

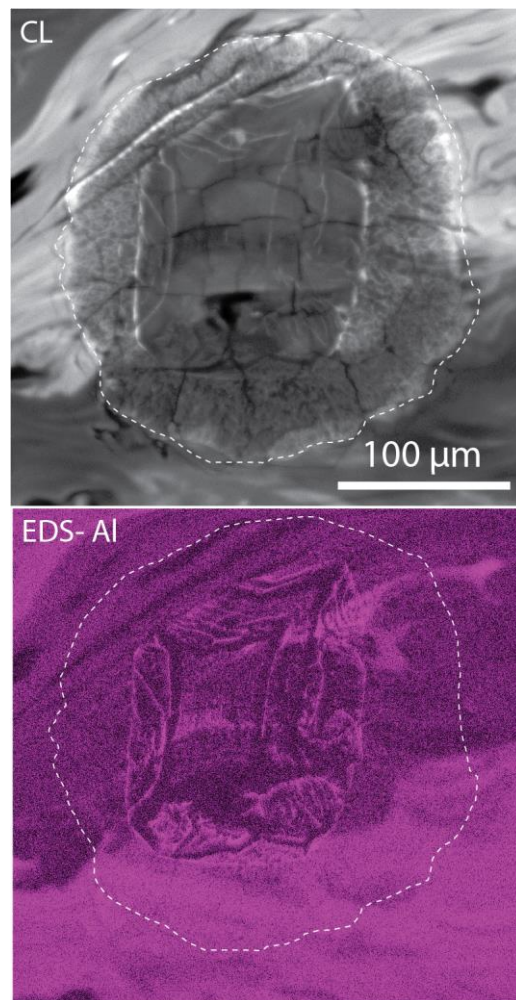
**FINGERPRINT OF  $\beta$ -CRISTOBALITE IN LIBYAN DESERT GLASS- THE HOTTEST NATURALLY OCCURRING SILICA POLYMORPH?** A. J. Cavosie<sup>1</sup>, W. D. A. Rickard<sup>2</sup>, N. J. Evans<sup>2</sup>, K. Rankenburg<sup>2</sup>, M. P. Roberts<sup>3</sup>, and C. Koeberl<sup>4</sup>, School of Earth and Planetary Sciences (Space Science and Technology Centre, The Institute for Geoscience Research), Curtin University, Perth, WA 6102, Australia, <sup>2</sup>John de Laeter Centre, Curtin University, Perth, WA 6102, Australia, <sup>3</sup>Centre for Microscopy, Characterisation, and Analysis, University of Western Australia, Perth, WA 6009, <sup>4</sup>Department of Lithospheric Research, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria. Corresponding author email: [aaron.cavosie@curtin.edu.au](mailto:aaron.cavosie@curtin.edu.au)

**Introduction:**  $\beta$ -cristobalite, the high-temperature silica polymorph [1], is rarely preserved due to transformation to  $\alpha$ -cristobalite at low temperature. Here we report a geochemical and microstructural study of  $\alpha$ -cristobalite in Libyan Desert Glass (LDG), a nearly pure silica natural glass of impact origin found in western Egypt [2]. Elemental mapping and imaging show that LDG is layered, mostly corresponding to variations in Al, and that the layering continues across cristobalite grains, which have conspicuous cores and rims. The Al layering is disrupted in cristobalite cores, where the Al distribution records oscillatory growth zoning. In rims, Al defines fine grain boundaries. Cristobalite cores thus nucleated within layered LDG at conditions that allowed mobility of Al into crystallographically-controlled growth zones. Analysis of 37 trace elements by LAICPMS shows that both materials are highly depleted relative to upper continental crust, with abundance variations correlating to layering in LDG. Orientation analysis of twinning in cristobalite by EBSD identifies {112} twins, and confirms that cristobalite cores were formerly large single  $\beta$ -cristobalite crystals. Combined with published experimental studies, our data provide compelling evidence for high-temperature (>1350 °C) magmatic crystallization of oscillatory zoned  $\beta$ -cristobalite in LDG. These results represent the highest formation temperature estimate thus far reported for naturally occurring cristobalite, which we attribute to the near pure silica composition of LDG and anomalously high temperatures generated during melting by meteorite impact processes.

**Sample/Methods:** Sample LDG-2018-4 was collected in western Egypt and described previously [3]. In this study, we applied electron microprobe analysis (EMPA), laser ablation inductively coupled mass spectrometry (LAICPMS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), scanning electron microscopy (SEM), and electron backscatter diffraction (EBSD) to both cristobalite in LDG and LDG.

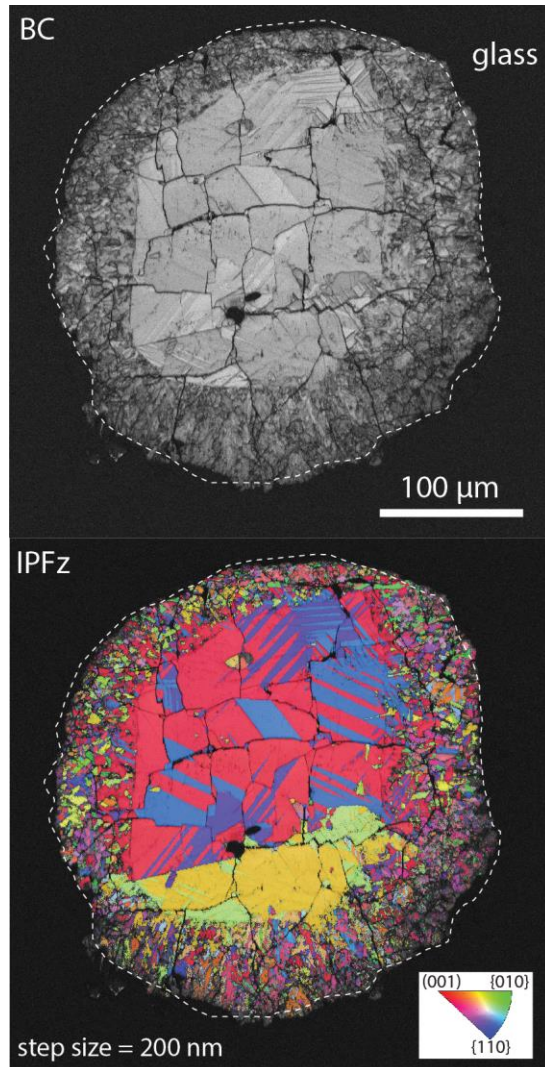
**Results:** The studied cristobalite grain is ~250  $\mu\text{m}$  across. A core and rim structure is visible in CL (Fig. 1). EDS and ToF-SIMS mapping shows that layering in LDG corresponds to Al variation, and that Al zoning

in LDG is preserved across the cristobalite grain (Fig. 1). However, Al in the core records oscillatory zoning, unlike the rim, where it is undisturbed. Oscillatory zoning has not been reported previously in cristobalite, and the Al zoning pattern appears to define a crystalline form (Fig. 1).



**Figure 1.** Cristobalite in layered LDG. Top: CL image, showing core-rim structure, and that layering in LDG cuts across cristobalite. Bottom: Al distribution corresponds to layering in LDG. However, the core of the cristobalite grain records oscillatory zoning in Al. The zoning pattern appears to define a crystalline form.

**Results (cont.):** EBSD orientation analysis further reveals a distinct core-rim structure (Fig. 2). A band contrast (BC) image shows the core has a sharp boundary, and orientation mapping reveals a complex array of  $\{112\}$  twins (Fig. 2). Phase heritage analysis [4] of the systematic twin relations shows that the  $\{112\}$  twins result from the  $\beta$ -cristobalite to  $\alpha$ -cristobalite transformation during cooling [5].



**Figure 2.** EBSD orientation maps for cristobalite in LDG. Top: Band contrast (BC) image, showing quality of diffraction patterns. Bottom: Inverse pole figure (IPF) map showing crystallographic orientation. The different colors indicate twinning.

Analysis of cristobalite by EMPA shows that CL-light domains are  $\sim 99.9$  wt.%  $\text{SiO}_2$ , whereas CL-dark domains are  $\sim 98.5$  wt.%  $\text{SiO}_2$ . Few impurities were detected other than Al, Fe, and Ti. LAICPMS analysis shows that both LDG and cristobalite are highly depleted relative to upper continental crust [6].

**Discussion:** Analysis of orientation data for  $\alpha$ -cristobalite in LDG confirms the predicted systematic  $\{112\}$  twin relations for the  $\beta$ -to- $\alpha$  transformation during cooling. Oscillatory zoning in cores of (former)  $\beta$ -cristobalite grains further shows that the cores grew in layered LDG, at conditions where Al was mobile in nearly pure molten silica.

We propose that the cores of  $\alpha$ -cristobalite grains in LDG represent former  $\beta$ -cristobalite grains that crystallized at high-temperature in LDG as euhedral, oscillatory zoned magmatic grains. Experimental heating studies conducted with vitreous silica from 1350-1625 °C show that euhedral cristobalite grains form internally within silica (rather than at a boundary exposed to atmosphere) at temperatures  $>1350$  °C [7]. Such experiments provide a close analog to LDG; we thus interpret that cristobalite in LDG initially crystallized at  $T > 1350$  °C. We note that this minimum estimate is below the thermodynamic stability of  $\beta$ -cristobalite [1], but still higher than any previous temperature estimates for naturally occurring cristobalite. Cristobalite occurs in a wide variety of impact melt rocks [8], however, no other impactites with cristobalite are as high in silica as LDG. The nearly pure  $\text{SiO}_2$  composition of cristobalite in LDG further rules out non-stoichiometry as a significant factor for metastable crystallization of  $\beta$ -cristobalite at low temperature, as often occurs in siliceous volcanic rocks [e.g., 9].

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