

https://dspace.org/

Mineralogy and geochemistry of the impact breccias of the Bosumtwi impact structure, Ghana : genesis and secondary proccesses

Coney, Louise

2009-05-28T10:56:53Z
http://hdl.handle.net/10539/6991

Downloaded from a DSpace repository. https://dspace.org/

The Meteoritical Society

Meteoritics & Planetary Science 42, Nr 4/5, 743–753 (2007)
Abstract available online at http://meteoritics.org

Search for a meteoritic component in drill cores from the Bosumtwi impact structure, Ghana: Platinum group element contents and osmium isotopic characteristics

Iain McDONALD[1*], Bernhard PEUCKER-EHRENBRINK[2], Louise CONEY[3], Ludovic FERRIÈRE[4], Wolf Uwe REIMOLD[5], and Christian KOEBERL[4]

[1]School of Earth, Ocean & Planetary Sciences, Cardiff University, Park Place, Cardiff CF10 3YE, UK
[2]Department of Marine Chemistry & Geochemistry, Woods Hole Oceanographic Institution, 360 Woods Hole Road, Mail Stop 25, Woods Hole, Massachusetts 02543–1541, USA
[3]Impact Cratering Research Group, School of Geosciences, University of the Witwatersrand, Private Bag 3, Johannesburg 2050, South Africa
[4]Department of Geological Sciences, University of Vienna, Althanstrasse 14, Vienna A-1090, Austria
[5]Mineralogy, Museum for Natural History, Humboldt University in Berlin, Invalidenstrasse 43, D-10115 Berlin, Germany
*Corresponding author. Email: iain@earth.cf.ac.uk

(Received 18 October 2006; revision accepted 01 January 2007)

Abstract–An attempt was made to detect a meteoritic component in both crater-fill (fallback) impact breccias and fallout suevites (outside the crater rim) at the Bosumtwi impact structure in Ghana. Thus far, the only clear indication for an extraterrestrial component related to this structure has been the discovery of a meteoritic signature in Ivory Coast tektites, which formed during the Bosumtwi impact event. Earlier work at Bosumtwi indicated unusually high levels of elements that are commonly used for the identification of meteoritic contamination (i.e., siderophile elements, including the platinum group elements [PGE]) in both target rocks and impact breccias from surface exposures around the crater structure, which does not allow unambiguous verification of an extraterrestrial signature. The present work, involving PGE abundance determinations and Os isotope measurements on drill core samples from inside and outside the crater rim, arrives at the same conclusion. Despite the potential of the Os isotope system to detect even small amounts of extraterrestrial contribution, the wide range in PGE concentrations and Os isotope composition observed in the target rocks makes the interpretation of unradiogenic, high-concentration samples as an impact signature ambiguous.

INTRODUCTION

The Bosumtwi impact structure, centered at 06°30′N, 01°25′W, is a well-preserved complex impact structure in south-central Ghana. It is ~10.5 km in diameter, has a pronounced rim with elevations of up to ~300 m above the lake level, and is almost completely filled by Lake Bosumtwi, which is 8 km in diameter. A detailed review, describing all aspects of Bosumtwi and a new geological map, has recently been published by Koeberl and Reimold (2005). The Bosumtwi impact structure has an age of only 1.07 Myr and is thus one of the youngest and best-preserved terrestrial crater structures. Bosumtwi is also important as the source crater of the Ivory Coast tektites, one of only four known tektite strewn fields. The Ivory Coast tektite strewn field extends beyond occurrences on land, as microtektites related to those found on land have been found in deep-sea cores off the coast of West Africa. The similar age, as well as chemical and isotope data (see, e.g., Koeberl et al. 1997, 1998) and the magnetostratigraphic age of the microtektites (e.g., Glass et al. 1991), all indicate that the Ivory Coast tektites were generated in the Bosumtwi impact event.

Whereas the tektites represent distal ejecta from Bosumtwi, abundant proximal ejecta in the form of suevite (polymict impact breccia carrying cogenetic impact melt particles) and other impact deposits occur outside the crater rim as fallout ejecta, and as fallback ejecta in the interior of the structure (Dai et al. 2005). Limited exposures of massive suevite deposits have been observed just outside the northern and the southwestern crater rim sections. The Bosumtwi

© The Meteoritical Society, 2007. Printed in USA.

impact excavated lower greenschist facies metasediments (graywacke, quartzitic graywacke, meta-tuffs, phyllites, shales, and schists) of the 2.1–2.2 Gyr Birimian Supergroup (e.g., Leube et al. 1990; Koeberl and Reimold 2005). Rocks to the southeast of the crater contain altered basic intrusives (Birimian metavolcanics) in addition to metasediments. Further to the east and southeast, clastic Tarkwaian sediments thought to have been formed by erosion of Birimian rocks occur. Several Proterozoic granitic intrusions are found in the structure, and some strongly weathered granitic dikes occur in the crater rim (e.g., Reimold et al. 1998). The granitic complexes and dikes probably belong to the 2.2–2.0 Gyr old (e.g., Taylor et al. 1992; Hirdes et al. 1992; Feybesse et al. 2006) Kumasi-type granitoid intrusions. In addition, a few dikes of dolerite, amphibolite, and intermediate rocks (minor intrusives) occur around the crater (e.g., Koeberl and Reimold 2005). In the immediate environs of the crater, graywacke and sandstone/quartzitic rocks dominate, but especially in the northeastern and southern sectors, shale and mica schist are also present (e.g., Reimold et al. 1998). Quartz veins and stringers of up to 20 cm wide cut through all the rock formations in the area, or occur in the form of pods.

The present paper focuses on new geochemical studies of melt-rich suevite samples from two drill cores from north of the Bosumtwi crater, outside the crater rim (Boamah and Koeberl 2002, 2003, 2006), as well as samples from drill cores within the crater, which were analyzed with the aim of detecting evidence of a meteoritic component.

Drilling at Bosumtwi

In 1999, the University of Vienna, Austria, in cooperation with the Geological Survey Department of Ghana (GSD) and guided by airborne radiometry (cf. Plado et al. 2000; Pesonen et al. 2003), undertook a shallow drilling program outside the northern crater rim of Bosumtwi. Seven holes were drilled to the north of the crater to a maximum depth of 30 m and at a distance of 2.5–8 km from the lake shore (see Boamah and Koeberl 2002, 2003, 2006). Relevant for the present study are drill holes BH1 and BH3. These were sited not very far from known suevite outcrops, and where cores of fallout suevite deposits of about 15 m thickness were recovered (for core locations, see Fig. 1).

The success of the work from the mid-1990s to early 2000s triggered an international and multidisciplinary drilling project, financed mainly by the International Continental Scientific Drilling Program (ICDP) (cf. Koeberl et al. 2005, 2006, 2007). The project had two main scientific goals: paleoenvironmental and impact studies. From July to October 2004, 16 boreholes were drilled at 6 locations within Lake Bosumtwi as part of the ICDP drilling project. At five sites, 14 separate holes were drilled into the lake sediments; at two sites, LB-07A and LB-08A, thick sequences of impactites and fractured bedrock were recovered. Core LB-07A was sited within the moat between central uplift and rim, to penetrate the thickest possible impactite sequence, and core LB-08A was drilled on the flank of the central uplift. In both cores, suevitic breccias (in the top part of the recovered cores) were intersected.

Meteoritic Components in Impactites

The detection and verification of an extraterrestrial component in impact-derived melt rocks or breccias can be of diagnostic value to provide confirming evidence for an impact origin of a geological structure (see the review by Koeberl 1998). Generally, a very small amount of meteoritic melt or vapor is mixed with a much larger quantity of target rock vapor and melt, and this mixture later is incorporated into impact melt rocks or melts breccias, suevite, or impact glass. In most cases, the extraterrestrial contribution to these impactite lithologies is very small—mostly much less than one percent by weight. Detecting such small amounts of meteoritic matter is extremely difficult and only elements that have high abundances in meteorites, but correspondingly low abundances in terrestrial crustal rocks (e.g., siderophile elements such as Ni, Cr, and the platinum-group elements [PGE]) are used in such studies. Distinctly higher siderophile element contents in impact melts, compared to target rock abundances, can be indicative of the presence of either a chondritic or an iron meteoritic component (Palme et al. 1978; Evans et al. 1993; McDonald et al. 2001). Complications may arise, first, because meteorites have a range of compositions within each class and some are better constrained than others (see McDonald 2002), second, if the target rocks have variable siderophile element concentrations, or third, if siderophile element concentrations in the impactites are very low. Furthermore, the contribution of the target rock (the indigenous component) to the composition of impactites can only be well understood if either a well-constrained mixing relationship exists between the impactor and the target rocks that produces a reliable regression and a lower intercept that reflects the average PGE concentration in the target rocks (e.g., McDonald et al. 2001; Tagle and Claeys 2005), or if all contributing target rocks have been identified and their relative contributions to the melt mixture are known—something that is extremely difficult to achieve in practice.

The Os and Cr isotope systems can be used to establish the presence of a meteoritic component in impactites. Both methods are based on the observation that the isotopic compositions of the elements Os and Cr, respectively, are different between most meteorites and terrestrial rocks and that these differences are sufficiently large to permit detection of relatively small amounts of meteoritic Os or Cr present in the impact rock (see reviews by Koeberl and Shirey 1997 and Shukolyukov and Lugmair 1998 for applications of the Os and Cr systems, respectively).

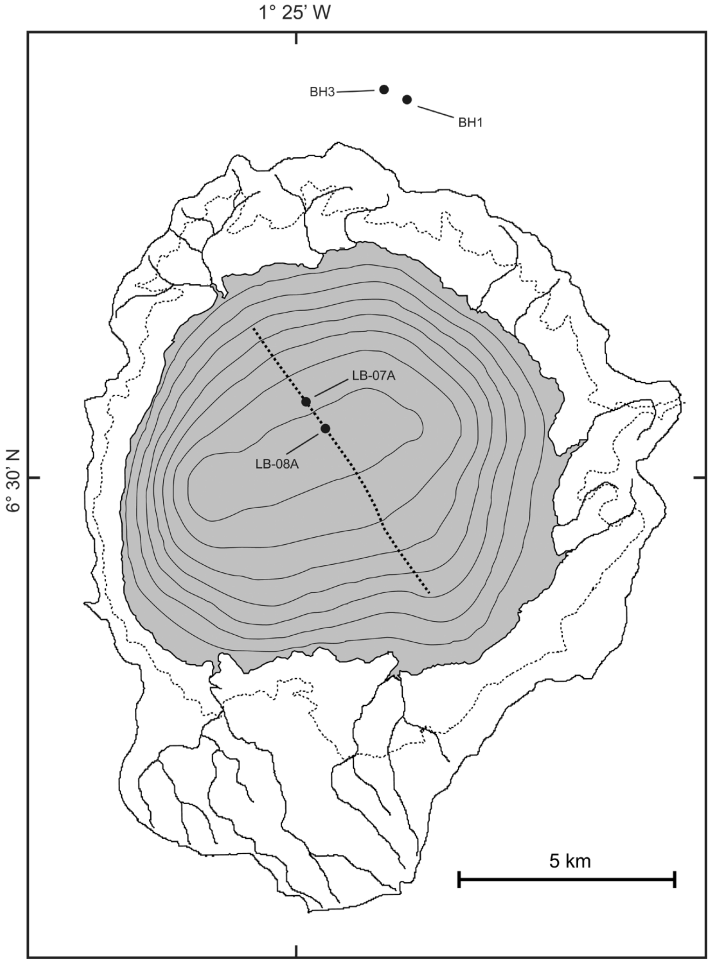


Fig. 1. An outline of the Bosumtwi impact structure and drainage area, with location of the drill holes from which the core samples studied were taken. The lake is shaded, and the seismic line along which the two cores LB-07A and LB-08A are located is shown as well. The dotted line indicates the approximate high points of the crater rim.

Search for a Meteoritic Component at Bosumtwi

El Goresy (1966) noted the presence of Ni-rich spherules in some Bosumtwi impact glass (presumably isolated from suevite) and took this as evidence of an impact origin of the structure. Palme et al. (1978) found that Ivory Coast tektites have high contents of siderophile elements, in particular Ir and Os (both on the order of 0.3–0.4 ppb), which, because of the nonchondritic interelement ratios, they interpreted as evidence of iron meteorite contamination. In contrast, Jones (1985) noted that the high siderophile element contents in the tektites could be the result of high indigenous contents in the Bosumtwi target rocks due to local ore mineralization. Koeberl and Shirey (1993) measured Os and Re concentrations and isotope ratios of Os in four Ivory Coast tektites, two Bosumtwi impact glasses, and five different target rocks from the Bosumtwi crater. The tektites have major- and trace- element compositions, as well as large negative ε_{Nd} (−20) and positive ε_{Sr} (+260 to +300), which are characteristic of old continental crust. Both tektites and target rocks have Os concentrations ranging from 0.09 to 0.30 ppb, and 0.021 to 0.33 ppb, respectively. However, the $^{187}Os/^{188}Os$ ratios in the tektites are close to meteoritic values at about 0.155 to 0.213, whereas the Bosumtwi crater rocks have much more radiogenic values of 1.52–5.01, which is typical of old continental crust. The low $^{187}Os/^{188}Os$ in the tektites are unambiguous evidence for the existence of a small meteoritic component (on the order of 0.1–0.6 wt%). A meteoritic component in the Ivory Coast tektites was also confirmed by the Cr isotope method (Koeberl et al. 2004).

In these investigations, the geochemistry of target rocks and breccias from the Bosumtwi crater structure was studied for comparison with Ivory Coast tektites. The studies of Koeberl and Shirey (1993) confirmed the suspicion of Jones (1985) that the target rocks have Os concentrations equal to or higher (21–327 pg/g) than average continental crust (~31 pg/g, Peucker-Ehrenbrink and Jahn 2001). More

Table 1. Major- and selected trace-element data for the samples from core LB-7A. All data in wt%, except Cr, Co, and Ni in ppm.

	Depth	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total	Cr	Co	Ni
KR7-1	334.91	66.21	0.51	15.62	5.18	0.04	1.65	1.13	3.02	1.79	0.09	3.64	98.88	104	9	33
KR7-9	377.46	46.38	0.26	5.98	7.23	0.14	14.95	6.84	0.00	0.00	0.05	17.24	99.07	2023	77	1122
KR7-14	398.44	63.97	0.47	14.61	5.46	0.05	2.24	1.88	2.56	1.58	0.09	5.79	98.70	172	21	466
KR7-43b	384.84	56.66	0.38	13.21	4.88	0.02	3.79	10.06	2.81	1.32	0.18	7.85	101.16	389	20	177
KR7-21	413.13	54.92	0.50	12.44	6.50	0.10	6.40	5.19	1.66	1.27	0.12	9.53	98.63	457	26	292
KR7-22	420.86	56.01	0.51	12.69	6.46	0.12	4.44	6.48	1.88	1.13	0.13	8.99	98.84	459	20	110
KR7-31	512.15	62.18	0.54	15.17	4.85	0.05	2.67	2.78	2.84	1.94	0.13	5.63	98.78	94	10	74
KR7-29A	487.36	49.72	0.46	10.37	6.87	0.11	9.28	6.89	0.36	0.79	0.14	13.87	98.86	785	30	316
KR7-43c	384.84	59.22	0.59	13.73	5.41	0.07	3.44	3.57	3.71	1.49	0.13	8.53	99.89	114	16	33
KR7-11b	383.74	53.76	0.29	5.02	5.50	0.12	12.73	6.40	0.11	0.00	0.07	15.07	99.07	1765	31	605

recently, Dai et al. (2005) tried to calculate the meteoritic contribution by subtracting the PGE content of the target rocks from the samples. However, this study revealed that target rock PGE concentrations were highly variable, and in some cases were very high (e.g., Ir up to 3 ppb and Pt up to 39 ppb). The PGE abundance pattern in these samples are fractionated when normalized to chondritic (meteorite) abundances and are enriched in the more volatile PGE and Au, in common with most crustal rocks (Barnes et al. 1985; Schmidt et al. 1997; Farago et al. 2005). It should be noted that in the wider region around Bosumtwi there are several gold mines, and elevated siderophile element abundances are found in many regional country rocks (cf. Osae et al. 1995; Jones 1985; Dai et al. 2005).

The recent drilling projects afforded an opportunity to expand the search for a meteoritic signature to previously unavailable impact rocks within the Bosumtwi crater and test new predictions (Artemieva et al. 2004) of the amount of meteoritic material within fallback ejecta and crater fill. Similar studies are also being undertaken by other groups and preliminary results on different samples have recently been published by Goderis et al. (2006).

Samples

For the present work we selected 11 samples of breccias from core LB-07A for PGE analyses, along with 5 samples from core LB-08A, and 2 samples from outside the crater rim for combined Os isotope and related PGE content measurements. For core locations see Fig. 1. In each case, whole samples were taken for analysis (i.e., no attempt was made to separate clasts from matrix) and samples were prepared and powdered according to the guidelines established by Montanari and Koeberl (2000). The former sample set was analyzed at Cardiff University and the latter at the Woods Hole Oceanographic Institution. Samples were selected based on relatively high contents of siderophile elements, such as Cr, Co, and Ni that had been determined previously by X-ray fluorescence and neutron activation analysis. A few samples with comparatively low siderophile element contents were included as controls. Two samples of suevite from the shallow drill cores BH1 and BH3, about 1.5 km north of the northern crater rim, were also studied: sample BH1-1500, from 15.00 m depth, and sample BH3-0865, from 8.65 m depth. Both are melt- and glass-rich suevites with relatively high siderophile element contents. Details about these samples and the two drill cores were reported by Boamah and Koeberl (2003, 2006). Details about the samples from LB-07A and LB-08A are given in Coney et al. (2007) and Ferrière et al. (2007), respectively. The following paragraphs provide short petrographic sample descriptions for the LB-07A and LB-08A samples. Statements about the general siderophile element content refer to concentrations of Ni, Cr and Co in Table 1.

LB-07A Samples

KR7-1: (depth: 334.91 m; lithic breccia) Polymict- and clast-rich lithic breccia. The clast component is dominated by one large (2 cm) mylonitic quartz-rich meta-graywacke clast. Other clasts: phyllosilicate, quartz, plagioclase. The clasts are angular. The breccia has ~10 vol% matrix. Quartz contains a maximum of 2 PDF sets and approximately 20% of the quartz grains are shocked, with usually 1 PDF set. Low siderophile contents.

KR7-9 and KR7-9d: (depth: 377.46 m; suevite) Contact between lithic breccia and suevitic breccia. Polymict lithic breccia with angular to subrounded clasts of up to 6 mm in the longest dimension. Melt particles contain flow structures, and in most cases are not fully melted. Melt particles are up to 5 mm wide. The other clasts are shale (with lamination), meta-graywacke, and fine-grained quartz. Only 1 quartz grain was found to contain a single PDF set. Less than 10 vol% matrix. High siderophile element concentrations.

KR7-11b: (depth: 383.74 m; suevitic breccia) Suevitic breccia with subrounded to angular clasts of graywacke, laminated shale (containing pyrite), other metapelite and quartz. Forty vol% matrix. Three melt particles, which vary in size from 0.1 to 1 mm. No other shock effects noted. High siderophile element concentrations.

KR7-43b and KR7-43c: (depth: 384.84 m; suevitic breccia) Suevitic breccias containing mylonitic graywacke, laminated shale, phyllite, quartz, and phyllosilicates. Particles are rounded to angular. Melt: black to brown melt particles, with 5 small particles, 1 particle of 1 mm size, and 2 larger melt particles. No other shock effects noted. KR7-43c is more melt-rich than KR7-43b. Medium to low siderophile element concentrations.

KR7-14: (depth: 398.44 m; suevitic breccia) Suevitic breccia containing mylonitic graywacke, metapelite including laminated shale, quartz, carbonate, feldspars, phyllosilicates. Clasts are angular to subrounded; 60 vol% matrix. Many small brown-black melt particles. Shocked quartz (1–2 PDF sets; about 7% of the quartz grains are shocked). Plagioclase with ladder structure observed. Diaplectic quartz glass is present but rare. High siderophile element concentrations.

KR7-21: (depth: 413.13 m; suevitic breccia) Suevitic breccia with quartz and meta-graywacke clasts. Less than 10 vol% matrix, angular lithic clasts. Unable to make thin section due to the crumbly state of sample. Medium to high siderophile element concentrations.

KR7-22: (depth: 420.86 m; monomict breccia) Monomict breccia, composed entirely of meta-graywacke. Unable to make thin section due to the crumbly state of sample. Medium to low siderophile element concentrations.

KR7-29A and KR7-31: (depth: 487.36 and 512.15 m, respectively; basement) Both are fragile samples, partly disintegrated. The first sample is shale-dominated and has high siderophile element contents, whereas KR7-31 is dominated by meta-graywacke and has low siderophile element concentrations.

LB-08A Samples

KR8-004: (depth: 240.65 m; suevite) Suevite with variety of clasts: phyllite, slate, mylonitic graywacke, quartzite, melt particles (up to 1 cm in size), carbon-rich organic shale, and altered feldspathic graywacke clasts. Minerals identified include quartz, feldspar, plagioclase, muscovite, chlorite, biotite, and opaques. Most of the biotite is altered to chlorite. Some quartz grains show undulatory extinction and some PFs and PDFs (1–2 sets). Feldspar grains are altered to sericite and are cloudy. Some fractures filled with iron oxides and calcite flakes are present. Moderate siderophile element concentrations.

KR8-030: (depth: 272.47 m; gritty graywacke) Shocked (PDFs in quartz) gritty graywacke, composed mainly of quartz, feldspar, plagioclase, muscovite, biotite, epidote, zircon, sphene, and opaques (pyrite). Most of the biotite is altered to chlorite and feldspar to sericite. Quartz grains show cracks and undulatory extinction, and abundant PDFs (1 or 2 sets). Feldspar and plagioclase grains are shocked and show cracks and undulatory extinction. Some feldspar grains are partially isotropic. Presence of calcite flakes. Low siderophile element concentrations.

KR8-043: (depth: 297.39 m; altered suevite) Strongly altered suevite with phyllite, slate, graywacke (mylonitic, fine- to medium-grained graywacke), melt particles, quartzite, and calcite clasts. Minerals identified include quartz, feldspar, plagioclase, muscovite, chlorite, epidote, and opaques. Most of the feldspar is altered to sericite. Few quartz grains with PDFs (1 or 2 sets). One clast contains abundant chlorite. High siderophile element concentrations.

KR8-107: (depth: 422.51 m; suevite) As above. High siderophile element concentrations.

KR8-122: (depth: 447.06 m; graywacke/basement) Altered, weakly shocked/fractured medium-grained graywacke with intense local cataclasis. Composed mainly of quartz, feldspar, plagioclase, muscovite, chlorite, and opaques. Quartz grains show cracks and some display undulatory extinction. Feldspar and plagioclase grains are partially altered to sericite (with cloudiness). Few roundish plagioclase clasts in the brecciated part of the section. A lot of calcite flakes. No PDFs seen. Low siderophile element concentrations.

ANALYTICAL METHODS

The contents of the PGE and Au were determined in Cardiff by ICP-MS after Ni-sulfide fire assay with Te coprecipitation, using signal intensity calibration. All details regarding the procedures for these analyses, as well as related precision and accuracy values, are given in Huber et al. (2001) and McDonald and Viljoen (2006) and in Table 2.

Samples at WHOI were prepared by NiS fire assay (Ravizza and Pyle 1996; Hassler et al. 2000). A few grams of rock powder were spiked with a mixed PGE tracer enriched in ^{99}Ru, ^{105}Pd, ^{190}Os, ^{191}Ir, and ^{198}Pt. A flux mixture of sodium tetraborate, high-purity nickel powder and sublimed elemental sulfur was mixed with the sample powder in a glazed ceramic crucible. The crucible was covered with a glazed ceramic lid and the mixture fused at 1000 °C for ~1.5 h. After cooling, the sulfide bead was separated from the glass and dissolved under reducing conditions in 6.2N HCl at ~150 °C. The solution containing insoluble PGE-rich particles was then filtered through a 0.45 µm cellulose filter and the filter paper was transferred to a Teflon vial and digested in 1 mL concentrated HNO_3. To fully dissolve the PGE-rich particles and oxidize Os to volatile OsO_4, the closed Teflon vial was heated to ~100 °C for about 60 min. After chilling the vial in ice water and diluting the solution five-fold

Table 2. Data for platinum group elements and Au, by ICP-MS (Cardiff), for samples from core LB-07A and in reference materials Wits-1 (see McDonald and Viljoen 2006) and TDB1 (see Govindaraju 1994; Peucker-Ehrenbrink et al. 2003). All data in ppb.

	Ru	Rh	Pd	Ir	Pt	Au
KR7-1	0.093	0.19	1.30	0.038	2.99	1.43
KR7-9	1.52	1.29	25.9	0.68	22.4	6.86
KR7-9d	1.36	1.25	25.1	0.65	23.6	7.76
KR7-14	0.45	0.34	4.85	0.21	7.90	10.4
KR7-43b	0.096	0.088	1.43	0.059	1.32	2.90
KR7-21	0.080	0.13	1.51	0.050	3.60	4.78
KR7-22	0.065	0.056	1.50	0.033	2.17	1.58
KR7-31	0.059	0.088	0.74	0.028	2.75	4.99
KR7-29A	0.071	0.21	1.53	0.039	2.44	1.24
KR7-43c	0.11	0.17	0.84	0.035	2.16	6.23
KR7-11b	0.23	0.21	4.19	0.10	3.33	22.7
Wits1	3.83	1.18	5.19	1.38	7.02	5.73
TDB1	0.21	0.54	22.4	0.11	4.92	7.07
Wits1 preferred	3.9 ± 0.8	1.1 ± 0.2	5.0 ± 1.2	1.4 ± 0.3	5.7 ± 1.6	4.9 ± 2.6
TDB1 certified	0.3	0.7	22.4 ± 1.4	0.15	5.8 ± 1.1	6.3 ± 1.3

with Millipore water, the Teflon lid was replaced with a two-port cap, one end of which was connected to the Ar supply for the plasma and the other to the torch of a multicollector ICPMS (ThermoElectron NEPTUNE). Volatile OsO_4 was carried with the Ar stream into the plasma, allowing the determination of Os. Osmium isotopic composition was determined using three channeltrons in a multi-dynamic acquisition routine that corrects for variable channeltron counting efficiencies and instrumental mass fractionation. Complementary PGE concentrations were determined on a single collector, magnetic sector ICPMS (ThermoFinnigan ELEMENT 2) in the liquid residue after it was taken to dryness and redissolved in 5% HNO_3. Osmium, Pt, and Pd concentrations were calculated using at least two isotope ratios each to check for consistency. Concentrations generally agree within a few percent of each other and are not listed when the standard deviation of the two results exceeds 20%. The precision, accuracy, and procedural blanks of the analytical method have been documented in detail by Peucker-Ehrenbrink et al. (2003).

RESULTS AND DISCUSSION

The results of the PGE analyses by ICP-MS of samples from core LB-07A are reported in Table 2. Related major-element and selected trace-element data (for Cr, Co, and Ni) of the same samples are reported in Table 1. In agreement with elevated siderophile element data (for Cr, Co, and Ni), on which the sample classification was based, some of the samples show fairly high PGE contents. For example, suevite KR7-9 (and its duplicate KR7-9d), which has the highest Ni and Cr concentrations, has the highest PGE contents of all analyzed samples. The Ru/Ir ratio (2.1–2.2) is within a factor of two of the chondritic ratio (1.42) but the Pt/Ir and Pd/Ir ratios in this sample (36.6 and 39.2, respectively) are more than 15 times the corresponding chondritic ratios. Similarly, the PGE contents of the Ni-rich samples KR7-11b and KR7-14 (both are suevitic breccias) are relatively high. The ranges of the individual PGEs show a wide variation. For example, Ir values range from 0.028 to 0.68 ppb, Pt values range from 1.3 to 23.6 ppb, and Pd values from 0.87 to 26.2 ppb. Gold abundances—of particular interest because the Bosumtwi crater structure is located near the gold-mineralized zones of the Ashanti Belt (see also discussion in Dai et al. 2005)—range from 1.2 to 22.7 ppb. Interestingly, the highest Au values do not correlate with the highest PGE values, indicating that gold may have a different carrier phase than the PGEs or that Au, which is more mobile than the PGEs, was affected by hydrothermal alteration.

The chondrite-normalized PGE and Au abundance patterns for these samples are shown in Fig. 2. It is immediately evident that all samples, irrespective of lithology, show fairly similar patterns, all of which are fractionated and nonchondritic. The lowest abundances are found for those PGE with the highest volatilization temperature and the patterns show a reasonably steep slope (over two orders of magnitude) from the left to the right of the diagram, with a consistent positive Pt anomaly. These pattern shapes are typical of many crustal rocks, including many sediments and soils, and basic magmas and associated sulfide mineralization where Pt is enriched over Rh (e.g., Barnes et al. 1985; Schmidt et al. 1997; McDonald et al. 2001; Farago et al. 2005; Kinnaird 2005). Despite the presence of relatively high Ir and Ru contents, for some samples, the normalized abundance patterns do not provide any unambiguous evidence for the presence of an extraterrestrial component. In contrast, some low-temperature mobility of the PGE might have influenced the distribution patterns (e.g., Colodner et al. 1993). No clear-cut distinction exists between the impact breccia and basement samples.

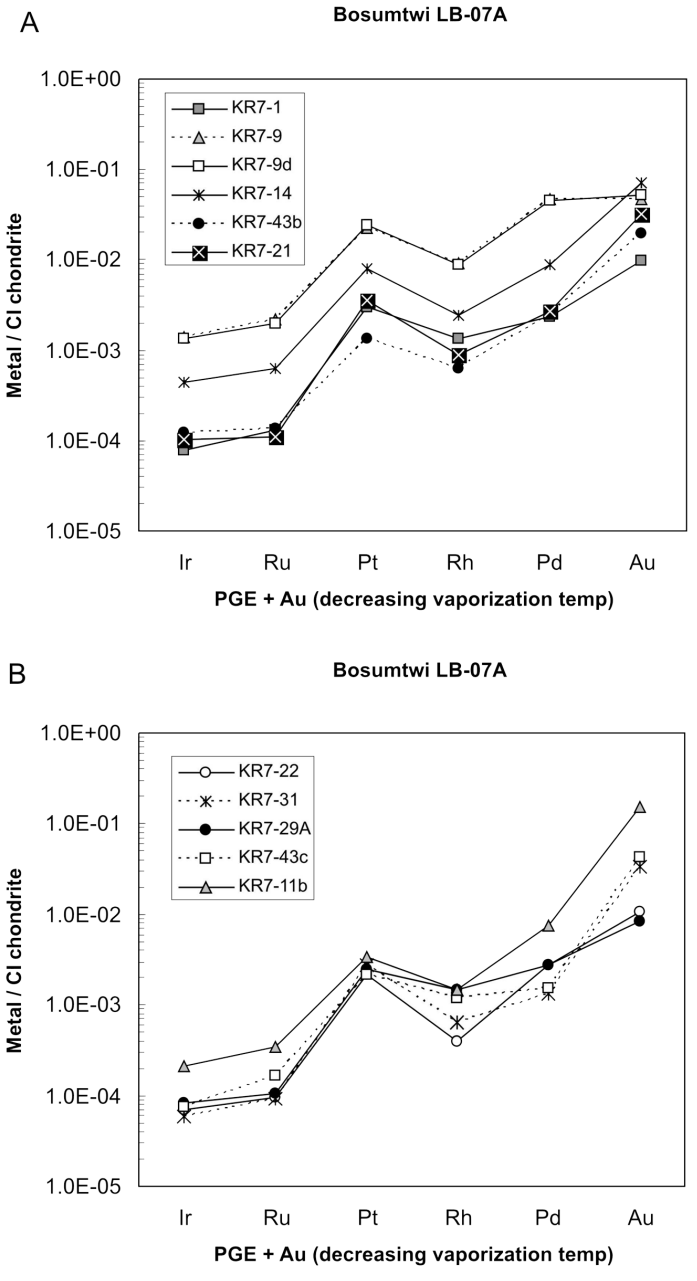


Fig. 2. Chondrite-normalized PGE abundance patterns for Bosumtwi rocks from the LB-7A core. Normalization data from Jochum (1996), except Pd from Anders and Grevesse (1989). Even though these have somewhat lower overall PGE contents, the patterns of all rocks are non-chondritic. Plots split in two panels (A and B) for clarity.

The PGE contents of the suevite samples are very variable, similar to those of the basement samples. Even though the overall contents of the PGE in the target rocks (samples KR7-22, 29a, 31) are somewhat lower than the abundances in the impact breccias, the contents of the latter vary widely, and none show any near-chondritic abundance patterns or interelement ratios. All of those PGE and Au contents are higher than those of the average continental crust (Schmidt et al. 1997; Peucker-Ehrenbrink and Jahn 2001). However, no distinction exists in the overall patterns between the samples with higher or lower PGE contents, with the possible exception of suevite KR7-9, which does show a somewhat different pattern—no dip in the Pd contents and somewhat lower Au contents. However, the range on chondrite-normalized values is still close to two orders of magnitude, slightly greater than the range reported by Goderis et al. (2006) from their samples.

These results and those reported by Goderis et al. (2007) support the conclusion reached by Dai et al. (2005), namely that local indigenous mineralization at or near Bosumtwi may

Table 3. Data for Os isotopic composition and platinum group element abundances, measured by HR-ICDP-MS (Woods Hole), for samples of fallout suevites, as well as from cores LB-07A and LB-08A.

	$^{187}Os/^{188}Os$	2σ%	2σ abs.	Os ppt	Blank corr%	Ir ppt	Pd ppt	%dev	Pt ppt	%dev
BH1-1500	3.7404	0.86	0.032	135	0.6	56	2125	2	1601	0
BH3-0865	4.2438	0.66	0.028	64	1	39	1892	2	1366	0
KR7-29A	1.7891	0.25	0.0044	20	4	34	1899	0	1464	0
KR7-43C	2.8747	0.92	0.0265	27	3	19	646	1	418	1
KR8-04	3.7371	0.16	0.059	36	2	27	1279	3	1148	0
KR8-30	2.3265	0.59	0.0137	7	12	5	1062	3	403	1
KR8-43	2.8068	0.3	0.083	33	3	47	3143	1	2488	0
KR8-107	1.4503	0.19	0.0027	28	3	46	1854	2	1462	0
KR8-122	2.5589	0.29	0.075	19	4	32	2356	2	1457	0

The "%dev" values for Pd and Pt indicate, in %, the difference of the concentrations that were calculated using two different isotope ratios. In the ideal case this agreement is very good (0–2%, i.e., the resulting concentrations are independent of the isotope ratio used). For Ir there are only two isotopes, and the Os content is calculated using three isotope ratios (Peucker-Ehrenbrink et al. 2003). "Blank corr%" indicates the magnitude of the blank correction (in %) for the Os isotope data.

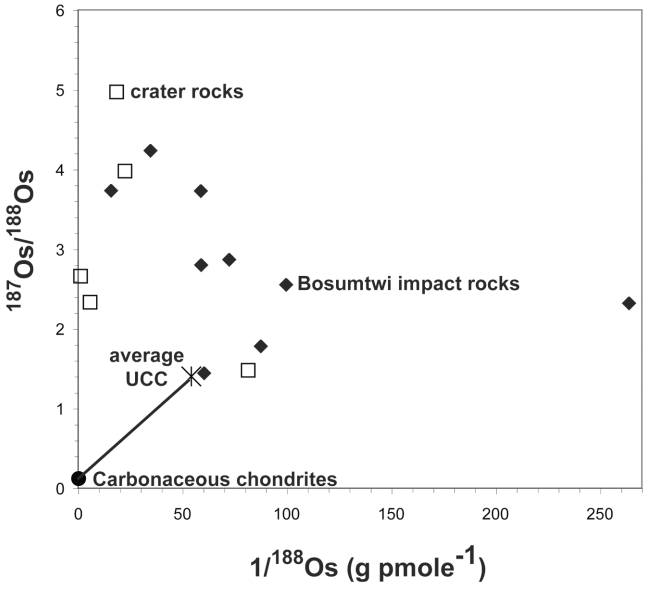


Fig. 3. Plot of inverse ^{188}Os (i.e., common Os) concentration ($1/^{188}Os$) versus $^{187}Os/^{188}Os$ for the Bosumtwi drill core samples. A straight mixing line between radiogenic, Os-poor (= upper crustal) target crater rocks (open squares, Koeberl and Shirey 1993) and an unradiogenic, Os-rich component (= carbonaceous chondrites, solid black circle) is shown schematically for mixing with average upper continental crust (star, Peucker-Ehrenbrink and Jahn 2001). The data for the Bosumtwi impact rocks (black diamonds) overlap significantly with the target crater rocks and do not follow a linear trend indicative of two-component mixing.

have been responsible for the high PGE contents in the Bosumtwi rocks, and that the PGE abundances and patterns do not provide an unambiguous answer regarding the presence and identity of a meteoritic component—even in samples taken from as close as possible to the center of the crater.

Dai et al. (2005) also suggested that an Os isotopic study of the Bosumtwi impact breccias might reveal a meteoritic component, in analogy to the study of Ivory Coast tektites by Koeberl and Shirey (1993), who did find, from Os isotopes, clear evidence for an extraterrestrial component. Therefore, we selected several samples for an Os isotope study. The assumption was that the surface samples analyzed by Dai et al. (2005) might have been subjected to more severe alteration than the core samples studied here, and also that the Os isotope method, which is more selective than the PGE abundance measurements, would produce evidence for a meteoritic signal. The results of these analyses of fallout suevite (to the north of the crater rim), two samples from core LB-07A, and five samples from core LB-08A are given in Table 3. Unfortunately, the $^{188}Os/^{187}Os$ values of all samples are radiogenic, and none shows any clear evidence of a meteoritic component. Figure 3 shows a plot of the isotopic ratio versus the inverse Os content. In such a diagram, mixing between an unradiogenic, Os-rich meteoritic component with radiogenic, Os-poor crustal rocks creates linear mixing trends. This is not observed and our data indicate that in this case terrestrial Os dominates the mixtures. Thus both the Os and PGE abundances reported in Table 3, as well as the Os isotopic ratios, do not show any evidence for a meteoritic component in these samples.

It is thus difficult to quantify the amount of an extraterrestrial component actually present in the Bosumtwi suevites, because of the dominance of the terrestrial PGE. The products of local mineralizations probably dominate the budgets for Pt, Pd, and Au, which may not be the case for Ir (cf. Dai et al. 2005, who found that mineralized samples from the region contained negligible Ir). The low Ir contents in some breccia samples indicate no or a negligible meteoritic component, but those samples that do contain appreciable amounts of Ir (e.g., KR7–9 at ~0.7 ppb Ir) may contain several tenths of a percent of a meteoritic component—but this cannot be unambiguously quantified and resolved from a crustal contribution. The small (or absent) meteoritic component in the fallback breccia deposited directly into the

crater agrees with the suggestion by Artemieva et al. (2004) that this could be the effect of an oblique impact (angle between about 30 to 45° from the horizontal), which has also been invoked to explain the asymmetric distribution of the tektites relative to the crater location. Numerical models of impacts at oblique angles also predict that, due to the large component of horizontal motion, most projectile material will be ejected downrange of impact site in the first few seconds after impact and would therefore be expected to be present in tektites but largely absent from the crater itself (Pierazzo and Melosh 1999). On the other hand, Artemieva et al. (2004) also predicted the presence of appreciable amounts of melt rock within the crater fill, which were not found.

SUMMARY AND CONCLUSIONS

The detection of meteoritic signatures at impact craters is important because, under ideal conditions, it allows constraints to be placed on the types of impactors that form terrestrial impact structures. Previous work at Bosumtwi has shown a clear meteoritic signature only in Ivory Coast tektites, which are distal ejecta that formed during the Bosumtwi impact event. Analyses of proximal ejecta near the crater rim failed to detect a clear meteoritic signature, because of rather high (compared to average crustal) and variable abundances of the siderophile elements, in particular the PGE, in the target rocks. In the present work we attempted a new search for such a meteoritic component in drill-core samples from both inside and outside the crater structure, using both PGE abundances and Os isotope characteristics.

Ten breccia and basement samples from drill core LB-07A, which was drilled in the deepest part of the crater fill, were analyzed for their PGE contents, and two samples from fallout suevite (to the north of the crater rim), two samples from core LB-07A, and five samples from core LB-08A, were subjected to an Os isotope study. No clear distinction between the basement and breccia samples was found at any of these locations. The chondrite-normalized PGE abundance patterns are nonchondritic, and the PGE abundances in both target rocks and breccias are very high compared to average crustal values. This is in agreement with other studies (Dai et al. 2005; Goderis et al. 2007). More surprisingly, the Os isotopic compositions of all samples are dominated by terrestrial Os and the presence of a meteoritic component cannot be resolved even with this more sensitive technique. In contrast to craters such as Morokweng, Clearwater East, and Popigai (McDonald et al. 2001; McDonald 2002; Tagle and Claeys 2005) where there is an obvious meteoritic signature recorded by PGE in the impact melt rocks, the determination of the type of impactor at Bosumtwi hinges on data obtained for the Ivory Coast tektites. Bosumtwi is a good example of the complexity of, and problems associated with, the determination of a meteoritic component at terrestrial impact structures.

Acknowledgments–We are grateful to the Geological Survey of Ghana for logistical support. This research was supported by the Austrian FWF, project 17194-N10 (to C. K.), by the NSF (to B. P.-E.), and by The Leverhulme Trust (to I. McD.). We thank Tracy Atwood for sample preparation and data analysis, as well as Lary Ball and Dave Schneider in the WHOI ICP Facility for the use of the mass spectrometers. Drilling at Bosumtwi was supported by the International Continental Drilling Program (ICDP), the U.S. NSF-Earth System History Program under grant no. ATM-0402010, Austrian FWF (project P17194-N10), the Austrian Academy of Sciences, and by the Canadian NSERC. Drilling operations were performed by DOSECC.

Editorial Handling—Dr. Bernd Milkereit

REFERENCES

Anders E. and Grevesse N. 1989. Abundances of the elements: Meteoritic and solar. *Geochimica et Cosmochimica Acta* 53: 197–214.

Artemieva N. A., Karp T., and Milkereit B. 2004. Investigating the Lake Bosumtwi impact structure: Insight from numerical modeling. *Geochemistry, Geophysics, Geosystems* 5, doi: 10.1029/2004GC000733.

Barnes S.-J., Naldrett A. J., and Gorten M. P. 1985 Origin of the fractionation of platinum-group elements in terrestrial magmas. *Chemical Geology* 53:197–214.

Boamah D. and Koeberl C. 2002. Geochemistry of soils from the Bosumtwi impact structure, Ghana, and relationship to radiometric airborne geophysical data. In *Meteorite impacts in Precambrian shields*, edited by Plado J. and Pesonen L. Impact Studies, vol. 2. Heidelberg-Berlin: Springer. pp. 211–255.

Boamah D. and Koeberl C. 2003. Geology and geochemistry of shallow drill cores from the Bosumtwi impact structure, Ghana. *Meteoritics & Planetary Science* 38:1137–1159.

Boamah D. and Koeberl C. 2006. Petrographic studies of "fallout" suevite from outside the Bosumtwi impact crater, Ghana. *Meteoritics & Planetary Science* 41:1761–1774.

Colodner D. C., Boyle E. A., and Edmond J. M. 1993. Determination of rhenium and platinum in natural waters and sediments and iridium in sediments by flow injection isotope dilution inductive coupled plasma mass spectrometry. *Analytical Chemistry* 65: 1419–1425.

Coney L., Gibson R. L., Reimold W. U., and Koeberl C. 2007. Lithostratigraphic and petrographic analysis of ICDP drill core LB-07A, Bosumtwi impact structure, Ghana. *Meteoritics & Planetary Science* 42. This issue.

Dai X., Boamah D., Koeberl C., Reimold W. U., Irvine G., and McDonald I. 2005. Bosumtwi impact structure, Ghana: Geochemistry of impactites and target rocks, and search for a meteoritic component. *Meteoritics & Planetary Science* 40: 1493–1511.

El Goresy A. 1966. Metallic spherules in Bosumtwi crater glasses. *Earth and Planetary Science Letters* 1:23–24.

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. *Geochimica et Cosmochimica Acta* 57:3737–3748.

Farago M. E., Hutchinson E. J., Simpson P. R., and Thornton I. 2005. Recent increases in platinum metals in the environment from

vehicle catalytic converters. *Applied Earth Science (IMM Transactions section B)* 114:182–192.
Ferrière L., Koeberl C., and Reimold W. U. 2007. Drill core LB-08A, Bosumtwi impact structure, Ghana: Petrographic and shock metamorphic studies of material from the central uplift. *Meteoritics & Planetary Science* 42. This issue.
Feybesse J.-L., Billa M., Guerrot C., Duguey E., Lescuyer J.-L., Milesi J.-P., and Bouchot V. 2006. The Paleoproterozoic Ghanaian province: Geodynamic model and ore controls, including regional stress modeling. *Precambrian Research* 149: 149–196.
Glass B. P., Kent D. V., Schneider D. A., and Tauxe L. 1991. Ivory Coast microtektite strewn field: Description and relation to the Jaramillo geomagnetic event. *Earth and Planetary Science Letters* 107:182–196.
Govindaraju K. 1994. 1994 compilation of working values and samples description for 383 geostandards. *Geostandards Newsletter* 18:1–158.
Goderis S., Tagle R., Claeys P., Schmitt R. T., and Erzinger J. 2006. Platinum-group elements in the ICDP cores from the Bosumtwi crater, Ghana (abstract #1035). 37th Lunar and Planetary Science Conference. CD-ROM.
Goderis S., Tagle R., Schmitt R. T., Erzinger J., and Claeys Ph. 2007. Platinum group elements provide no indication of a meteoritic component in the ICDP cores from the Bosumtwi crater, Ghana. *Meteoritics & Planetary Science* 42. This issue.
Hassler D. R., Peucker-Ehrenbrink B., and Ravizza G. E. 2000. Rapid determination of Os isotopic composition by sparging OsO_4 into a magnetic-sector ICP-MS. *Chemical Geology* 166:1–14.
Hirdes W., Davis D. W., and Eisenlohr B. N. 1992. Reassessment of Proterozoic granitoid ages in Ghana on the basis of U/Pb zircon and monazite dating. *Precambrian Research* 56:89–96.
Huber H., Koeberl C., McDonald I., and Reimold W. U. 2001. Geochemistry and petrology of Witwatersrand and Dwyka diamictites from South Africa: Search for an extraterrestrial component. *Geochimica et Cosmochimica Acta* 65:2007–2016.
Jochum K. 1996. Rhodium and other platinum-group elements in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 60: 3353–3357.
Jones W. B. 1985. Chemical analyses of Bosumtwi crater target rocks compared with the Ivory Coast tektites. *Geochimica et Cosmochimica Acta* 48:2569–2576.
Koeberl C. 1998. Identification of meteoritic components in impactites. In *Meteorites: Flux with time and impact effects*, edited by Grady M. M., Hutchison R., McCall G. J. H., and Rothery D. A. Geological Society of London Special Publication #140. London: Geological Society of London. pp. 133–153.
Koeberl C. and Reimold W. U. 2005. Bosumtwi impact crater, Ghana (West Africa): An updated and revised geological map, with explanations. *Jahrbuch der Geologischen Bundesanstalt, Wien (Yearbook of the Austrian Geological Survey)* 145:1–70 (+1 map, 1:50,000).
Koeberl C. and Shirey S. B. 1993. Detection of a meteoritic component in Ivory Coast tektites with rhenium-osmium isotopes. *Science* 261:595–598.
Koeberl C. and Shirey S. B. 1997. Re-Os isotope systematics as a diagnostic tool for the study of impact craters and distal ejecta. *Palaeogeography, Palaeoclimatology, Palaeoecology* 132:25–46.
Koeberl C., Bottomley R. J., Glass B. P., and Storzer D. 1997. Geochemistry and age of Ivory Coast tektites and microtektites. *Geochimica et Cosmochimica Acta* 61:1745–1772.
Koeberl C., Reimold W. U., Blum J. D., and Chamberlain C. P. 1998. Petrology and geochemistry of target rocks from the Bosumtwi impact structure, Ghana, and comparison with Ivory Coast tektites. *Geochimica et Cosmochimica Acta* 62:2179–2196.
Koeberl C., Shukolyukov A., and Lugmair G. 2004. An ordinary chondrite impactor composition for the Bosumtwi impact structure, Ghana, West Africa: Discussion of siderophile element contents and Os and Cr isotope data (abstract #1256). 35th Lunar and Planetary Science Conference. CD-ROM.
Koeberl C., Milkereit B., Overpeck J. T., Scholz C. A., Peck J,. and King J. 2005. The 2004 ICDP Bosumtwi impact crater, Ghana, West Africa, drilling project: A first report (abstract #1830). 36th Lunar and Planetary Science Conference. CD-ROM.
Koeberl C., Milkereit B., Overpeck J. T., Scholz C. A., Reimold W. U., Amoako P. Y. O., Boamah D., Claeys, P., Danuor S., Deutsch A., Hecky R. E., King J., Newsom H., Peck J., and Schmitt D. R. 2006. An international and multidisciplinary drilling project into a young complex impact structure: The 2004 ICDP Bosumtwi impact crater, Ghana, drilling project—An overview (abstract #1859). 37th Lunar and Planetary Science Conference. CD-ROM.
Kinnaird J. A. 2005. Geochemical evidence for multiphase emplacement in the southern Platreef. *Applied Earth Science (IMM Transactions section B)* 114:225–242.
Leube A., Hirdes W., Mauer R., and Kesse G. O. 1990. The early Proterozoic Birimian Supergroup of Ghana and some aspects of its associated gold mineralization. *Precambrian Research* 46: 139–165.
McDonald I. 2002. Clearwater East structure: A re-interpretation of the projectile type using new platinum-group element data from meteorites. *Meteoritics & Planetary Science* 37:459–464.
McDonald I., Andreoli M. A. G., Hart R. J., and Tredoux M. 2001. Platinum-group elements in the Morokweng impact structure, South Africa: Evidence for the impact of a large ordinary chondrite projectile at the Jurassic-Cretaceous boundary. *Geochimica et Cosmochimica Acta* 65:299–309.
McDonald I. and Viljoen K. S. 2006. Platinum-group element geochemistry of mantle eclogites: A reconnaissance study of xenoliths from the Orapa kimberlite, Botswana. *Applied Earth Science (IMM Transactions section B)* 115:81–93.
Montanari A. and Koeberl C. 2000. *Impact stratigraphy—The Italian record.* Lecture Notes in Earth Sciences, vol. 93. Heidelberg: Springer-Verlag. 364 p.
Osae S., Kase K., and Yamamoto M. 1995. A geochemical study of the Ashanti gold deposit at Obuasi, Ghana. *Okayama University Earth Science Reports* 2(1):81–90.
Palme H., Janssens M. J., Takahashi H., Anders E., and Hertogen J. 1978. Meteorite material at five large impact craters. *Geochimica et Cosmochimica Acta* 42:313–323.
Pesonen L. J., Koeberl C., and Hautaniemi H. 2003. Airborne geophysical survey of the Lake Bosumtwi meteorite impact structure (southern Ghana)—Geophysical maps with descriptions. *Jahrbuch der Geologischen Bundesanstalt, Vienna (Yearbook of the Austrian Geological Survey)* 143:581–604.
Peucker-Ehrenbrink B. and Jahn B.-M. 2001. Rhenium-osmium isotope systematics and platinum group element concentrations: Loess and the upper continental crust. *Geochemistry, Geophysics, Geosystems* 2, doi:10.1029/2001GC000172.
Peucker-Ehrenbrink B., Bach W., Hart S. R., Blusztajn J. S., and Abbruzzese T. 2003. Rhenium-osmium isotope systematics and platinum group element concentrations in oceanic crust from DSDP/ODP Sites 504 and 417/418. *Geochemistry, Geophysics, Geosystems* 4, doi:10.1029/2002GC000414.
Pierazzo E. and Melosh H. J. 1999. Hydrocode modeling of Chicxulub as an oblique impact. *Earth and Planetary Science Letters* 165:163–176.
Plado J., Pesonen L. J., Koeberl C., and Elo S. 2000. The Bosumtwi meteorite impact structure, Ghana: A magnetic model. *Meteoritics & Planetary Science* 35:723–732.
Ravizza G. and Pyle D. 1997. PGE and Os isotopic analyses of single

sample aliquots with NiS fire assay preconcentration. *Chemical Geology* 141:251–268.

Reimold W. U., Brandt D., and Koeberl C. 1998. Detailed structural analysis of the rim of a large, complex impact crater: Bosumtwi crater, Ghana. *Geology* 26:543–546.

Schmidt G., Palme H., and Kratz K.-L. 1997. Highly siderophile elements (Re, Os, Ir, Ru, Rh, Pd, Au) in impact melts from three European impact craters (Saaksjärvi, Mien and Dellen): Clues to the nature of the impacting bodies. *Geochimica et Cosmochimica Acta* 61:2977–2987.

Tagle R. and Claeys P. 2005. An ordinary chondrite impactor for the Popigai crater, Siberia. *Geochimica et Cosmochimica Acta* 69: 2877–2889.