Supplementary material 1 – Methods

QEMSCAN®

Selected samples of miarolitic cavities from outcrop were prepared as polished thin sections (30 μm thickness) for microscale analysis. Following optical microscopy, section surfaces were carbon coated to a thickness of around 25 nm using an Emitech K950 carbon coater. The mineralogy of selected carbon-coated polished thin sections was determined using a QEMSCAN® 4300 automated mineralogical assessment system at Camborne School of Mines (Gottlieb et al., 2000; Goodall et al., 2005; Goodall and Scales, 2007). The system is based on a Zeiss Evo 50 SEM with 4 × Bruker SDD EDS detectors (XFlash) controlled by iMeasure v. 4.2SR1 software for data acquisition and iDiscover v. 4.2SR1 and 4.3 for spectral interpretation and data processing (Rollinson et al., 2011). The QEMSCAN® was operated at an accelerating voltage of 25 kV and a beam current of 5 nA, with a working distance of around 22 mm, in high vacuum mode and with automatic beam calibration every 30 min. Fieldscan measurement mode was used to obtain a mineralogical map of nearly the whole polished section area (39 × 20 mm) at an analytical point resolution, or pixel spacing, of 10 μm and with 1000 X-ray counts per pixel. The data from each point of analysis was automatically compared with a Species Identification Protocol (SIP) database of mineral and non-crystalline phase spectra to identify the minerals present. The SIP used was modified from the LCU5 SIP provided with the QEMSCAN®, which includes a range of oxide, sulphate, and silicate minerals. All mineral categories were checked by manually assessing elemental abundances, element ratios, and BSE signal. A boundary phase post-processor was applied to reduce edge effects and to resolve rogue pixels. Data collection and processing followed in house QA/QC procedures. The data were output as mineralogical maps and in a mineral associations matrix (Supplementary material 2).

SEM-EDS-CL

Scanning electron microscope (SEM)-based backscattered electron (BSE) and cathodoluminescence (CL) imaging and qualitative energy dispersive X-ray (EDS) elemental mapping of select thin sections were carried out using an FEI Quanta 650 Field Emission Gun-SEM equipped with a Gatan monochrome CL detector and 2x Bruker SDD EDS detectors (XFlash series 6 | 30) at the University of Exeter's Environment and Sustainability Institute. The instrument was operated at an accelerating voltage of 20 kV. Elemental maps were

obtained using a minimum of 4 scans and a dwell time of 32 μs, and processed using Bruker Esprit software version 1.9a. The CL images were collected from single scans with a 30 μs dwell time, a processing resolution of 3072 × 2048 pixels and 256 grey levels. CL brightness and contrast were optimized to reveal inhomogeneities in quartz; other phases therefore appear either white or black.

In the SEM-CL images, the different grey levels shown by quartz represent different luminescence colours. variability in CL colour and intensity of quartz can be attributed to defects in the lattice and/or trace elements in the crystal structure, (e.g. Wark and Watson, 2006; Müller et al., 2010; Kronz et al., 2012). Selected CL images were overlain over the area's respective EDS elemental for appreciation of different mineral phases' CL response. Some select CL images were retrospectively false-coloured using a 'fire' look-up table, using ImageJ software, to visually intensify differences in CL response from different quartz generations. Images are included in supplementary material 3

EPMA

Concentrations of Al, Ti and Fe in quartz in select polished thin sections were determined by Electron Probe Microanalysis (EPMA) using a JEOL JXA-8200 electron microprobe at Camborne School of Mines, University of Exeter. To mitigate any electron beam damage from prior SEM analysis, the thin sections used were re-polished and carbon coated to a thickness of 25 nm in an Emitech K950 carbon coater. Analyses were undertaken using a 20 kV, 80 nA beam, defocussed to 15 μm, running 12 accumulations measuring 30 s on peak and 30 s on each background (+/- 2 mm from peak), resulting in a total analysis time per spot of 18 minutes (6 m on peak, 12 m on background). The lower limit of detection for these conditions is 24 ppm Ti (3σ). This relatively large spot size was used due to the sensitivity of quartz at high current under a narrow beam (Kronz et al., 2012). SiO_2 was assumed to be 100%. Corundum (Geo MkII), rutile and hematite (Astimex) calibration standards were used for Al, Ti and Fe, respectively. For calibration at low concentrations or as ''blank''-control, some studies use a synthetic doped or pure SiO_2-glass. This was deemed inappropriate as their behaviour during electron irradiation is very different to that of quartz (e.g. Kronz et al., 2012). Al was measured over two TAP crystals simultaneously. Due to crystal line up, Ti and Fe were only measured with one spectrometer each (on PETJ and LIFH crystals respectively).

Repeat analyses of quartz reference material (smoky quartz from Shandong Province, China; Audétat et al., 2014) returned an average of 60 ± 15 (2σ, n= 13) ppm, compared to reported values (57 ± 4 ppm). These values were spaced across the whole crystal, and account for slight heterogeneity in the standard. Repeat analyses of a single location of the same quartz crystal returned an average of 58 ± 14 (2σ, n= 31) ppm Ti, indicating slightly higher precision for individual points (and removing uncertainty surrounding standard heterogeneity). From this, we express our analytical uncertainties for Ti as ± 14 ppm. Data is presented in supplementary material 4.

Ti-in-quartz geothermometry

Using the EPMA data (Appendix 3), Ti-in-quartz geothermometry (TitaniQ, method of Wark and Watson, 2006) was used to assess the crystallisation temperatures of quartz. TitaniQ was shown to be affective for crystallisation temperatures of between 600°C and 1,000°C, at 10 kbar (Wark and Watson, 2006). Whether and how TitaniQ can be applied at other pressures has been strongly debated (e.g. Thomas et al., 2010; Huang and Audétat, 2012; Wilson et al., 2012). Wark and Watson (2006) reported that there was little temperature effect on Si-Ti interdiffusion, i.e. on temperatures derived from TitaniQ, between experiments carried out at 1 atm (Cherniak et al., 2007) and those predicted at 10 kbar. In addition to this, there is general agreement that calculated temperatures vary little across the limited 1-3 kbar pressure range typical of the porphyry environment (e.g. Seedorff et al., 2005). As such, the TitaniQ method was deemed appropriate for use in the current study without applying a pressure correction. Based on the consistent presence of rutile in the granitic assemblage, the activity of $TiO2$ (aTiO2) was assigned a value of 1 (Wark and Watson, 2006). We acknowledge that the aTiO2 may have changed during crystallisation history of the system, we note small changes in the aTiO2 will have a minor effect on the calculated crystallisation temperature. At ~700 °C, a decrease in aTiO$_2$ of 0.1 would increase the temperature by only 17°C. We use our repeat analysis of the quartz reference material (from Audétat et al., 2014) to calculate precision – at 682 °C, +24 °C / -29 °C.

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