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MATERIALS AND METHODS

Samples of LDG were collected by one of us (CK) during field work in western Egypt in 2006 at N25°28.23' and E25°32.28'. The seven LDG samples surveyed in this study are mounted in epoxy resin, polished to a sub- μ m finish, and they include characteristics previously described, such as locally containing optically dark and/or light-colored layering. The samples were imaged and analyzed for orientation by scanning electron microscopy (SEM) using a Tescan Mira3 FE-SEM in the John de Laeter Centre (JdLC) at Curtin University. Images collected include secondary electron (SE), backscattered electron (BSE), and panchromatic cathodoluminescence (CL) images; operating conditions for imaging typically used an accelerating voltage from 10-20 kV, with variable beam currents. Acquisition of orientation data for cristobalite by electron backscatter diffraction (EBSD) used similar protocols for other silicate minerals analyzed with an Oxford NordlysNano EBSD detector at Curtin University (e.g., Cavosie et al., 2018a), including 20 kV accelerating voltage, sample tilted to 70° and a thin (~5 nm) carbon coat. No other phases were detected in cristobalite grains (cf., Greshake et al., 2018). The match unit used for indexing α -cristobalite is from the American Mineralogist database using data from Downs and Palmer (1994); LDG cristobalite grains indexed well, and yielded high-quality diffraction patterns (average mean angular deviation values <0.5°). Orientation data were collected with the Oxford Instruments AZtec software program (v. 3.3). The EBSD map was collected with a step size of 200 nm, which yielded 2.4 M points. A 'wildspike' noise reduction algorithm was applied, which removes an individual pixel from the data set if it is different than the 8 surrounding adjacent pixels; no other noise correction was applied. Figures showing pattern

quality (band contrast, BC), orientation (inverse pole figure, IPF) and stereonet were plotted using the Tango and Mambo modules in the Oxford Instruments/HKL Channel5 software program (v. 5.12). Electron backscatter diffraction (EBSD) orientation maps and energy dispersive spectroscopy (EDS) elemental maps were collected simultaneously. The EDS elemental abundances were not calibrated.

Analysis of LDG and cristobalite by electron microprobe analyser (EMPA) was conducted using a JEOL JXA-8530F field emission microscope with Probe For EMPA acquisition software at the Centre for Microscopy, Characterization and Analysis at the University of Western Australia. Operating conditions included a 15 kV accelerating voltage, 15 nA current, and a 10 μm defocused beam. Analysis spots made on both LDG and cristobalite were spaced at least 25 μm apart to avoid overlap. The count time for all elements was 30 s. Intensity data were corrected for time dependent intensity (TDI) loss (or gain) using a self-calibrated correction for Al K α , Mn K α , Ti K α , and K K α x-rays. Background corrections were accomplished using the mean atomic number method (MAN, Donovan and Tingle, 1996). The MAN background intensity data were calibrated and continuum absorption corrected for K α of all 12 elements analyzed. Unknown and standard intensities were corrected for deadtime. Interference corrections were applied to Mn for interferences by Cr, and to Fe for interference by Mn (Donovan et al., 1993; Donovan et al., 2016); however, in all but two analyses, both Mn and Cr were below detection limit. The ZAF, or Phi-Rho-Z, algorithm utilized was from Armstrong (1988).

A combination of glass and mineral standards were employed; the element, standard, and crystal used include: Ca (wollastonite, PETJ), Si (Kakanui pyrope, TAP), Mg (periclase, TAP), Al (spessartine, TAP), Mn (Mn, LiF), Na (jadeite, TAP), Ti (rutile, LiFH), K (orthoclase, PETJ), Cr (Cr₂O₃, LiFH), Fe (San Carlos olivine, LiF), P (Durango apatite, PETJ), S (barite, PETJ). In

addition, a Smithsonian Institution basaltic glass (NMNH111240-52 VG2) was analyzed to estimate precision. Calculated error based on nine analyses of the basaltic glass are 0.1 rel% (Ti), 1-3 rel% (Si, Ca, Mg, Mn, Na, Fe), and 6-8 rel% (Al, K, P). Elements are expressed as molecular oxides (Tables 1 and 2). Analyses were made adjacent to holes produced during laser ablation analysis. The EMPA data are available in Table 1 (LDG), Table 2 (cristobalite) and Supplementary Tables 1 and 2.

Analysis of LDG and cristobalite by laser ablation inductively coupled plasma mass spectrometry (LAICPMS) was accomplished using a RESolution M-50A-LR incorporating a Compex 102 excimer laser, coupled to an Agilent 8900 QQQ ICP-MS at the GeoHistory Facility, JdLC, Curtin University. Following 2 cleaning pulses and a 30s period of background analysis, samples were spot ablated for 35 s at a 4 Hz repetition rate, using a 50 μm spot size and laser energy of 8 J cm^{-2} . Analysis spots made on both LDG and cristobalite were spaced at least 10 μm apart to avoid overlap. Oxide polyatomic interferences were minimized by tuning flow rates for a ThO/Th of < 0.5%. The sample cell was flushed with ultrahigh purity He (350 ml min^{-1}) and N₂ (3.6 ml min^{-1}) and high purity Ar was employed as the plasma carrier gas. Glass standard NIST 612 was used as the primary reference material to calculate elemental concentrations (using stoichiometric ²⁹Si as the internal standard element with an EMPA-determined Si content for LDG of 46.34 wt.% Si) and to correct for instrument drift. Reproducibility of secondary standard glass analyses (ATHO-G, BCR-2G and GSD-1G, see Jochum et al., 2005, 2010) yielded an accuracy of between 0.5 and 5 rel%. Standard blocks were run every 3 unknowns. The mass spectra were reduced using Iolite (Paton et al., 2011 and references therein). Data were collected for 38 isotopes (⁷Li, ¹¹B, ²³Na, ²⁵Mg, ²⁷Al, ²⁹Si, ³⁹K,

^{43}Ca , ^{45}Sc , ^{47}Ti , ^{51}V , ^{52}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{85}Rb , ^{88}Sr , ^{89}Y , ^{91}Zr , ^{93}Nb , ^{137}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{163}Dy , ^{166}Er , ^{173}Yb , ^{178}Hf , ^{208}Pb , ^{232}Th and ^{238}U).

Elemental abundance data (in ppm) are presented in Tables 3 (LDG), Table 4 (cristobalite), and Supplementary Tables 3 and 4.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) maps of Al distribution were collected using a Tescan Lyra3 focused ion beam scanning electron microscope (FIB-SEM) fitted with a ToFwerks compact ToF-SIMS detector located in the JdLC at Curtin University. Data were collected using a monoisotopic ^{69}Ga primary ion source operated with an accelerating voltage of 30 kV and a beam current of 300 pA, resulting in a nominal lateral resolution of ≤ 100 nm. ToF-SIMS maps and spectra were collected by scanning $15 \times 15 \mu\text{m}$ areas (effective pixel size ~ 60 nm) for 20 frames. During data collection the electron beam of the SEM was used to partially charge compensate the FIB scanned surface using an accelerating voltage of 2 kV and a beam current of 1 nA. The 2D elemental maps showing Al distribution were extracted from the volume analyzed using the ToFwerk's ToF-SIMS Explorer software (v. 1.3.). The ToF-SIMS Al abundances were not calibrated.

REFERENCES CITED

Armstrong, J.T. (1988) Quantitative analysis of silicates and oxide minerals: Comparison of Monte-Carlo, ZAF and Phi-Rho-Z procedures. In: Newbury, D.E. (Ed), Proceedings of the Microbeam Analysis Society, San Francisco Press, San Francisco, p 239-246.

Donovan, J.J. and Tingle, T.N. (1996) An improved mean atomic number correction for quantitative microanalysis. *Journal of Microscopy*, 2, 1-7.

Donovan, J.J., Singer, J.W., and Armstrong, J.T. (2016) A new EPMA method for fast trace element analysis in simple matrices. *American Mineralogist*, 101, 1839-1853.

Donovan, J.J., Snyder, D.A., and Rivers, M.L. (1993) An improved interference correction for trace element analysis. *Microbeam Analysis*, 2, 23-28.

Downs, R.T., and Palmer, D.C. (1994) The pressure behavior of α cristobalite. *American Mineralogist*, 79, 9-14.

Jochum, K.P., Nohl, U., Herwig, K., Lammel, E., Stoll, B., and Hofmann, A.W. (2005) GeoReM: A new geochemical database for reference materials and isotopic standards. *Geostandards and Geoanalytical Research*, 29, 333-338.

Jochum, K.P., et al. (22 authors) (2010) GSD-1G and MPI-DING reference glasses for in situ and bulk isotopic determination. *Geostandards and Geoanalytical Research*, 35, 193-226.

Paton, C., Hellstrom, J., Paul, B., Woodhead, J. and Hergt, J. (2011) Iolite: freeware for the visualization and processing of mass spectrometer data. *Journal of Analytical Atomic Spectrometry*, 26, 2508-2518.