Use of $\gamma$-$\gamma$ coincidence spectrometry in the geochemical study of diamicites from South Africa

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We used $\gamma$-$\gamma$ coincidence spectrometry to investigate the possible presence of a meteoritical component in 27 samples of South African diamicites. Recently, several studies have suggested that some tillites/diamicites may represent impact breccias, but a petrographical study by our group found no evidence for the presence of impact-characteristic shocked minerals. The siderophile elements, such as Cr, Co, Ni, and, especially, the platinum group elements, have high abundances in meteorites, but low abundances in terrestrial crustal rocks. The Ir content of the diamicites was measured with the new iridium coincidence spectrometer (ICS) at the University of Vienna, with detection limits of around 0.02 ppb. No enrichments in the contents of Ir and other siderophile elements compared to average crustal concentrations were found; thus, no unequivocal evidence for an impact origin of these diamicites of the South African Dwyka Group can be documented.

Introduction

Multiparameter $\gamma$-$\gamma$ coincidence spectrometry is used to determine Ir abundances in the sub-ppb range, in relatively small samples ($\leq$100 mg). The present work includes the first results on natural samples (South African diamicites) measured with our iridium coincidence spectrometry (ICS) system to determine the possible presence of a meteoritic component in these rocks. Diamicites are defined as “A comprehensive, nongenetetic term proposed by FLINT et al. 1 for a nonsorted or poorly sorted, noncalcareous, terrigenous sedimentary rock that contains a wide range of particle sizes, such as rock with sand and/or larger particles in a muddy matrix.” Some diamicites have been regarded as having formed by lithification of glacial till (termed tillites). OBERBECK et al. 3 and RAMPINO 4 suggested that large-scale impact events could have produced the Dwyka deposits of the Karoo Supergroup in South Africa. These suggestions were made without any petrographic studies of the rocks to determine the possible presence of characteristic shock deformation indicators, such as the so-called planar deformation features (PDFs), which are only formed during impact events (e.g., FRENCH). 5

REIMOLD et al. 6 searched for PDFs in some 75,000 rock and mineral clasts from Dwyka Group diamicites. No evidence for shock metamorphism was observed in any of these clasts. Here we use geochemical methods to clarify a possible impact relation of the South African Dwyka Group diamicites. We studied the chemical composition of 27 samples including a sample of diamicite from the collar of the Vredefort Dome and several samples from the Government Subgroup of the Witwatersrand Supergroup.

If diamicites represent impact breccias, they should contain traces of the meteoritic projectile. In the early phases of crater formation, the impacting body undergoes almost total vaporization, and only a small amount of the meteoritic vapor may be incorporated with a much larger quantity of target rock vapor and melt. In most cases, the contribution of meteoritic matter to impact melt or melt bearing rocks or glasses is very small (commonly <1%). Only elements that have high abundances in meteorites, but low abundances in terrestrial crustal rocks, can be used to detect such a meteoritic component. Studies of the abundances and inter-element ratios of the siderophile elements, such as Cr, Co, Ni, and, especially, the platinum group elements (PGEs), have been used for these investigations. Addition of only 0.1% of a meteoritic (chondritic) component (containing about 500 ppb Ir) to a crustal rock (containing about 0.02 ppb Ir) would yield an enrichment of about 0.5 ppb in the resulting impact breccia. 7 Because of these low abundances, conventional instrumental neutron activation analysis (INAA) rarely yields usable Ir values; thus, inductively coupled plasma source mass spectrometry (ICP-MS) with chemical pre-separation of the noble metals and ICS were used in the present study.

Experimental

Samples

The specimens analyzed were 23 Dwyka diamicites of the Late Carboniferous-Jurassic Karoo Supergroup of Southern Africa. Sixteen samples were taken from the Umlas Road Quarry (near Pietermaritzburg) and seven additional diamicites from other localities of the Dwyka
group. V-1 to V-5 were collected at Sjambokkraal at the southern cape near Merweville, whereas EGH 270 and Ma-Ca-1/2 come from the Matla coal mine in Mpumalanga Province in the northeastern part of the Karoo basin. These 23 samples were compared with a breccia from the collar of the Vredeport structure (K10E) and three diamicrites from the Wits-Government Supergroup collected near the town of Heidelberg in the East Rand Basin of the Witwatersrand Basin (HE-1, HE-2/A and HE-3). For further details on Dwyka diamicites see REIMOLD et al., and references therein.

**Analytical procedures**

Major, minor and trace element abundances were analyzed by instrumental neutron activation analysis (INAA). Due to the low Ir abundances encountered during INAA, the iridium content was measured with the ICS system at the Institute of Geochemistry at the University of Vienna. This method is specially designed to determine iridium contents in the sub-parts-per-billion (ppb) range. The ICS method has a number of advantages compared to other techniques used to determine Ir concentrations in this range, and may represent one of the best techniques to determine ultra-low iridium abundances in very small samples of geological material.

The main purpose of a coincidence setting is background reduction and removal of spectral interferences. The method is based on the counting of coincident events from two γ-rays from the decay cascade of 192Ir. The coincidence system consists of two detectors (low energy planar HPGe-detectors), two preamplifiers, two amplifiers, two analog-to-digital converters (ADCs) and a multiparameter analyzer small bus box (Fast Com Tec MPA-SBB). Only signals occurring within a certain time (the so-called coincidence time) from both detectors are accepted by the MPA and plotted in a 1024×1024 matrix (see Fig. 1). Then the regions of the iridium peaks (316.5 keV×468.1 keV) are extracted and fitted and the resulting peak volumes are corrected (live time correction, decay time correction, flux correction, background subtraction) and compared with the standards.

Seven crushed and powdered samples of about 50 mg each, as well as a series of Allende meteorite reference samples, mixed with pure quartz powder, were sealed into Suprapur quartz glass tubes. The five standards contained 6.93 ppb, 5.27 ppb, 316.8 ppb, 112.6 ppb, and 35 ppb iridium. Samples and standards were wrapped with aluminum foil, placed into an aluminum capsule, and irradiated for 48 hours at the Astra Reactor of the Forschungszentrum Seibersdorf at a flux of about $7 \times 10^{13}$ n cm$^{-2}$ s$^{-1}$. After a cooling period of ten weeks the samples were first measured for five to eight hours. The samples that reached the detection limit were measured for another 24 hours. For the standard dilution series a regression analysis was done to obtain the interpolated values of their peak volumes.

For comparison, and to provide additional data, the concentrations of iridium, ruthenium, rhodium, platinum, palladium, and gold were determined by ICP-MS using a Ni sulfide fire assay with Te co-precipitation. This method was modified by JACKSON et al. to accommodate a small sample mass (typically 7–14 g), enhance detection limits, and minimize the reagent blank. Typically, 6 g of Na-carbonate, 12 g borax, 0.9 g sulfur, 1.08 g carbonyl-purified Ni, and 3.5 g of silica were required for fusion of a 10 g sample aliquot. Masses of sulfur and Ni were fixed, but masses of the other reagents were proportionally increased or decreased to accommodate larger or smaller samples. The reagents were thoroughly mixed and transferred into a fire clay crucible before being fired for 90 minutes at 1000 °C. After cooling, the crucibles were broken open and the Ni sulfide buttons were separated from the silicate slag and weighed. The button masses spanned a small range (1.48–1.54 g; mean = 1.505±0.017 g), indicating a very consistent separation of Ni sulfide from the molten silicate across the different sample aliquots.

Following fire assay, each button was sealed inside a plastic bag, cracked using a sharp tap from a hammer, and the fragments transferred to a 500 ml beaker containing 120 ml of concentrated HCl. Moderate heat was applied using a hotplate and the buttons were dissolved in the HCl. After the sulfide had dissolved, any noble metals which had entered solution were co-precipitated with Te using SnCl$_2$ as a reductant. After co-precipitation, the insoluble noble metal-bearing residue was filtered under vacuum through a Whatman 0.45 μm nitrocellulose filter paper and washed with 10% HCl and warm distilled water. Each filter paper was then placed inside a 7 ml screw-top Teflon vial. 2.5 ml of concentrated HNO$_3$ was added, the vial was tightly sealed and placed in a refrigerator for 12–15 hours. Taking care to keep the solution cold using an ice slurry bath, 2.5 ml of chilled concentrated HCl was added along with 3–4 crystals (>0.001 g) of salt, NaCl, which promotes the formation of soluble PGE chlorocomplexes. The vial was re-sealed and allowed to stand at room temperature for a further 2 hours, after which it was opened and the solution containing the dissolved noble metals was diluted to 100 g with cold distilled water. Despite attempts to minimize losses of Os as volatile OsO$_4$ during dissolution of the filter paper, Os recoveries were erratic with variations of up to 40% between some standard replicates. For this reason, Os data are not reported in this study.
Finally, the solutions were spiked with Cd and Tl as internal standard monitors for instrumental drift and noble metal concentrations were determined by external calibration on a VG Element PQ2\textsuperscript{+} Plasmaquad ICP-MS. The accuracy of the analysis was determined by analysis of the reference materials Peridotite-WPR1\textsuperscript{14} and Komatiite-Wits1.17

### Results

Five samples from the Umlaas Quarry, two from Sjambokkraal and one from Vredefort and the Heidelberg area, respectively, were analyzed by ICP-MS. The results are shown in Table 1. Normalizing these data to CI, E4, H5 and L6 meteoritic abundances did not show chondritic PGE abundance patterns. Figure 2 shows the abundances normalized to CI chondrite abundances of the Orgueil meteorite\textsuperscript{18} (480 ppb Ir, 690 ppb Ru, 130 ppb Rh, 1050 ppb Pt, 530 ppb Pd and 140 ppb Au). The normalized PGE patterns are similar for most of the samples, with an increase in slope from Ir to Au, but no significant differences within any group of samples. Only one diamicite sample (HE-3) shows a slight enrichment in all of the PGEs. The highest gold abundance is observed in a sample from the Vredefort structure (K10E), whereas the Umlaas Quarry samples usually have the lowest abundance of gcld.
A routine INAA procedure\textsuperscript{19} was used to determine 36 major and trace elements. In addition, the major elements Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P, and the trace elements Y, Nb, V, and Cu were measured by X-ray fluorescence (XRF) spectrometry. The contents of Fe, Ni, Sr, Ba, and Zr were calculated as the average of the XRF and INAA results. All chondrite-normalized rare earth element (REE) patterns\textsuperscript{19} from the Dwyka Group diamicites resemble each other closely. Samples HE-1 and HE-3 (from the Witwatersrand Subgroup) generally show decreased abundances of the REE. (HUBER et al., in preparation).

In short, the abundances of lithophile elements, such as the rare earth elements (as well as major element abundances), are all typical of terrestrial upper crustal rocks. The contents of siderophile elements, such as Cr, Ni, and Co, were measured to obtain additional information on the possible presence of a meteoritic component. The CI-normalized siderophile element abundance patterns (Fig. 3) show no enrichment in the contents of Ni or Ir compared to average crustal concentrations. Compared with the abundances of the other siderophile elements, the Ir and Ni content is significantly decreased. The patterns of all samples, irrespective of their origin, are identical.

Iridium abundances determined by ICS for samples UQ-2, UQ-7, UQ-16, UQ-17, EGH270 and two Witwatersrand samples HE-1 and HE-3 are presented in Table 2. Values are calculated to lie within the 95\% confidence interval (counts $\pm 1.96 \sqrt{\text{counts}}$). Comparing the results of the different methods to determine iridium investigated in this study, there is a good relationship between the ICS and ICP-MS data for the samples UQ-17, EGH270 and HE-3, against the differences for UQ-2 and UQ-7, that may be due to inhomogeneity of the sample.
Table 2. Comparison of iridium concentrations in South African Diamictites from the Karoo Basin determined by INAA, ICS and ICP-MS. Concentration in ppb, 1σ values

<table>
<thead>
<tr>
<th>Sample</th>
<th>INAA</th>
<th>ICS</th>
<th>ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample locality: Umlaas Road Quarry</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>UQ-2</td>
<td>&lt;1.0</td>
<td>0.093 ± 0.019</td>
<td>0.26 ± 0.04</td>
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<tr>
<td>UQ-7</td>
<td>&lt;1.0</td>
<td>0.070 ± 0.016</td>
<td>0.24 ± 0.05</td>
</tr>
<tr>
<td>UQ-16</td>
<td>&lt;0.8</td>
<td>0.066 ± 0.016</td>
<td>–</td>
</tr>
<tr>
<td>UQ-17</td>
<td>&lt;2.1</td>
<td>0.086 ± 0.018</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td>EGH270</td>
<td>&lt;2.1</td>
<td>0.373 ± 0.048</td>
<td>0.28 ± 0.08</td>
</tr>
<tr>
<td>Sample locality: Heidelberg town in East Rand Basin of Witwatersrand Basin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HE-1</td>
<td>&lt;2.2</td>
<td>0.209 ± 0.048</td>
<td>–</td>
</tr>
<tr>
<td>HE-3</td>
<td>&lt;2.7</td>
<td>0.512 ± 0.060</td>
<td>0.42 ± 0.07</td>
</tr>
</tbody>
</table>

INAA — Instrumental neutron activation analysis.
ICS — Iridium coincidence spectrometry.
ICP-MS — Noble metal analysis by NiS fire assay with Te coprecipitation, followed by ICP-MS.

Conclusions

A set of 23 Dwyka diamictite samples from the Late Carboniferous-Jurassic Karoo Supergroup of Southern Africa were chemically analyzed. The chondrite normalized PGE contents show no evidence for the presence of a meteoritic component in any of the samples analyzed so far. The siderophile element concentration patterns also show no enrichment in the contents of Ni or Ir compared to average crustal concentrations. Thus, we conclude that no chemical evidence exists for a meteoritic component in the diamictites of the Dwyka Group, casting further doubt on a connection between these rocks and an impact event.

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References

9. C. KOEBERL, H. HUBER, this issue.