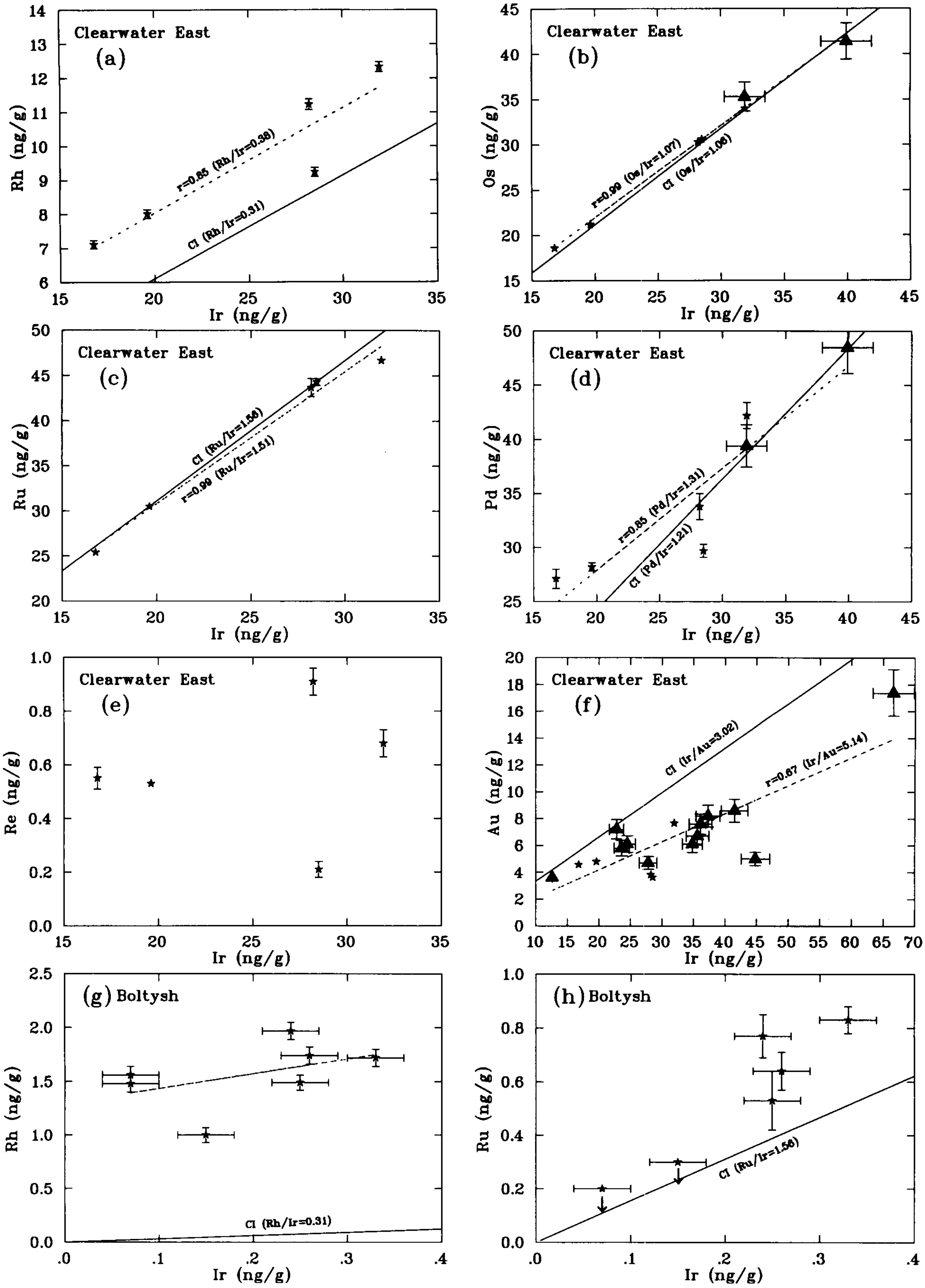
An alternative explanation for the excess Os would be the addition of a terrestrial component with high Os/Ir. Since both Os and Ir are highly refractory elements, large fractionations (a factor of two have been determined in a plagioclase-wherlite from Zabargad) between Os and Ir have never been observed in terrestrial rocks. Nevertheless, proper interpretation of siderophile element contents in the Clearwater East impact melt requires the assumption of a small fraction of a Ni- and Cr-bearing ultramafic component, which had not been sampled (Palme, 1980).

Rhenium may be volatilized during terrestrial impact processes (Morgan, 1978). The five samples studied in this work may have also lost Re and Au during terrestrial weathering. The Re concentrations in this study contrast with values obtained by Palme *et al.* (1979). The average of five analyses from Palme *et al.* (1978) and Palme *et al.* (1979) gives a Ir/Re ratio of 15 ± 1.7, which is only slightly higher than the CI-ratio of 12. The corresponding Ir/Re ratio from this work, without the high ratio of sample DCW-2-63-1005, is 37 ± 8 (Table 1, Fig. 1e). In contrast, the Re concentration of the basement sample DCW-1-64-472 from this work is 0.16 ng/g, which is 4× the content obtained by Palme *et al.* (1978). There is,

TABLE 2. Element ratios of melt rocks from East Clearwater (Canada) and Boltysh (Ukraine) compared to CI ratios.

Samples	Os/Ir	Ru/Ir	Rh/Ir	Pd/Ir	Ir/Au	Ru/Rh	Ir/Re
DCW-2-63-965	1.09	1.49	0.42	1.60	3.72	3.57	31
DCW-2-63-972	1.06	1.45	0.38	1.31	4.19	3.79	47
DCW-2-63-1005	1.07	1.54	0.32	1.03	7.93	4.79	137
DCW-2-63-1039	1.07	1.54	0.40	1.19	7.44	3.89	31
DCW-2-63-1110	1.07	1.54	0.40	1.42	4.14	3.81	37
Average	1.07	1.51	0.38	1.31	5.48	3.97	57
Std. Dev. (σ)	0.01	0.04	0.04	0.21	2.03	0.48	45
Net ratio*	1.07	1.51	0.31	1.22	5.36	4.84	60
50/580	<1.43	<2	21.1	30.0	0.13	<0.14	>3.5
50/658.5	<0.40	2.12	5.96	10.4	0.21	0.36	4.2
50/574	<0.38	2.46	6.69	7.7	0.38	0.37	>3.7
50/627.8	<1.43	<2	22.3	34.4	0.10	<0.13	1.4
50/600.3	<0.42	3.21	8.21	9.1	0.31	0.39	3.0
50/734	<0.30	<4.2	5.21	8.0	0.40	0.37	2.9
50/696	<0.67	2.00	6.67	18.9	0.33	0.02	1.4
Average		2.4	10.9	16.9	0.3	0.30	2.6
Std. Dev. (σ)		0.5	7.5	11.2	0.1	0.16	1.2
CI-chondrite	1.06	1.56	0.31	1.21	3.02	5.1	12

*Net ratio = indigenous component (DCW-1-64-472; Table 1) is subtracted.


Clearwater East
(a)
Rh (ng/g)
14
13
12
11
10
9
8
7
6
r=0.85 (Rh/Ir=0.38)
CI (Rh/Ir=0.31)
15
20
25
30
35
Ir (ng/g)
Clearwater East
(b)
Os (ng/g)
45
40
35
30
25
20
15
r=0.99 (Os/Ir=1.07)
CI (Os/Ir=1.06)
15
20
25
30
35
40
45
Ir (ng/g)
Clearwater East
(c)
Ru (ng/g)
50
45
40
35
30
25
20
CI (Ru/Ir=1.56)
r=0.99 (Ru/Ir=1.51)
15
20
25
30
35
Ir (ng/g)
Clearwater East
(d)
Pd (ng/g)
50
45
40
35
30
25
r=0.85 (Pd/Ir=1.31)
CI (Pd/Ir=1.21)
15
20
25
30
35
40
45
Ir (ng/g)
Clearwater East
(e)
Re (ng/g)
1.0
0.8
0.6
0.4
0.2
0.0
15
20
25
30
35
Ir (ng/g)
Clearwater East
(f)
Au (ng/g)
20
18
16
14
12
10
8
6
4
2
0
CI (Ir/Au=3.02)
r=0.67 (Ir/Au=5.14)
10
15
20
25
30
35
40
45
50
55
60
65
70
Ir (ng/g)
(g) Boltysh
Rh (ng/g)
2.5
2.0
1.5
1.0
0.5
0.0
CI (Rh/Ir=0.31)
.0
.1
.2
.3
.4
Ir (ng/g)
(h) Boltysh
Ru (ng/g)
1.0
0.8
0.6
0.4
0.2
0.0
CI (Ru/Ir=1.56)
.0
.1
.2
.3
.4
Ir (ng/g)

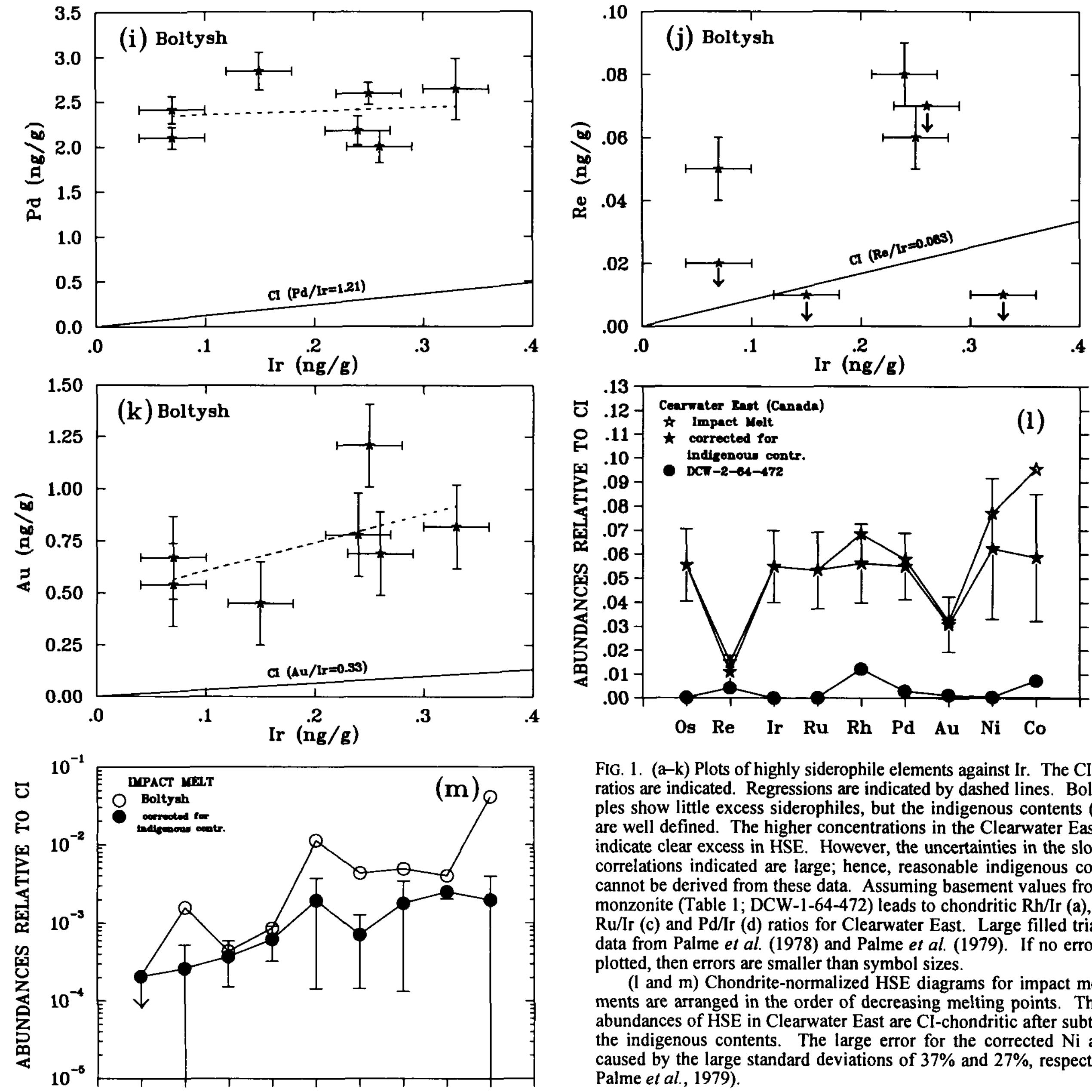


FIG. 1. (a–k) Plots of highly siderophile elements against Ir. The CI-chondrite ratios are indicated. Regressions are indicated by dashed lines. Boltysh samples show little excess siderophiles, but the indigenous contents (at Ir = 0) are well defined. The higher concentrations in the Clearwater East samples indicate clear excess in HSE. However, the uncertainties in the slopes of the correlations indicated are large; hence, reasonable indigenous components cannot be derived from these data. Assuming basement values from quartz-monzonite (Table 1; DCW-1-64-472) leads to chondritic Rh/Ir (a), Os/Ir (b), Ru/Ir (c) and Pd/Ir (d) ratios for Clearwater East. Large filled triangles are data from Palme *et al.* (1978) and Palme *et al.* (1979). If no error bars are plotted, then errors are smaller than symbol sizes.

(l and m) Chondrite-normalized HSE diagrams for impact melts. Elements are arranged in the order of decreasing melting points. The relative abundances of HSE in Clearwater East are CI-chondritic after subtraction of the indigenous contents. The large error for the corrected Ni and Co is caused by the large standard deviations of 37% and 27%, respectively (see Palme *et al.*, 1979).

however, some discrepancy between the absolute abundances of Re found in the two different studies. The difference indicates that Re is quite heterogenously distributed in the samples. Similar results were obtained for the distribution of Os and Ir within impact melts from Chicxulub crater, Mexico (Sharpton *et al.*, 1992; Koeberl *et al.*, 1994) and the Manson crater, USA (Pernicka *et al.*, 1996), where significantly different abundances of Ir and Os were found in different splits. Two core samples of melt rocks from drill hole DCW-2-63 (5 g sample) were also analyzed by Evans *et al.* (1993), who found strong enrichment of PGEs in sample DCW-2-63-1045 (Ir = 29 ng/g, Au = 35 ng/g, Pd = 124 ng/g; in this sample, Palme *et al.* (1979) obtained 35.8 ng/g Ir and 6.7 ng/g Au; see also Fig. 1f), which contrasted sharply with the value for DCW-2-63-1022 (Ir = 0.12 ng/g) and confirms heterogeneously distributed Ir and Au in the melt samples from Clearwater East.

The average Os/Ir, Ru/Ir and Pd/Ir ratios of the melt samples are CI-chondritic, if we take into consideration the estimated accuracy for Ru and Pd of 10% for CI-chondrites (see Table 1). The average Rh/Ir ratio is ~23% higher and the average Ru/Rh ratio is ~22% lower than the CI-ratio (Table 2). After subtraction of the indigenous Rh content of 1.71 ng/g (Table 1), the Rh/Ir and Ru/Rh ratio is 0.31 and 4.84, which is not different from the CI ratios (Table 2).

The amount of meteoritic component corresponds to 4 to 7% of a nominal CI component (Fig. 1). The HSE patterns from Clearwater East are flat (CI-chondritic) with some depletion of Re and Au and some Cr enrichment relative to CI-chondrites. From Ni-Ir correlations, Palme (1980) calculated indigenous Ni and Co contents of 158 ± 38.6 ug/g and 18.59 ± 4.84 ug/g, respectively. The Ni content derived by correlation is much higher than the highest Ni content determined in a basement sample (34 μg/g Ni, Palme *et al.*

1979). The Co content of 21.5 μg/g from this sample is in agreement with the value derived by correlation. Hische (1994) reported for basement lithologies in drill core 164 Ni and Co contents in the range of 5 to 155 μg/g and 30 to 164 μg/g, respectively (XRF analyses; n = 20).

After correcting the Ni and Co contents for indigenous Ni and Co, the CI-normalized values are 0.062 and 0.058, which is not significantly different from the CI-normalized PGE values of the five melt samples analysed in this work (0.053 to 0.056; see Fig. 1).

The CI-normalized Cr of the melt samples is 0.113 (not shown here), which is 2× the PGE values. On the basis of the Cr/Ir ratio, we cannot argue that the projectile is a chondrite, although a high fraction of a meteoritic component is diluted in the melt, and in former studies Cr has been shown to be critical for distinguishing between stony and iron projectiles (Palme, 1982). On the other hand, iron meteorites have much lower Cr/Ir ratios than chondrites. Therefore, we conclude that a large fraction of ~130 μg/g Cr in the samples is terrestrial in origin.

In summary, I conclude that the nonfractionated CI-chondritic PGE ratios from Clearwater East are compatible with a chondritic meteorite as projectile.

Boltysh

Chemically, the melt rocks are relatively homogeneous and correspond to a mixture of Kirovograd granites and gneisses in the ratio of five to one (Grieve *et al.*, 1987, Table 2). The contents of highly siderophile elements obtained in the present study are plotted *vs.* Ir in Fig. 1g–k. The excess siderophiles in the seven borehole samples from Boltysh are very low (Ir = 0.2 ± 0.1 ng/g), which is barely above the background.

Figure 1g–m demonstrates that the low fraction of meteoritic components in Boltysh impact melts can, if at all, only be seen in Ir, which is the most sensitive indicator element for most types of meteoritic material, due to the low indigenous abundances in crustal rocks of 0.03 ± 0.02 ng/g. However, the Rh/Os ratio of Boltysh melts (Rh/Os > 15.7) is clearly nonchondritic (Rh/Os_{CI} = 0.29). Subtracting the unusually high content of 1.3 ng/g of Rh from these samples does not bring them to the chondritic line. There is excess Rh compared to Os and Ir.

Five of seven impact melt samples have lower Os/Ir ratios than the chondritic value of 1.06 (Table 2). In most meteorite groups, both elements are found in CI-ratios (Kallemeyn and Wasson, 1981; Kallemeyn *et al.*, 1989). In magmatic iron meteorites, low Os/Ir ratios are not uncommon (Pernicka and Wasson, 1987). Depletion of Os was also observed in melt rock samples from Rochechouart (France) by Janssens *et al.* (1977), in impact melt samples from Wanapitei Lake (Canada) by Wolf *et al.* (1980) and in impact melt samples from Brent (Canada) by Palme *et al.* (1981). Recently, we have measured low Os/Ir ratios in three Scandinavian craters (Sääksjärvi, Mien and Dellen; Schmidt *et al.*, 1997a). If the low Os/Ir ratios in the analysed melt samples would reflect original fingerprints of surviving relicts of the projectile, I would favour a magmatic iron meteorite as projectile. However, I cannot exclude loss of Os during the impact.

The indigenous content of Pd (2.32 ± 0.30 ng/g) is in agreement with other estimates of Pd in the upper crust (Schmidt *et al.*, 1997a). As can be seen from Fig. 1h, the indigenous component of Ru is more difficult to evaluate. The two samples lowest in Ir show only upper limits for Ru. The five samples highest in Ir have Ru concentrations (Ru = 0.62 ± 0.21 ng/g) in the range of the upper crust.

In Fig. 1m, I have plotted both the average CI-normalized concentrations of meteoritic elements in Boltysh melt rock samples and concentrations after subtraction of the indigenous component. For Ni and Co, I have taken the concentrations from Grieve *et al.* (1987) (melt samples: Ni = 43 μg/g, Co = 21 μg/g, Cr = 56 μg/g, average of four basement samples: Ni = 16 μg/g, Co = 25 μg/g, Cr = 26 μg/g). Hölker and Deutsch (1996) have found in the impact melt rocks (drill cores B-50, and B-11475) 30 ± 3 μg/g Ni, 5 ± 1 μg/g Co and 36 ± 2 μg/g Cr (n = 11). As pointed out in an earlier paper (Schmidt *et al.*, 1997a), the identification of Cr as a meteoritic element requires a comparatively high fraction of a meteoritic component (in general >3% of a nominal CI-component). Impact melts should have at least 100 μg/g Cr of meteoritic origin to identify meteoritic Cr. Therefore, in the case of the Boltysh impact melt, we can rule out an extraterrestrial Cr contribution. The HSE pattern from Boltysh is somewhat fractionated relative to CI-chondrites. The amount of meteoritic component would correspond to 0.015 to 0.07% of a nominal CI component. Normalized abundances increase from the refractory to the more volatile siderophile elements (Os < Ir < Ru < Rh ~ Pd ~ Au ~ Ni < Co). Because of the low Ir anomaly and uncertainties in making corrections (correlations are weak) for indigenous siderophile elements, no clear projectile assignment can be made.

CONCLUSION

Impact melt rock samples from Clearwater East (Canada) and Boltysh (Ukraine) were analyzed for highly siderophile elements. Melt rock samples from Clearwater East are strongly enriched in Os, Ir, Ru, Rh and Pd relative to crustal concentrations. This work confirms earlier findings and demonstrates similarly high enrichments of Ru and Rh. The average Os/Ir, Ru/Ir, Rh/Ir, Pd/Ir ratios of the melt samples from Clearwater East are CI-chondritic. The nonfractionated, flat (CI-chondritic) HSE pattern from Clearwater East is compatible with a chondritic meteorite as projectile. The amount of meteoritic component corresponds to 4 to 7% of a nominal CI component for Clearwater East. The Boltysh samples are, if at all, only slightly enriched in Ir (0.2 ± 0.1 ng/g). No clear projectile assignment can be made for this crater.

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REFERENCES

CANMET (1994) WMG-1, Certificate of analysis. *Canadian Certified Reference Materials Project.* Ottawa, Canada.

Choi B-G., Ouyang X. and Wasson J. T. (1995) Classification and origin of IAB and IIICD iron meteorites. *Geochim. Cosmochim. Acta* **59,** 593–612.

Esser B. K. and Turekian K. K. (1993) The osmium isotope composition of the continental crust. *Geochim. Cosmochim. Acta* **57,** 3093–3104.

Evans N. J., Gregoire D. C., Grieve R. A. F., Goodfellow W. D. and Veizer J. (1993) Use of platinum-group elements for impactor identification: Terrestrial impact craters and Cretaceous-Tertiary boundary. *Geochim. Cosmochim. Acta* **57,** 3737–3748.

Grieve R. A. F. (1987) Terrestrial impact structures. *Ann. Rev. Earth. Planet. Sci.* **15,** 245–270.

Grieve R. A. F. (1991) Terrestrial impact: The record in the rocks. *Meteoritics* **26,** 175–194.

GRIEVE R. A. F. AND E. M. SHOEMAKER (1994) The record of past impacts on Earth. In *Hazards Due to Comets and Asteroids* (ed. T. Gehrels), pp. 417–462. Univ. Arizona Press, Tucson, Arizona.

GRIEVE R. A. F., PALME H. AND PLANT A. G. (1980) Siderophile-rich particles in the melt rocks at E. Clearwater impact structure, Quebec: Their characteristics and relationship to the impacting body. *Contrib. Mineral. Petrol.* **75,** 187–198.

GRIEVE R. A. F., RENY G., GUROV E. P. AND RYABENKO V. A. (1987) The melt rocks of the Boltysh impact crater, Ukraine, USSR. *Contrib. Mineral. Petrol.* **96,** 56–62.

GUROV E. P., KOLESOV G. M., GUROVA E. P. (1986) The composition of impactites of the Boltysh astrobleme (in Russian). *Meteoritika* **45,** 150–155.

HISCHE R. (1994) Geologie der Clearwater-Impaktstruktur/Quebec. Ph.D. thesis, Univ. Münster. 146 pp. and 113 pp. Tabellenanhang.

HÖLKER TH. AND DEUTSCH A. (1996) The Boltysh impact structure, Ukraine: Geochemistry of the melt sheet (abstract). *Lunar Planet. Sci.* **27,** 555–556.

JANSSENS M-J., HERTOGEN J., TAKAHASHI A. H., ANDERS E. AND LAMBERT P. (1977) Rochechouart meteorite crater: Identification of projectile. *J. Geophys. Res.* **82,** 750–758.

JOCHUM K. P. (1996) Rhodium and other platinum-group elements in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **60,** 3353–3357.

KALLEMEYN G. W. AND WASSON J. T. (1981) The compositional classification of chondrites I. The carbonaceous chondrite groups. *Geochim. Cosmochim. Acta* **45,** 1217–1230.

KALLEMEYN G. W., RUBIN A. E., WANG D. AND WASSON J. T. (1989) Ordinary chondrites: Bulk compositions, classification, lithophile-element fractionations, and composition-petrographic type relationships. *Geochim. Cosmochim. Acta* **53,** 2747–2767.

KOEBERL C., SHARPTON V. L., SCHURAYTZ B. C., SHIREY S. B., BLUM J. D. AND MARTIN L. E. (1994) Evidence for a meteoritic component in impact melt rock from the Chicxulub structure. *Geochim. Cosmochim. Acta* **58,** 1679–1684.

KOMAROV A. N. AND RAYKHLIN AI (1976) Comparative study of ages of impactites by fission track and potassium-argon dating methods (in Russian). *Dokl. Akad. Nauk. SSSR* **240/6,** 1407–1410.

MASAITIS V. L. (1974) Some ancient meteorite craters of the USSR (in Russian). *Meteoritika* **33,** 64–68.

MORGAN J. W. (1978) Lonar crater glasses and high-magnesium australites: Trace element volatilization and meteoritic contamination. *Proc. Lunar Planet. Sci. Conf.* **9th,** 2713–2730.

PALME H. (1980) The meteoritic contamination of terrestrial and lunar impact melts and the problem of indigenous siderophiles in the lunar highland. *Proc. Lunar Planet. Sci. Conf.* **11th,** 481–506.

PALME H. (1982) Identification of projectiles of large terrestrial impact craters and some implications for the interpretation of Ir-rich Cretaceous/Tertiary boundary layers. In *Geological Implications of Impacts of Large Asteroids and Comets* (eds. L. T. Silver and P. H. Schultz), pp. 223–233. GSA Spec. Pap. **190,** Boulder, Colorado.

PALME H. AND BEER H. (1993) Abundances of the elements in the solar system. In *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, Vol. 3* (ed. H. H. Voigt), pp. 196–206. Springer-Verlag, Berlin, Germany.

PALME H., JANSSENS M.-J., TAKAHASHI H., ANDERS E. AND HERTOGEN J. (1978) Meteoritic material at five large impact craters. *Geochim. Cosmochim. Acta* **42,** 313–323.

PALME H., GÖBEL E. AND GRIEVE R. A. F. (1979) The distribution of volatile and siderophile elements in the impact melt of East Clearwater (Quebec). *Proc. Lunar Planet. Sci. Conf.* **10th,** 2465–2492.

PALME H., GRIEVE R. A. F. AND WOLF R. (1981) Identification of the projectile at the Brent crater, and further considerations of projectile types at terrestrial craters. *Geochim. Cosmochim. Acta* **45,** 2417–2424.

PERNICKA E. AND WASSON J. T. (1987) Ru, Re, Os, Pt and Au in iron meteorites. *Geochim. Cosmochim. Acta* **51,** 1717–1726.

PERNICKA E., KAETHER D. AND KOEBERL C. (1996) Siderophile element concentrations in drill core samples from the Manson Crater. In *The Manson Impact Structure, Iowa: Anatomy of an Impact Crater* (eds. C. Koeberl and R. Anderson), pp. 325–330. GSA Spec. Pap. **302,** Boulder, Colorado.

SCHMIDT G. AND PALME H. (1997) Abundances of Os, Ir, Ru, Rh, Pt and Pd in the Earth's crust. In *The Origin and Fractionation of Highly Siderophile Elements in the Earth's Mantle* (eds. G. Brügmann, J. P. Lorand and H. Palme), pp. 71–72. Max-Planck-Institut for Chemistry, Mainz, Germany.

SCHMIDT G. AND PERNICKA E. (1994) The determination of platinum group elements (PGE) in target rocks and fall-back material of the Nördlinger Ries impact crater (Germany). *Geochim. Cosmochim. Acta* **58,** 5083–5090.

SCHMIDT G., PALME H. AND KRATZ K-L. (1997a) Highly siderophile elements (Re, Os, Ir, Ru, Rh, Pd, Au) in impact melts from three European impact craters (Sääksjärvi, Mien and Dellen): Clues to the nature of the impacting bodies. *Geochim. Cosmochim. Acta* **61,** in press.

SCHMIDT G., KRATZ K-L. AND PALME H. (1997b) Os, Re, Ir, Ru, Rh, Pd, Au in borehole samples from the Clearwater East crater (Canada) and the Boltysh impact crater (Ukraine) (abstract). *Lunar Planet. Sci.* **28,** 1255–1256.

SCOTT E. R. D. (1972) Chemical fractionation in iron meteorites and its interpretation. *Geochim. Cosmochim. Acta* **36,** 1205–1236.

SHARPTON V. L., DALRYMPLE G. E., MARTIN L. E., RHYDER G., SCHURAYTZ B. C. AND URRUTIA-FUCUGAUCHI J. (1992) New links between the Chicxulub impact structure and the Cretaceous/Tertiary boundary. *Nature* **359,** 819–821.

TUREKIAN K. K. AND LUCK J. M. (1984) Estimation of continental ^{187}Os/^{186}Os values by using ^{187}Os/^{186}Os and ^{143}Nd/^{144}Nd ratios in marine manganese nodules. *Proc. Natl. Acad. Sci. USA* **81,** 8032–8034.

WALKER R. J., MORGAN J. W., NALDRETT A. J., LI C. AND FASSETT J. D. (1991) Re-Os isotope systematics of Ni-Cu sulfide ores, Sudbury Igneous Complex, Ontario: Evidence for a major crustal component. *Earth Planet. Sci. Lett.* **105,** 416–429.

WOLF R., WOODROW A. B. AND GRIEVE R. (1980) Meteoritic material at four Canadian impact craters. *Geochim. Cosmochim. Acta* **44,** 1015–1022.

YURK Y., YEREMKO G. K. AND POLKANOV Y. (1975) The Boltysh depression–A fossil meteorite crater (in Russian). *Sov. Geol.* **2,** 138–144.