MAXIMISING SCIENCE RETURN FROM RYUGU USING ATOM PROBE TOMOGRAPHY. L. Daly[1,2,3], J. R. Darling[4], M. R. Lee[1], L. J. Hallis[1], J. Cairney[2], I. McCarrol[2], L. Yang[2], P. A. Bland[3], G. K. Benedix[3], L. V. Forman[3], W. D. A. Rickard[3], D. Fougerouse[3], S. Reddy[3], D. Saxey[3] and P. A. J. Bagot[5] [1]School of Geographical and Earth Sciences, University of Glasgow, UK. (luke.daly@glasgow.ac.uk) [2]Australian Centre for Microscopy and Microanalysis, The University of Sydney, Sydney, Australia, [3]Space Science and Technology Centre, School of Earth and Planetary Sciences, Curtin University, Perth, Australia, [4]School of the Environment, Geography and Geosciences, University of Portsmouth, UK. [5]Department of Materials, University of Oxford, UK.

Introduction: JAXA's Hayabusa2 mission will soon return samples of the C-type asteroid Ryugu. This body has spectroscopic affinities to CM2-like carbonaceous chondrites that that have undergone static or shock heating and thermal alteration [1]. From ground-based observations, [2] found that the CM carbonaceous chondrite Allan Hills (ALH) 83100 is a good match for Ryugu.

Given the quantity of material that will be returned by Hayabusa2, maximizing the data that can be obtained from these small sample volumes is imperative. As phyllosilicates comprise ~56–88 vol. % of the CM carbonaceous chondrites [3], these minerals and/or their thermal alteration products are likely to comprise around two-thirds by volume of the returned material.

Atom probe tomography (APT) is relatively new technique in planetary science. As it gives 3D atomic information from ~100×100×1000 nm sample volumes, APT has enormous potential for nanoscale chemical and isotopic analysis of precious extraterrestrial materials. The capability of APT to chemically and isotopically analyse anhydrous minerals from primitive meteorites and terrestrial impactites has been demonstrated [4, 5], but its applicability to hydrous minerals including phyllosilicates has yet to be evaluated. Such tests are important because APT information on mineral compositions including OH/H_2O contents can provide unique insights into processes including dehydroxylation and recrystallization due to parent body heating. Here we evaluate the capabilities of APT in analyzing terrestrial serpentine and the fine-grained matrix of ALH 83100.

Methods: The terrestrial serpentine (precise minerlogy being determined) is from the Ronda peridotite in southern Spain, and ALH 83100 was loaned by ANSMET. This CM carbonaceous chondrite has been highly aqueously altered with a petrologic subtype of CM2.1 [6]. Bulk ALH 83100 contains 83 vol. % phyllosilicate comprising 62 vol. % Mg-rich serpentine and 21 vol. % cronstedtite. APT work focused on the phyllosilicate-rich matrix.

Serpentine veins within the Ronda sample and ALH 83100 matrix were characterized using a Zeiss Sigma SEM at the University of Glasgow (UoG). Five needle shaped APT samples were extracted using a plasma focused ion beam (FIB) instrument at the University of Sydney (UoS). These samples were made into needles by annular milling using a Ga-FIB the UoS following the approach of [7]. Needles were analyzed using a LEAP 4000X atom probe at the UoS. Samples will also be prepared under cryogenic conditions to evaluate the effectiveness of different preparation strategies.

Results: Large datasets were successfully acquired from two of the five needles extracted from each sample: Ronda serpentine datasets had 8.5 million and 10 million atoms, and ALH 83100 datasets contained 14.5 million and 9 million atoms prior to sample failure. The mass spectra obtained were challenging to interpret owing to complexities of their molecular compositions and the nanophases and structures present.

Ronda serpentine: Phyllosilicates are Mg-rich with an average chemical composition (in wt. %) of ~42 SiO_2, 39 MgO, 4 FeO [8]. APT datasets highlight the chemistry of this serpentine, and also reveal the presence of evenly distributed rounded particles 20 nm in size that are rich in SiO (Fig 1, <20 At % Mg isoconcentration surface, red).

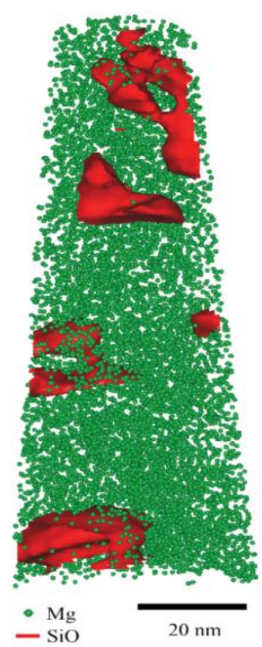

Figure 1. APT dataset from the Ronda serpentine that has been processed to highlight the distribution of Mg (green), and inclusions of SiO nanoparticles (red).

ALH 83100. The phyllosilicate-rich matrix of this meteorite is composed of interlocking cell-like structures, each up to a few tens of micrometers in size (Fig. 2). The cells have an average chemical composition (in wt. %) of ~33 SiO_2, 22 MgO, 20 FeO, 2 Al_2O_3, 2 S, and 1 NiO. Each cell has a narrow rim that is enriched in Fe, and a core that is enriched in Mg. For consistency with the Ronda dataset, the Mg-rich phyllosilicates were targeted for APT.

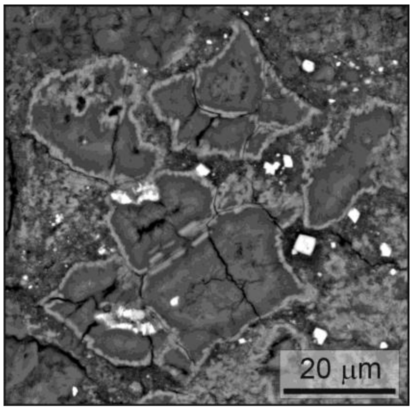

Figure 2. Backscattered electron image of interlocking phyllosilicate 'cells' within ALH 83100 matrix. The rim of each cell is Fe-rich and the core is Mg-rich.

Figure 3. APT dataset from ALH 83100 matrix serpentine. The pink isosurfaces are relatively rich in Mg and Si, and depleted with respect to H, O and Fe.

The two APT needles are quite different in chemical composition and nanostructure. One is composed of a material that is Fe-rich and H-poor. The other needle has higher concentrations of Mg and H (up to 14 at. %), and also has nanoscale heterogeneities in density (Fig. 3, >9 atoms/nm^3 Mg isodensity surface, purple). The high density regions are tabular, ~5 nm in thickness, relatively rich in Mg, Al and Si, and have lower concentrations of H, O and Fe. H is bonded as OH and H_2O.

Discussion: Results demonstrate that serpentine can be successfully analysed by APT, and that these minerals contain nanoscale phases and structures with the potential to provide unique insights into the composition and evolution of samples returned from Ryugu.

Ronda serpentine contains nanoscale inclusions of a SiO-rich material. These inclusions could be quartz or opaline silica ($SiO_2.nH_2O$). The latter possibility is consistent with the finding using transmission electron microscopy of nanoparticles of opal 5–29 nm in size (average 12 nm) within veins of smectite from the Nakhla (Martian) meteorite [9]. Although these findings may not appear to be directly applicable to Ryugu, the identification of nanoparticles could indicate the start of thermal recrystallization of phyllosilicates.

The two ALH 83100 APT needles were quite distinct despite being extracted from phyllosilicates that are homogeneously Mg-rich at the SEM scale (Fig. 2). The nanoscale layers of Mg- and Fe-rich material within the needle in Figure 3 are intriguing. Whilst they could reflect an interstratification of different phyllosilicate minerals (e.g., chrysotile with cronstedtite), the observed depletion of the Mg-rich layers in OH and H_2O could suggest incipient dehydroxylation, despite the bulk hydrogen composition of this meteorite being inconsistent with post-hydration heating [10].

Conclusions: APT has the potential to provide a wealth of information from Ryugu samples including phyllosilicates and/or their thermal decomposition products that will probably comprise most of the returned material. Moreover, preparation of APT needles is straightforward and does minimal damage to the bulk sample. Whilst results described here were obtained from phyllosilicates that had been extracted and analysed at ambient temperature, cryogenic APT techniques being developed at the UoS can potentially further enhance our ability to analyse materials rich in OH, H_2O and organics.

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References: [1] Kitazato K. et al. (2019) *Science* 364, 272–275. [2] Le Corre et al. (2018) *Month Not. Royal Astron. Soc.* 475, 614–623. [3] Howard K. et al. (2015) *Geochim. Cosmochim. Acta* 149, 206–222. [4] White L.F. et al., (2017) *Nat Comms.* 8, 15597. [5] Daly L. et al. 2017 *Geology,* 45, 847–850. [6] de Leuw S. et al. (2010) *Meteoritics & Planet. Sci.* 45, 513–530. [7] Thompson K. et al. (2007) *Ultramic.* 107, 131–139. [8] Bucher K. et al. (2015) *Contribs. Min. Pet.* 169, 52. [9] Lee M. R. et al. (2015) *Meteoritics & Planet. Sci.* 50, 1362–1377. [10] Alexander C. M. O'D (2013) *Geochim. Cosmochim. Acta* **123**, 244–260.