

## Supplementary material A: Analytical methods

### A1. Scanning Electron Microscope (SEM) spot analyses

Eight polished thin sections were made at Rhodes University, while another three were made by Richard Harrison (University of Western Cape). SEM spot analyses performed at Central Analytical Facility's Electron Microbeam Unit, Stellenbosch University (all in RSA). The minerals in these were analysed by means of quantitative ED analysis with a Zeiss EVO MA 15 Scanning Electron Microscope (SEM). Phase compositions were quantified *via* EDX analysis using an Oxford Instruments® X-Max 20 mm<sup>2</sup> detector and Oxford INCA software. Energy dispersive spectroscopy is only suitable for determining elements at concentrations >0.1 mass % for heavy elements using Oxford INCA software. Beam conditions during quantitative analyses were 20 kV and approximately 1.0 A, with a working distance of 8.5mm and a specimen beam current of -20 nA. Natural mineral standards (Astimex, Scientific Limited & MINM25-53) were used for standardization and verification of analyses. The system is designed to perform high-resolution imaging concurrently with quantitative analysis, with element errors ranging from ± 0.6 to 0.01mass % using EDS.

### A2. Scanning Electron Microscope (SEM) elemental mapping

SEM phase mapping was performed at Central Analytical Facility's Electron Microbeam Unit, Stellenbosch University. Element mapping performs the simultaneous acquisition of X-ray data for all possible elements from each pixel on a defined area of an image. The Zeiss EVO MA 15 SEM utilize backscattered electrons (BSE) and energy dispersive X-ray spectra (EDS) to create digital mineral images, identifying the elemental phase composition of minerals. The EDX detector is an X-Max 80 mm<sup>2</sup> Silicon Drift Detector (SDD) from Oxford Instruments that performs high count rate mapping and phase identifications within mineral assemblages. Backscatter electron images were collected at a 20 kV voltage and -20 nA current at a 8.5 mm working distance. BSE elemental mapping and point analyses were conducted to acquire relevant elemental data. The EDS elemental phase mapping was also performed at a 20 kV voltage and a beam current of -20 nA. An Oxford INCA software was used to collect compositional maps and point spectrum analyses.

### A3. Whole rock sample processing (crushing and milling)

Sample processing was done by the second author at the Central Analytical Facility's processing laboratory, Stellenbosch University. A steel jaw crusher and a steel mill pot were used for the crushing and milling, respectively, of the rocks. Table A1 reports tests that were performed in the laboratory to assess contamination induced by grinding/powdering during sample milling. The tests were performed on clean quartz in the various mill pots to test for maximum contamination. Quartz chips were too small for the steel jaw crusher, but the maximum contamination due to steel was simulated by using the steel mill pot.

**Table A1: Contaminations in wt% determined on CAF's XRF instrument (see below).**

Sample	Al <sub>2</sub> O <sub>3</sub>	CaO	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Sum
Quartz Standard	0.168	0.035	0.003	0.015	0.027	0.065	0.003	0.151	0.015	99.823	0.004	100.31
Quartz (Steel mill)	0.041	0.013	0.056	0.392	0.003	0.035	0.002	0.012	0.005	99.966	0.000	100.53

The composition of the quartz used in this milling experiment is not known, because the ICP unit uses the same preparation instruments. The bought standard SARM 49 (South African

Reference Material) was already milled by the manufacturer. Fusions were prepared with a Claisse Fluxer, platinum ware crucibles and with Li-Meta/Tetraboride flux, which possibly also contain some traces.

These tests show that the steel mill may introduce significant amounts of Fe<sub>2</sub>O<sub>3</sub> and Cr, as well as smaller amounts of Ni, Pb and Zr. The results in Tables A1 and A2 represent “worst case scenarios” due to the hardness of the tested material, and generally it is believed that the contamination is minor. No correlation has been attempted implemented to the analysed samples.

Similar tests were performed for LA-ICPMS analyses on fused glass discs (Table A2). Maximum contamination was determined on milled clean quartz, whereas minimum values where indicated were calculated from more than 400 samples processed in the same way but with hardness less than quartz. From these results we see that the Steel mill pot does contaminate mainly with Co and to a much lesser extent with Ni, Cu and Sc.

**Table A2: Contaminations in ppm determined on CAF’s XRF instrument (see below).**

Element (ppm)	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Nd	Pb	Th	U
Quartz Standard	4	9	0	6	2	5	1	2	8	3	89	3	16	2	2	2	11	1	1
Quartz (Steel mill)	0	217	1	33	2	3	1	2	5	1	13	2	5	2	9	5	11	2	3

Results reflect any impurities present in the quartz as well. Red numbers emphasize the greatest contaminants.

#### A4. Fusion bead method for major element analysis:

Whole rock fusion beads (or glass disks) were made at the Central Analytical Facility’s XRF unit (Stellenbosch University), using the following procedure:

- Weigh 1.0000 g ± 0.0009 g of milled sample
- Place in oven at 110 °C for 1 hour to determine H<sub>2</sub>O
- Place in oven at 1000 °C for 1 hour to determine LOI (loss on ignition)
- Add 10.0000 g ± 0.0009 g Claisse flux and fuse in M4 Claisse fluxer for 23 minutes.

Loss on Ignition (LOI) comprises contributions from the volatile compounds of H<sub>2</sub>O<sup>+</sup>, OH<sup>-</sup>, CO<sub>2</sub>, F, Cl, S; as well as added O<sub>2</sub> due to oxidation (mainly of FeO to Fe<sub>2</sub>O<sub>3</sub>). One or more of the following standard reference materials were used: NIM-N, NIM-G, NIM-S, NIM-P, NIM-D, AGV-1, BHVO-1, GA, GH, GSN, SY-2, SY-3, and BCR.

**Table A3: Detection limits and uncertainties for major oxides (all in wt%).**

Analyte	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	MnO	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	SiO <sub>2</sub>	Na <sub>2</sub> O	TiO <sub>2</sub>	LOI
Uncertainty	0.11688	0.07288	0.14672	0.02416	0.00904	0.3506	0.0172	0.3506	0.10448	0.02096	0.03
LOD	0.06	0.04	0.01	0.04	0.01	0.01	0.01	0.03	0.01	0.02	0.01

#### A5. Major oxide analysis on XRF instrument

Major element compositions (in wt%) were obtained at the Central Analytical Facility’s XRF unit (Stellenbosch University) by X-Ray Fluorescence (XRF) analysis, using a Phillip’s PW1404w instrument (Axios from PANalytical with a 2.4 kWatt Rh X-ray Tube). The gas-flow proportional counting detector and scintillation detector, or a combination of the two, was used to cover the elements from fluorine to uranium. Major elements (Na<sub>2</sub>O, MgO, SiO<sub>2</sub>, K<sub>2</sub>O, CaO, TiO<sub>2</sub>, MnO, P<sub>2</sub>O<sub>5</sub>, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub><sup>T</sup> (total iron) were analysed on La-free fused glass beads. A wide range of international (NIST®) and national (SARM®) standards is used in the calibration procedures and quality control (precision and accuracy). Detection

limits for the elements quoted, depending on the matrix (combination of elements present), are approximately 0.001 wt% for major elements on these fused beads (**Table A3**).

#### **A6. Trace element analysis on LA-ICPMS instrument**

Trace element compositions (in ppm) were obtained at the Central Analytical Facility's XRF unit (Stellenbosch University) from the same whole rock fused beads as the major elements. By applying the method described by Eggins (2003), a mounted bead fragment was analysed using an Agilent 7500ce ICP-MS coupled with a Nd-YAG 223 nm New Wave LASER ablation (LA) system operating at a 12 Hz frequency with a mixed He-Ar carrier gas. Three spot analyses (each comprising a 30 s blank followed by data collection for 60 s) on each bead fragment were obtained using a 100 µm diameter aperture, and the results averaged.

After every three samples (i.e., every 10<sup>th</sup> analysis) a National Institute on Standards and Technology NIST612 (Pearce et al., 1996) glass bead (in this case BCR, Table 1d) was analysed as calibration standard, in addition to fused discs of Nim-G (granite) and BhVO-1 (basalt) as secondary standards. Data were collected in the time-resolved mode and, were reduced using an Excel calculation spreadsheet using the SiO<sub>2</sub> content measured by XRF as the internal standard. For each element the reproducibility of replicate analyses of the samples, and deviation from the certified values of the secondary standards are better than 10%, and mostly below 5% relative (Table A4).

**Table A4: Accuracy of trace element analysis of BCR standard glass (LA-QC-std)**

Element	Sc	V	Cr	Co	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb
<b>LA QC std</b>	<b>33</b>	<b>425.00</b>	<b>17</b>	<b>38</b>	<b>13</b>	<b>21</b>	<b>125</b>	<b>47</b>	<b>342</b>	<b>35</b>	<b>184</b>	<b>12.5</b>
Av. analysed	38.08	435.54	15.47	38.09	11.98	17.02	159.18	46.90	359.52	37.15	199.72	13.20
% Deviation	<b>15.39</b>	<b>2.48</b>	<b>9.02</b>	<b>0.25</b>	<b>7.88</b>	<b>18.95</b>	<b>27.34</b>	<b>0.21</b>	<b>5.12</b>	<b>6.15</b>	<b>8.54</b>	<b>5.64</b>
Element	Mo	Sn	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
<b>LA QC std</b>	<b>270</b>	<b>2.6</b>	<b>1.16</b>	<b>683</b>	<b>24.7</b>	<b>53.3</b>	<b>6.7</b>	<b>28.9</b>	<b>6.59</b>	<b>1.97</b>	<b>6.71</b>	<b>1.02</b>
Av. Analysed	265.30	2.12	1.14	711.42	27.35	54.91	7.02	31.39	7.32	2.09	7.29	1.10
% Deviation	<b>1.74</b>	<b>18.54</b>	<b>1.40</b>	<b>4.16</b>	<b>10.71</b>	<b>3.03</b>	<b>4.80</b>	<b>8.61</b>	<b>11.01</b>	<b>6.12</b>	<b>8.58</b>	<b>7.52</b>
Element	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Pb	Th	U
<b>LA QC std</b>	<b>6.44</b>	<b>1.27</b>	<b>3.7</b>	<b>0.51</b>	<b>3.39</b>	<b>0.503</b>	<b>4.84</b>	<b>0.78</b>	<b>0.50</b>	<b>11</b>	<b>5.90</b>	<b>1.69</b>
Av. Analysed	7.14	1.44	4.03	0.59	3.81	0.57	5.30	0.89	0.56	10.98	7.12	1.73
% Deviation	<b>10.87</b>	<b>13.09</b>	<b>8.92</b>	<b>15.28</b>	<b>12.47</b>	<b>12.92</b>	<b>9.49</b>	<b>13.68</b>	<b>12.28</b>	<b>0.19</b>	<b>20.59</b>	<b>2.22</b>

#### **References**

- EGGINS, S.M. (2003). Laser ablation ICP-MS analysis of geological materials prepared as lithium borate glasses. *Geostandards Newsletter* **27**, 147-162.
- PEARCE, N.J., WESTGATE, J.A. & PERKINS, W.T. (1996). Developments in the analysis of volcanic glass shards by laser ablation ICP-MS: quantitative and single internal standard-multielement methods. *Quaternary International* **34**, 213-227.