ATOMIC SCALE ANALYSIS OF EXTRATERRESTRIAL FLUIDS BY ATOM PROBE TOMOGRAPHY.

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Introduction: Primitive astromaterials are fundamental record keepers of early solar system physical and chemical processes, preserving records usually destroyed through reprocessing in the solar system during solar nebula evolution. Studies of meteorites and interplanetary dust particles indicate some primitive parent bodies experience a significant degree of thermal and aqueous alteration. Direct measurements of aqueous fluid samples in primitive astromaterials are fundamental for constraining the nature, location, and timing of aqueous alteration on primitive parent bodies [1-4]. However, direct measurements have been challenging due to the surviving trapped fluid inclusions usually being nanoscale and volatile, leaving the bulk of our understanding primarily constrained by theoretical modelling, analysis of icy grains from Enceladus during the Cassini mission and aqueous leaching experiments of carbonaceous chondrites [5-9]. Consequently, this has left fundamental gaps in our understanding of early solar system aqueous fluids.

The first direct analyses of aqueous fluids in primitive astromaterials were in halite crystals in ordinary chondrites (OC) Monahans (1999) and Zag, as these crystals were purple megacryst, distinguishing them from the matrix [2]. Freezing experiments inferred halite bearing fluids comprised divalent cations, e.g., Fe^{2+}, Ca^{2+} or Mg^{2+} in addition to Na^{+} and K^{+}. These results were later strengthened by inductively coupled plasma mass spectrometry measurements which revealed Ca, Mg and Fe ions barely above background, later confirmed through the recent application of time-of-flight secondary ion mass spectrometry (ToF-SIMS) [1-4]. The introduction of x-ray computed nanotomography in correlation with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in the search for trapped fluids has since led to the discovery of fluid inclusions in carbonates, sulphides, olivine, enstatite and calcite within primitive meteorites [1].

Here we present the first atom probe tomography (APT) study of fluid inclusions in extraterrestrial samples. The fluid inclusions are preserved in a pyrrhotite crystal returned to Earth by JAXA from Asteroid 162173 Ryugu, an asteroid essentially identical to Ivuna type (CI) carbonaceous chondritic meteorites. Collected during the Hayabusa 2 sample return mission, these samples are pristine, providing a unique opportunity to probe solar system fluids free from terrestrial influences. APT is a 3D sub-nanometer technique with a detection limit of 10 ppm or 0.001 at.%. Its application to fluid inclusions in astromaterials provides a lower detection limit and higher spatial resolution than achievable with current techniques.

Samples and Methods: A euhedral pyrrhotite crystal (~20 µm across) was targeted from the Ryugu sample C0011_A1, allocated by JAXA. We extracted a ~8×12 µm, 700 nm thick lamella from the center of the pyrrhotite crystal using the FEI Quanta 3D FEG dual beam focused ion beam (FIB)-SEM instrument at Astromaterials Research and Exploration Science (ARES), NASA JSC, and attached it to a Cu lift-out TEM grid. Using the Tescan Lyra3 FIB-SEM at the John de Later Centre (JdLC), three APT tips were FIB-milled and analysed in the CAMECA LEAP 4000X HR. The first needle fractured at a major fluid inclusion resulting in two separate acquisitions while the other two specimens remained intact throughout the run.

Results: The analysed phase was a pyrrhotite crystal with ~1 - 20 nm diameter fluid inclusions (Figure 1).

Mass resolution was high, and the acquisition stable enough to determine the composition of each fluid inclusion. Mass spectra of fluid inclusions revealed a composition of Na, Cl, Mg, Al, Si and P. Due to the high electronegativity of Cl, its elemental abundance is likely to be underrepresented in the spectra showing a disproportionately higher concentration minor and trace elements. Many of these elements can be seen distributed throughout the needle in Figure 2 below. Rare traces of Ca may be present, however, this is challenging to constrain due to the high concentration of Mg which overlaps at 20 Da (MgO^{++}) and 40 Da (MgO^{++}). Fluid inclusions are distinguished from background H_2O by the concentration of H_3O which is typically indicative of aqueous fluids within APT reconstructions.

The sub-nanometer ionic distributions and composition of each fluid were determined through 3D reconstructions and 1D concentration profiles. However, exact spatial relationships were likely impaired due to the nature of volatiles which are released towards the detector simultaneously once the acquisition reaches the fluid inclusion.

Conclusion: Here we presented the first results on APT analysis of fluid inclusions in the Ryugu pyrrhotite crystal. Measurements provided 3D spatial relationships in coordination with chemical signatures and detected elements not identified in previous ToF-SIMS analysis, *e.g.,* P, highlighting the benefit of correlating techniques and the application of APT to the study of fluid inclusions in astromaterials. The ability for APT to measure nm sized inclusions further expands the range of measurable fluid inclusions for chemical information. Continued studies will therefore considerably enhance our understanding of processes involving early solar system aqueous fluids. In particular, our results will further investigations into ocean worlds in our solar system.

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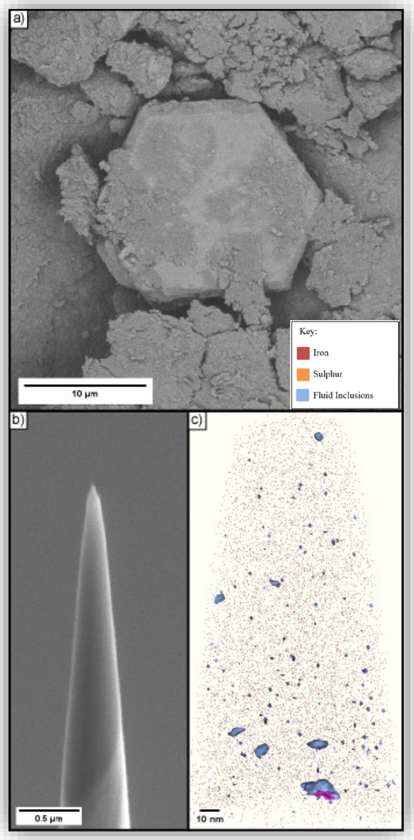

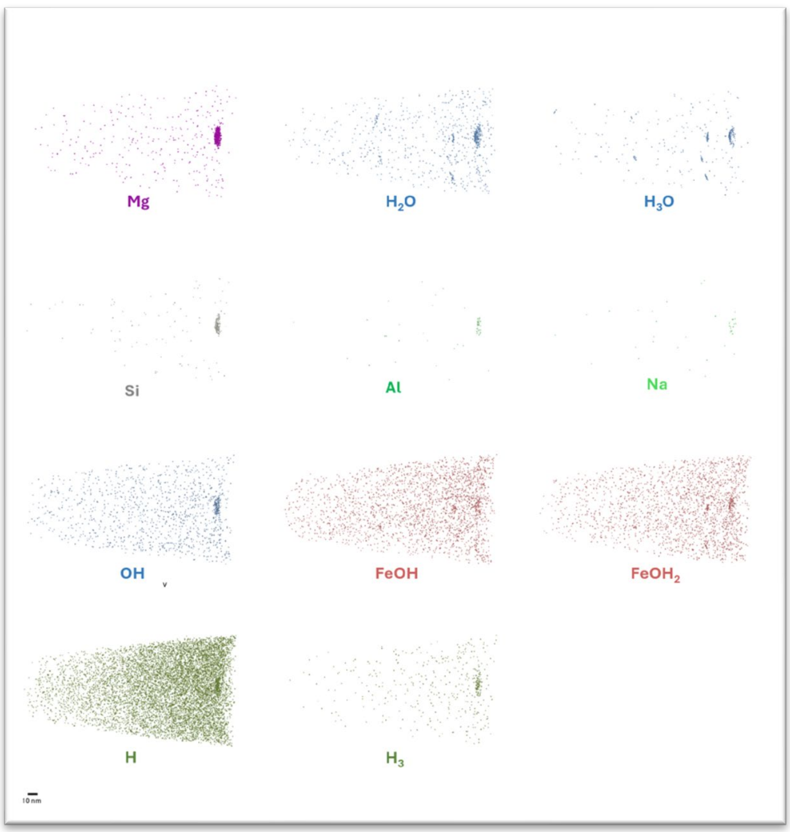

Figure 1 (Left): a) an SEM image collected at ARES of the studied pyrrhotite. b) An SEM image of the APT needle reconstructed in image c) prior to its acquisition. c) 3D APT atom map with 1 at.% H_3O (Blue) isosurfaces identifying trapped fluid pockets and a 4 at.% combined enrichment in Mg, Si, Al, H3O, H3 and Na (Pink) isosurface visible the largest inclusion.

Figure 2 (Right): 3D APT atom maps of the Ryugu pyrrhotite crystal showing some of minor and trace element distributions indicating their relative concentrations within each fluid inclusion.