ICE ICE BABY: IMPROVING WATER QUANTIFICATION OF HYDROUS MINERALS BY CRYO-FOCUSSED ION BEAM AND CRYO VACCUM TRANSFER TO ATOM PROBE.

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Introduction: Phyllosilicate mienrals are key targets for sample return missions including NASA's OSIRIS-REx and JAXA's Hayabusa2 mission to water-rich asteroids Bennu and Ryugu, respectively [1,2]. Phyllosilicates are abundant on these asteroids [1,2] and preserve evidence for water-rock reactions in the early Solar System (e.g. [3]). However, characterizing phyllosilicates in the returned samples will be challenging as their structure and composition rapidly changes during electron microscopy imaging [4]. We recently outlined a novel approach to extract nanostructural information and estimate the water content of serpentine from the terrestrial Ronda peridotite using atom probe tomography (APT; [5]). However, the water content of serpentine was consistently underestimated in the APT data [5]. This is likely because of room temperature sample preparation and brief exposure to the atmosphere during sample transfer [5]. Here we expand on our approach by preparing and measuring APT samples of serpentine under cryogenic conditions.

Methods: A portion of a serpentine vein from the Ronda peridotite was extracted, and 1 µm wedges were welded to pre-grown Si posts using a Plasma focused ion beam (P-FIB). The wedges were thinned to a needle like shape following the needle geometry recommendations for APT analysis of serpentine from of Daly et al., [5] using an annular milling pattern with a Ga-FIB under cryogenic conditions. The prepared needles were transferred from the FIB to the atom probe under vacuum and maintaining cryogenic temperatures. The samples were then measured on the LEAP 4000 atom probe at the University of Sydney following the recommendations of Daly et al., [5]. Surviving APT tips were warmed to room temperature then analysed again. The APT data were reconstructed using IVAS and the water content was calculated following the approach of Daly et al., [5].

Results: All cryogenically preparered samples ran substantially better during APT measurements than the same samples prepared at room temperature [5], and yielded multi-million ion datasets. Identical nanostructures of SiO rich low density volumes were detected in both room temperature and cryogenic samples [5]. The water content of the cryogenically prepared samples was higher (9-13 atomic % (at. %) than those prepared at room temperature (~6 at. % [5]; Fig 1).

Discussion and Conclusion: Serpentine typically contains ~13 wt. % water. The cryo-prepared APT samples are very close to this value while the room temperature samples yielded a lower water content. These results indicate that in the case of water-rich minerals some water within the crystal structure is lost during room temperature FIB-based preparation of APT specimens; importantly however water is preserved during cryogenic sample preparation. Thus we propose that cryo-FIB transfer should be incorporated into the workflow to characterize delicate water-rich minerals within meteorites and sample return materials.

References: [1] Lauretta D., et al., (2015) *Meteoritics and Planetary Science*, 50, 834-849, [2] Perna D. et al., (2017) *Astronomy and Astrophysics*, 599, L1. [3] Browning L. et al., (1996) *Geochimica et Cosmochimica Acta,* 60, 2621-2633, [4] Lee M. R. and Lindgren P. (2016) *Meteoritics and Planetary Science*, 51, 1003–1021. [5] Daly L. et al., (2021) *Geostandards and Geoanalytical Research.*

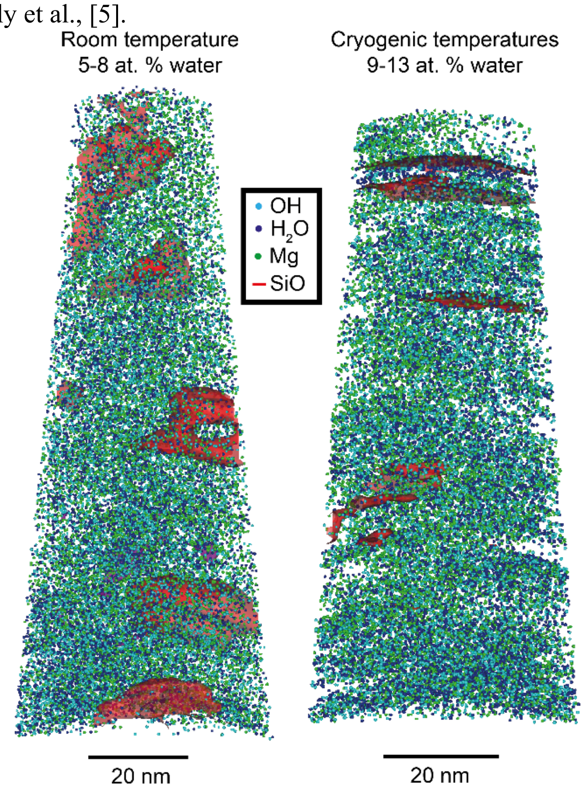

Figure 1. APT data of serpentine from the Ronda peridotite prepared at room temperature (left) and under cryogenic conditions (right).