PERGAMON

Planetary and Space Science 49 (2001) 831–837

Planetary and Space Science

www.elsevier.nl/locate/planspasci

Are Ir anomalies sufficient and unique indicators for cosmic events?

U. Kramar[a,*], D. Stüben[a], Z. Berner[a], W. Stinnesbeck[b], H. Philipp[a], G. Keller[c]

[a] *Institute of Mineralogy and Geochemistry, University of Karlsruhe, Kaiserstr. 12, 76128 Karlsruhe, Germany*
[b] *Institute of Geology, University of Karlsruhe, Kaiserstr. 12, 76128 Karlsruhe, Germany*
[c] *Department of Geosciences, Princeton University, NJ 08544, USA*

Received 21 September 2000; received in revised form 5 February 2001; accepted 5 March 2001

Abstract

Ir anomalies are often considered unique indicators for cosmic events. The present paper compares the contents and patterns of platinum group element (PGE) anomalies of magmatic and sedimentary origins with similar anomalies found in the Cretaceous–Tertiary (K/T) boundary impact clay and other PGE enriched layers across the K/T boundary and early Danian (*Parvularugoglobigerina eugubina zone*) at Beloc, Haiti. This analysis demonstrates that PGE patterns provide more conclusive evidence for the reconstruction of paleoevents than that can be achieved by Ir content alone.

1. Introduction

Meteorites are rich in iridium compared to the mean of Earth's crust. Consequently, high Ir concentrations in sedimentary layers are often used as evidence for meteorite impacts. Iridium contents in iron meteorites are reported to range from 24 to 30.000 ng/g (Wasson et al., 1989), whereas in chondritic meteorites the range is from 338 to 810 ng/g (Kalleymeyn et al., 1989).

Normalisation is often based on a content of 455 ng/g Ir (McDonough and Sun, 1995), the average of C1-chondrites. This is about 10.000 times higher than the average concentration of the Earth's crust, which is approximately 50 pg/g for the continental crust and 30 pg/g for the total crust. Other platinum group elements (PGEs) average at about 1 ng/g (Wedepohl, 1995). Iridium can be determined easily by instrumental neutron activation analysis (INAA), which has an extremely low detection limit of < 0.03 ng/g (30 pg/g) using γ–γ-coincidence counting (e.g., Alvarez, 1987; Koeberl and Huber, 2000). Other PGEs cannot be determined by INAA at crustal background levels.

Positive Ir anomalies in Cretaceous/Tertiary (K/T) boundary sequences are commonly referred to as being caused by the impact of a chondrite of about 10 km in diameter (Alvarez et al., 1980). The Ir content of this type of meteorite would have been sufficient to increase the Ir concentration in a 1 cm sediment layer to approximately 80 ng/g Ir on a global scale, if distributed homogeneously over the Earth's surface. Distinct, high Ir anomalies are present in Europe (e.g., at Stevns Clint, Denmark: 48 ng/g Ir; Caravaca, Spain: 56 ng/g Ir; e.g., Tredoux et al., 1989). Smaller Ir anomalies with concentrations of about 1 ng/g, or less, are reported by Smit (1999) for K/T- boundary sections around the Gulf of Mexico (e.g., Mimbral, La Ceiba, Lajilla and Coxquihui, Mexico; Fig. 1). Concentrations of 1 ng/g Ir exceed the average crustal background by a factor of at least 20. Few but nevertheless some magmatic and sedimentary rocks contain Ir concentrations well above 1 ng/g (Fig. 2).

Difficulties with the genetic interpretation of Ir anomalies as impact indicators have been previously discussed (Tredoux et al., 1989; Evans et al., 1993a, b). Tredoux et al. (1989) suggested that many of the Ir anomalies are artifacts related to the most commonly used analytical method (γ–γ-INAA) that allows the determination of only Ir, but not of the other PGEs. Evans et al. (1993a, b) proposed the use of Ru/Ir ratios for identification of impacts and deriving estimates of geographic distance between the Ir anomaly and impact site. Until about 10 years ago, data on PGE concentrations in rocks and sediments were restricted to a few areas. In recent papers related to impacts Ir measurements are commonly reported, whereas PGEs are rarely measured or discussed. The abundance of Ir data in studies over the past 10 years has revealed that Ir concentrations above average

* Corresponding author. Tel.: +49-721-608-6373; fax: +49-721-608-7247.

E-mail address: dgol@r3.uni-karlsruhe.de (U. Kramar).

0032-0633/01/$ - see front matter
PII: S0032-0633(01)00036-8

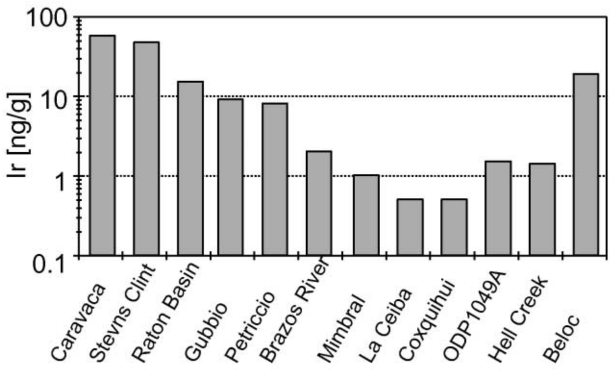

Fig. 1. Ir concentrations in the K/T-sites at Caravaca/Spain (1), Stevens Clint/Denmark (1), Raton Basin/New Mexico (2), Petriccio (3), and Gubbio (3)/Italy, Brazos/Texas (4), Mimbral (4), La Ceiba (4), Coxquihui (4)/Mexico, Beloc/Haiti (5), ODP 1049A (4). (Data from: (2) Gilmore et al. (1984); (3), Alvarez (1987); (1) Tredoux et al. (1989); (5), Jehanno et al. (1992); (4), Smit (1999)).

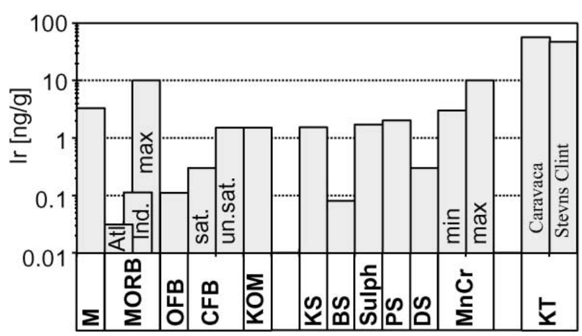

Fig. 2. Ir-concentrations in common magmatic and sedimentary rocks in comparison to K/T-sections. M = mantle (1), MORB = Mid Ocean Ridge Basalts (2a–c), OFB = Ocean Flood basalts (3), CFB (4) = continental flood basalts, KOM = komatiitic basalts (5), KS = Kupferschiefer (6), BS = Black shales (6), Sulph = sulphides and sulphates (6), PS = pelagic sediments (6), DS = Deep sea sediments (6), MnCr = hydrogenetic Mn-crusts (7). (Data from: (2a), Hamlyn et al. (1985); (3), Greenough and Fryer (1990); (2b), Fryer and Greenough (1992); (6), Sawlowicz (1993); (2c), Simonov and Lapukhov (1995); (1), McDonough and Sun (1995); (5), Rehkämper et al. (1999); (7), Stüben et al. (1999); (4), Philipp et al. (2001)).

crustal background are not as rare as previously believed, but occur in rocks of certain stages of magmatic evolution or in the sedimentary record under special sedimentation conditions. The present paper focuses on different depositional mechanisms that can lead to anomalous Ir concentrations in sedimentary sequences. Understanding these depositional mechanisms is helpful for the interpretation of low level Ir anomalies (<5 ng/g) as evidence of impact origin, when no other supporting evidence is present. Nevertheless, in interpreting the Ir data, not only the absolute peak level of the concentrations, but also the total flux of Ir in a given stratigraphic sequence has to be considered.

2. Ir contents of magmatic and sedimentary rocks

According to Barnes et al. (1988), the average Ir concentration of the Earth's mantle is 4.4 ng/g. However, measured Ir concentrations in most mantle-derived rocks are in the order of 0.1 ng/g or below (Barnes et al., 1985). For instance, MORB type basalts of the Mid Atlantic Ridge have generally very low Ir contents (<0.02 ng/g; Hamlyn et al., 1985). In Indian Ocean MORB Ir values average at 0.116 ng/g (Fryer and Greenough, 1992). Simonov and Lapukhov (1995) reported values of up to 10 ng/g Ir in MORB. Deccan trap flow basalts have a very low Ir content (<27 pg/g), whereas the "intertrappean" sediments (clays, marls and ashes) average at 50 pg/g, with maximum values of approximately 120 pg/g (Rocchia et al., 1988; Bhandari et al., 1993). Crocket (1981) reported on Deccan and Karroo floodbasalts that contain an average of 0.092 ng/g Ir. Continental flood basalts from Greenland average 0.3 ng/g Ir for sulphur-saturated melts, but undersaturated melts exist which average at 1.5 ng/g and reach maximum values above 5 ng/g Ir (Fig. 2; Philipp et al., 2001). Ocean flood basalts have concentrations of 0.1–0.3 ng/g (Greenough and Fryer, 1990). Concentrations in basalts from Iceland and La Reunion average at 0.2 ng/g Ir, whereas komatiitic basalts have concentrations between 1 and 4 ng/g Ir (Rehkämper et al., 1999). The latter are generally produced from melts that are undersaturated in sulphur. Barnes et al. (1997) report that Fe-rich sulphides in intraplate basalts are enriched in Ir, Os, Ru and Rh, (up to 400 ng/g Ir) as compared to Cu-rich sulphides that are enriched in Pt, Pd and Au, but have relatively low Ir concentrations (approx. 20 ng/g Ir).

Iridium in sedimentary rocks originates from extraterrestrial matter, continental weathering and volcanism. The extraterrestrial Ir-flux was estimated to be 7–13 $ng/cm^2/myr^1$ (Kyte and Wasson, 1986). Sedimentary rocks are generally low in Ir (~ 20 pg/g), but sediments rich in organic matter and sulphides reach Ir concentrations of the same order of magnitude as the K/T sections (e.g., Mimbral: 0.8 ng/g Ir), for example the Permian Kupferschiefer in Poland (2.1 ng/g Ir; Pfeifer et al., 1997), the "Rote Fäule" from Kupferschiefer in Poland (11 to 67 ng/g Ir; Bechtel et al., 2001) and sulphides from black shales (1.7 ng/g Ir; Sawlowicz, 1993). In sediments from deep sea environments Ir of cosmic origin may be enriched hydrogenetically up to 500 pg/g indicating low sedimentation rates (Kyte et al., 1993; Sawlowicz, 1993), thus the Ir concentration in sediments is being used as a tracer for sedimentation rates (Bruns et al., 1996). Iridium concentrations in hydrogenetic manganese crusts range from 3 to 10 ng/g (Stüben et al., 1999). These concentrations are of the same order of magnitude as impact-induced Ir anomalies at the K/T boundary (e.g., the Red Layer).

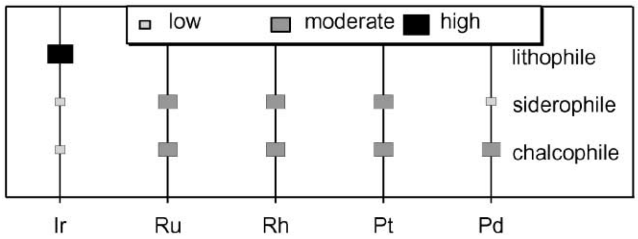

Fig. 3. Generalised and simplified behaviour of PGEs during magmatic and sedimentary evolution.

3. General chemical characterisation of PGEs

In a general sense, Ru, Rh and Pt behave chalcophile and siderophile, whereas Pd acts more like chalcophile elements (Campell et al., 1983; Copobianco and Drake, 1990; Peach et al., 1990, 1994, 1995; Copobianco et al., 1994), and Ir and Os like lithophile (Amossé and Alibert, 1993; Brügmann et al., 1987) (Fig. 3). As a result of this different chemical behaviours, the PGE distribution patterns are modified during endogenic (magmatic) and exogenic evolution. Normalised to CI chondrites, rock material from the Earth's mantle (McDonough and Sun, 1995), iron-meteorites (Sawlowicz, 1993; Kalleymeyn et al., 1989) and chondrites (e.g., Evans et al., 1993b; Wasson et al., 1989) show similar flat PGE patterns, but have ranges at different levels (between 0.001 and 1000-fold chondrite values).

The PGE distribution during magmatic evolution is mainly linked to the sulphur cycle (Keays, 1995). During the evolution from primitive to more evolved magmas, chondrite-normalised Ru, Rh, Pt and Pd tend to become increasingly enriched, as compared to Ir (Barnes et al., 1985; Keays, 1995). During differentiation of mantle-derived magmas by fractional crystallisation, the PGE distribution is largely controlled by the degree of sulphur saturation in the melt. In melts that are undersaturated in sulphur, Pd and Pt are incompatible elements that will be enriched, whereas Ir and Ru are compatible and will be depleted (Keays, 1995). In sulphur-saturated melts, Pd and Pt are preferentially partitioned into sulphides due to their high partition coefficient ($D[\mathrm{Pt, Pd}]_{\mathrm{sulphide\text{-}silicate}} \sim 10^4$). Gravity settling of the sulphides depletes the PGEs in the residual silicate magma (Philipp et al., 2001). Chondrite-normalised PGE values for sulphur-saturated flood-basalts show increasing trends from 6×10^{-4} for Ir to 4×10^{-3} for Pd. The PGE patterns of floodbasalts from undersaturated melts are quite similar at higher values, and Ir contents average around the same level as observed for samples from the Brazos K/T boundary (Smit, 1999; Philipp et al., 2001) (Fig. 4).

During hydrothermal processes, Ir as well as other PGEs are enriched in altered basalts and in sulphate condensates from volcanic exhalations (Crocket, 2000). For instance, Ir is drastically enriched in sulphate condensates as compared to Pd (19.6 ng/g Ir; 6.9 ng/g Pd). In high temperature sulphate condensates highest Ir concentrations are observed in condensation experiments between 250°C and 600°C (after Crocket, 2000). Iridium and Pd are considered to be dissolved in volcanic gases as IrO_3 and $PdCl_2$, respectively (Crocket, 2000).

In the sedimentary cycle, PGEs are removed from the water column by precipitation and co-precipitation with (bacterial) iron oxides and sulphides as well as by scavenging in ferromanganese phases (Wallace et al., 1990; Colodner et al., 1992; Sawlowicz, 1993; Anbar et al., 1996; Stüben et al., 1999). Secondary enrichment occurs during diagenesis of PGEs by remobilisation and redox-controlled re-precipitation (Evans et al., 1994; Piestrynski and Sawlowicz, 1999). Sediments rich in sulphur and/or organic matter, such as the Kupferschiefer or other black shales, can be enriched in PGEs. During diagenesis PGEs are fractionated according to their chalcophile behaviour (Sawlowicz, 1993). In hydrogenous manganese crusts the more siderophile PGEs are typically enriched due to scavenging by ferromanganese phases (Anbar et al., 1996; Stüben et al., 1999) (Fig. 4).

4. Case study: Multiple PGE anomalies at Beloc, Haiti

4.1. Geology

Three K/T boundary sections ≈ 1 km from the village of Beloc, Haiti, about 200 and 300 m apart and located on a steep slope, were investigated. The lithology and biostratigraphy of these sections is detailed in Stinnesbeck et al. (1999) and Keller et al. (2001). The three sections can easily be correlated from outcrop to outcrop, and various lithologically distinct layers are exposed over a visible distance of about 60 m. One of these sections (B2) has previously been described by Maurrasse and Sen (1991). The most expanded section (B3) was selected to establish a PGE profile. This section includes a 30 cm thick limestone of latest Maastrichtian age, and 200 cm of sediments of the early Danian *Parvularugoglobigerina eugubina* zone. The Danian sediments consist of spherule-rich layers, bioclastic limestones and pelagic lime-mudstones. The sediments are separated from the underlying late Maastrichtian limestone by an erosional surface marking disconformity. The spherule-rich layer contains evidence of reworked sediments, including common to abundant subrounded clasts of Maastrichtian limestone. The K/T transition is identified based on the first appearance of Danian species above the disconformity and at the base of the spherule-rich layer (Keller et al., 2001). Within the section four characteristic horizons (Marker Units MU1 to MU4) can be identified within the early Danian *P. eugubina* zone (Fig. 5, Keller et al., 2001):

- MU1 (Marker Unit 1) includes the basal 10–20 cm of the spherule-rich deposit that overlies the K/T disconformity.

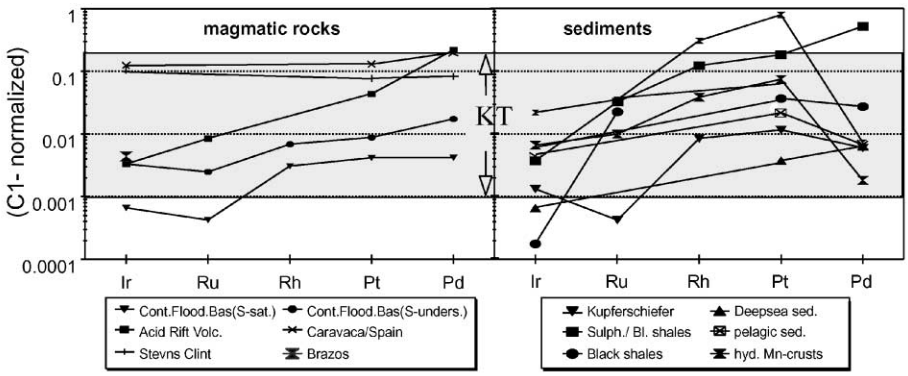

Fig. 4. Chondrite-normalised PGE patterns of magmatic (continental flood basalts (1) and rift-related volcanics (2)) sedimentary rocks (Kupferschiefer (3), sulphides, black shales (4), deep sea and pelagic sediments (3), hydrogenetic manganese crusts (5)) in comparison to K/T sections from Caravaca/Spain (6) and Stevns Clint/Denmark (6). (Data from: (2), Borg et al. (1988); (6) Tredoux et al. (1989); (4) Sawlowicz (1993); (3) Pfeifer et al. (1997); (5) Stüben et al. (1999); (1) Philipp et al. (2001)).

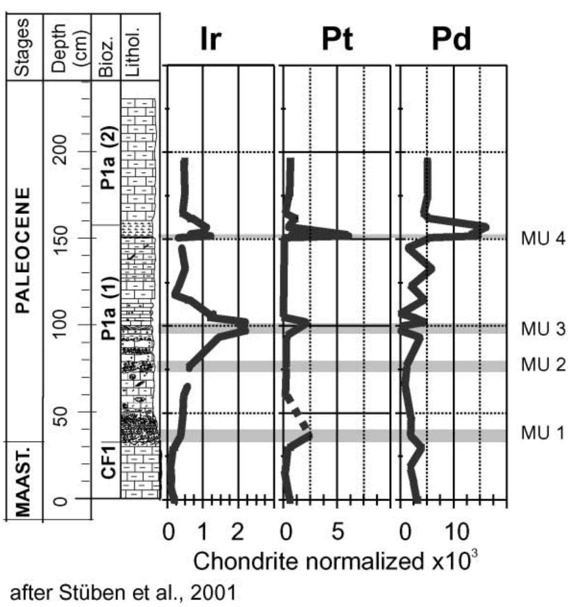

Fig. 5. Lithological section and chondrite-normalised Ir, Pd and Pt contents in the K/T-transition at Beloc 3/Haiti.

This layer is characterised by abundant spherules that are altered to blocky calcite and smectite.

- MU2 is a spherule layer at 70–80 cm above the base of the section and contains abundant black glass spherules.
- MU3 is a grey-green 2 cm thick shale with a thin rust-coloured layer that overlies the spherule-rich deposit at 100–102 cm from the base of the section. This layer contains a PGE anomaly and is labelled as the "lower PGE anomaly".
- MU4 is a thin rust-coloured layer with abundant amphiboles and situated within a pelagic limestone at 150 cm from the base of the section. This rust-coloured layer contains another PGE anomaly that has been labelled as "upper PGE anomaly".

A total of 50 cm of sediments separate MU3 and MU4. The lower 10 cm consist of alternating pelagic limestones and bioclastic limestones, whereas marly limestone with rare bioclastic limestone lenses form the upper 40 cm. The marly limestones show no signs of intense reworking or bioturbation.

4.2. Material and methods

A total of 28 samples were selected for PGE-analysis from the B3 section. About 30 g of each sample was dried at 105°C, mixed with 30 g of sodium carbonate, 100 g of sodium tetraborate, 10 g of nickel powder, 7.5 g of sulphur and 5–10 g of diatomite. The mixture was then fused for 1 h at 1140°C. The resulting melt segregates by liquation, leading to a Ni-sulfide phase ("Ni-button" or "regulus") which collects and concentrates the PGEs. After cooling, the regulus was crushed and its bulk (NiS) dissolved in HCl_{conc}. After filtration through a PTFE-membrane filter, the part of the residue containing the PGEs was dissolved in a mixture of H_2O_2 and HCl_{conc}. Undissolved particles were retained by filtration through a filter paper (white band quality). The solution containing the PGEs was slowly dried and taken up with 1% HNO_3 in 10 ml flasks. All chemicals used in the fire assay step were of reagent grade, those used in the digestion of the PGEs were of suprapure grade. PGEs were measured by ICP-MS.

Accuracy was checked by means of WPR-1 and SARM-7 standard reference materials. Based on reference samples analysed in the lab over several years, recovery was estimated to be better then 85%, which is in the range of the efficiency usually obtained by NiS fire assay (Date et al., 1987; Reddi et al., 1994; Zereini et al., 1994). Detection limits are 0.05 ng/g Ir, 0.1 ng/g Rh, 0.4 ng/g Pd and 0.4 ng/g Pt. Detection limits are mainly dependent on blanks of the NiS-fire assay.

4.3. Results

The PGE concentrations of the B3 samples display differences of nearly two orders of magnitude. The lowest PGE concentrations are observed in the Maastrichtian interval (basal 30 cm, 0.050 ng/g Ir, 0.2 ng/g Rh, < 0.5 ng/g Pt and 1 ng/g Pd) and represent background values for marine carbonates. Above the K/T disconformity, Ir increases slightly to 0.2 ng/g, whereas Pt, Rh and Pd remain at low levels. In the rust coloured layer of MU3 (102 cm), Ir is enriched 20 fold, as compared to local Maastrichtian background values, though the other PGEs are only slightly enriched. Iridium contents tail below and above this layer. In the limestones above, Ir decreases to 0.2–0.3 ng/g, but is still slightly higher than in the Maastrichtian limestones.

A second PGE anomaly is observed in the grey-green shale and rust-coloured layer of MU4. In this layer, Ir is only enriched by a factor of two, as compared to the marls below and above, whereas Pt is enriched to 6 ng/g and Pd to 9 ng/g. In the overlying limestones the PGE concentrations decrease to 0.2 ng/g Ir, 0.7 ng/g Pt and 2.8 ng/g Pd.

4.4. Discussion

The PGE profile displays two clear anomalies plus a minor enrichment at the base of the spherule layer above the K/T disconformity. The two anomalies display distinct, but different, patterns (Stüben et al., 2001). In the lower anomaly (MU3, Fig. 5) that directly overlies the top of the spherule-rich layer containing black glass, the chondrite-normalised PGE pattern is roughly chondritic (Ir: 2.2×10^{-3}, Pt: 2.1×10^{-3}, Pd: 4.5×10^{-3}). This contrasts with the PGE pattern from the upper anomaly and the rest of the section. The increased values for Pd can be explained by the overprint of a normal sedimentary PGE pattern, in addition to a meteoritic signature. The upper anomaly MU4 (Fig. 5) is completely different. The chondrite-normalised PGE pattern of this unit shows increasing values from Ir to Pd (Ir: 1.2×10^{-3}, Pt: 6×10^{-3}, Pd: 14.7×10^{-3}) that indicates similarity to ocean floor basalts, Kilauea basalts, or rift related volcanic rocks (Crocket, 2000; Rehkämper et al., 1999). A magmatic origin of this bentonite layer is also indicated by the presence of abundant amphiboles (Stinnesbeck et al., 1999).

The PGE patterns of both layers (MU3 and MU4) are significantly different. Lithologically they are separated by 50 cm of horizontally layered marly limestones that show no indication for reworking or bioturbation. It is therefore unlikely that the upper PGE anomaly resulted from reworking of the lower Ir anomaly. During late Cretaceous and early Tertiary, Haiti (southern Hispaniola) was part of the Caribbean arc that was tectonically active (Pindell and Barrett, 1990). Extensive arc and subduction-related volcanic and magmatic activity, associated with the production of tuff and pyroclasts, occurred in the area (Pindell and Barrett, 1990). Scott et al. (1999) report the presence of PGE-bearing ultramafites of "middle" and late Cretaceous age in Jamaica and Tobago; both these localities were located close to Haiti during the late Maastrichtian and early Paleocene (Pindell and Barrett, 1990). In Jamaica, the ultramafites are present in a dismembered ophiolite, whereas in Tobago they are part of an arc-related intrusion. These PGE-bearing rocks suggest that mantle heterogeneities existed below the Caribbean Plate with local PGE enrichments. Similar mantle heterogeneities with PGE enrichments have been described from the Ivrea Zone of the Italian Alps (e.g., Garuti et al., 1997) and from the Indian Ocean MORB (Fryer and Greenough, 1992).

Recent investigations of PGE distributions in magmatic rocks indicate that sulphur undersaturated magmas with higher Ir and PGE concentrations exist during magmatic evolution. The majority of magmatic and sedimentary rocks have Ir and PGE concentration ranges compatible with crustal background values. Nevertheless, a small but significant part of the magmatic and sedimentary rocks contains Ir concentrations of the same order of magnitude as observed in low-level anomalies at the K/T boundary (e.g., Mimbral). There is little doubt that the major Ir anomalies at the K/T (e.g. Stevns Clint, Denmark, Caravaca, Spain) originated from the impact of a meteorite. These major Ir-anomalies are characterised by flat chondrite-normalised PGE patterns. However, the small Ir-anomalies, especially from areas of extensive contemporaneous magmatic activity (such as Caribbean region), as well as sediment horizons rich in sulphides or iron and/or manganese oxides, have to be critically evaluated in the context of PGE distribution patterns and other impact markers. Iridium cannot be used as sole evidence for impact events.

5. Conclusions

Two PGE anomalies are present in early Danian sediments of the B3 section of Beloc and they most likely resulted from different sources. The lower anomaly (MU3) is within a thin rust-coloured clay layer directly overlying the spherule-rich layer in the lower part of the *Parvularugoglobigerina eugubina* zone of the early Danian. This anomaly is Ir-dominated and compatible with an impact as indicated by the flat PGE pattern.

The upper PGE anomaly is in the upper part of the *P. eugubina zone* in the early Danian (MU4), approximately 50 cm above the MU3 Ir anomaly. This PGE anomaly is characterised by Pt and Pd enrichments, but has low Ir values, and cannot be explained by an impact of a meteorite or by sediment reworking from the Ir anomaly below (MU3). The PGE pattern is similar to basalts derived from sulphur-undersaturated melts. A non-impact origin of the anomaly in this layer is also supported by the presence of amphiboles, zeolites and clay minerals.

During late Cretaceous and early Tertiary extensive volcanism took place in the entire Caribbean region. PGE-bearing ultramafites of “middle” and late Cretaceous age are known from the neighbouring Caribbean islands of Jamaica (dismembered ophiolites) and Tobago (arc related magmatism) (Scott et al., 1999). The occurrence of PGE-enriched magmas, ashes, tuffs or alteration products is therefore not surprising. Consequently, we propose a volcanic origin for the upper early Danian PGE anomaly.

The Haiti study shows that small Ir anomalies cannot be used as sole evidence in support of meteorite impacts. Ir anomalies have to be critically evaluated within the context of the overall PGE distribution pattern, the contemporaneous magmatic activity of the region, as well as possible enrichment of sediment horizons by sulphides, iron and manganese oxides.

Acknowledgements

This study was supported by the Deutsche Forschungsgemeinschaft (grants Sti128/2-1 to 2-4, and Stu 169/10-1), and the Swiss National Fund (grant 8220-028367). The laboratory assistance of F. Lindenmaier and R. Gehann in the analysis of the PGE, is greatly acknowledged. We thank the unknown reviewers for their comments.

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