

Methods

Samples were mounted in epoxy blocks, polished and coated with carbon. A Zeiss EVO MA15 scanning electron microscope (SEM) at the Geochemical Analysis Unit (GAU), Macquarie University, Sydney, Australia was used to capture Backscattered Electron (BSE) images and Energy Dispersive X-ray spectrometry (EDS) was used to map the elemental composition of the samples. An accelerating voltage of 15 keV and a beam current of 1 nA was used.

Major elements were determined by electron microprobe (EMP) using a CAMECA SX100 equipped with five wavelength-dispersive spectrometers at the Macquarie University GeoAnalytical (MQGA; formerly GAU), Macquarie University, Sydney, Australia. Analyses were performed using a focused beam (1-2 μm) with an accelerating voltage of 15 keV and a beam current of 20 nA. Standards were a suite of natural and synthetic minerals. Peak counting varied between 10 – 20 s, and background was counted for 5 – 10 s on either side of the peak. Oxygen and carbon were measured directly; matrix corrections were carried out by the ZAF software.

Major elements also were determined by electron microprobe (EMP) using a JEOL 8530F electron microprobe equipped with five wavelength dispersive spectrometers at the Centre for Microscopy Characterisation and Analysis (CMCA), The University of Western Australia, Perth, Australia. Analyses were performed using a fully focussed beam with an accelerating voltage of 15 keV, a beam current of 15 nA. Standards were a suite of natural and synthetic minerals. On-peak counting times were 30 seconds for all elements. X-ray intensity data was corrected for Time Dependent Intensity (TDI) loss (or gain) using a self-calibrated correction for Si $K\alpha$, Ti $K\alpha$, Mn $K\alpha$, Na $K\alpha$, K $K\alpha$ and mean atomic number (MAN) background corrections were used throughout (Donovan & Tingle, 1996; Donovan et al., 2016). Unknown and standard intensities were corrected for deadtime. Oxygen was measured, matrix corrections and ZAF correction were applied throughout.

Trace elements were obtained using a Photon Machines Excite 193 nm ArF EXCIMER laser system coupled to an Agilent 7700x ICP-MS at the GAU, Macquarie University, Sydney, Australia. Detailed method descriptions have been given by (Jackson et al., 2004). The ablation conditions included beam size (50 μm), pulse rate (5Hz) and energy density (7.59 J/cm²). Ablation was performed in an HelEx II cell and helium was used as the carrier gas at a total flow rate of 0.825L/min.

Average analytical runs comprised of 20 analyses, 2 analyses of reference materials and 10 analyses of unknowns, bracketed by two analyses of NIST610 standard glass at the beginning and end of each run. Analyses consisted of 60 second of background and 120 seconds of ablation. Trace element concentrations were calculated from the raw signal data using the on-line software package GLITTER ((Griffin et al., 2008); www.mq.edu.au/GEMOC). GLITTER calculates the element concentrations and relevant isotopic ratios for each mass sweep and displays them as time-resolved data. This allows homogeneous segments of the signal to be selected for integration. GLITTER then corrects the integrated ratios for ablation-related fractionation and instrumental mass bias by calibration of each selected time segment against the identical time-segments of the standard glass (NIST610 using the GeoReM values). An appropriate major element was used as an internal standard to quantify trace element concentrations and the synthetic BCR2 and NIST612 glasses were used as reference materials (GeoReM).

FIB foils from the region of interest were prepared for TEM using a dual-beam FIB system (FEI Nova NanoLab 200). High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) imaging and element mapping were carried out using an FEI Titan G2 80-200 TEM/STEM with ChemiSTEM Technology operating at 200 kV at the Centre for Microscopy Characterisation and Analysis (CMCA), The University of Western Australia, Perth, Australia. The element maps were obtained by energy dispersive X-ray spectroscopy using the Super-X detector on the Titan with a probe size ~1 nm and a probe current of ~0.25 nA. Total acquisition times of 20-30 minutes were used to obtain good signal-to-noise ratios. Electron diffraction was carried out using a field limiting aperture that selected an area approximately 400nm in diameter.

For X-ray micro-computed tomography (μ CT), the grain was mounted on a finger of rigid PVC plastic with double-sided tape and a separate tomogram was collected for each grain using a μ CT system (Versa 520 XRM, Zeiss) running Scout and Scan software (v11.1.5707.17179, Zeiss) at the CMCA. Samples were scanned at 50 kV and 77 μ A with the source detector positions set to -17.7 and 117 mm, respectively. An LE1 source filter was applied to screen out low energy X-rays. A 0.4X objective lens was used together with 2x camera binning to achieve an isotropic voxel resolution of 9 μ m. Each scan comprised 2501 projections through 360° with

an exposure of 3s for each projection. Raw data were reconstructed using XMReconstructor software (v11.1.5707.17179, Zeiss) following a standard centre shift and beam hardening correction. The standard 0.7 kernel size recon filter setting was also used. The visualization and analysis of data generated from μ CT scans were performed using Avizo (v8.1.1, FEI) software.