

ATOMIC SCALE DEPTH PROFILE OF SPACE WEATHERING IN AN ITOKAWA OLIVINE GRAIN.

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Introduction: Space weathering is an important process in modifying the physical and chemical properties of the regoliths of airless worlds [1]. This process is mostly due to bombardment from ions within the solar wind (SW), with minor contributions from solar flares and micrometeorite impacts [1]. Transmission electron microscopy (TEM) studies of Itokawa grains indicate that space weathering typically produces 20-40 nm thick amorphous and vesiculated rims, together with occasional Fe nanoparticles [2, 3]. Space weathering also causes the implantation of elements, in particular the noble gasses He and Ne [4], as well as volatile elements such as H [5]. SW implanted H is particularly important as it may react with silicates to produce OH and H₂O, which have been observed in interplanetary dust particles (IDPs) [5]. In turn, these reactions may have significant implications for the origin of water in the inner solar system. Therefore, it is important to quantify the distribution and speciation of SW-implanted H, and here we present the first atom probe microscopy (APM) study of Itokawa particles, revealing the attenuation depth and profile of SW irradiation.

Methods: Itokawa particle RA-QD02-0279, a 164 μm diameter grain consisting of olivine and plagioclase, was mounted onto a 100 μm diameter glass rod with araldite. The grain was sputter coated with 200 nm of Cr, to dissipate charge, and protect the immediate surface of the grain from any electron or ion beam damage (Fig. 1). Two APM specimens were extracted normal to the surface of the olivine portion of the grain (Fig. 1), and sharpened to a needle-shape with a 10-15 nm Cr cap using focused ion beam (FIB) milling using a TESCAN LYRA3 FIB-Scanning electron microscope (SEM), at Curtin University. These specimens were analysed on the Cameca LEAP 4000X HR Geoscience atom probe at Curtin University.

Results: 51.5 and 55.9 million atoms were collected from each specimen. In both APM data sets evaporation commenced within the protective Cr coating ensuring the outermost portion of the grain was analysed, where any space weathering features may be present. No feldspar was observed. The composition of olivine was Fe₃₀. Helium and Ne were absent from both datasets. However, small reductions and spikes in density were detected in the outermost 20-30 nm of the tip in both specimens (Fig. 2). The high-density regions in each dataset

are enriched in Mg relative to the rest of the specimen. Furthermore, a gradual enrichment in OH and H₂O ions was detected extending from the outer surface of the grain to a depth of ~ 50 nm (Fig. 3).

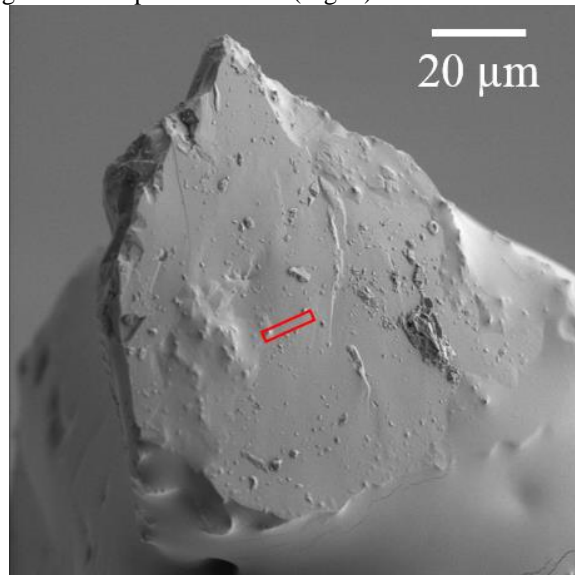


Figure 1: Itokawa particle RA-QD02-0293. Atom probe specimens were extracted from the red box.

Discussion: Vesiculated textures and Fe nanoparticles have previously been described in space-weathered rims of Itokawa [6]; such features are not detected here. Density variations detected here may either represent a new atomic-scale feature of space weathering, or immature examples of the features described in [6]. The absence of typical space weathering features previously described in Itokawa grains imply that this rim is immature and has not been exposed to SW as long as other Itokawa grains (e.g. [6]).

Hydrogen ions are a main component of SW [5], and so implantation of H⁺ ions from SW is interpreted to be the cause of anomalously high levels of OH and H₂O ions detected in the outer 50 nm of the particle. The penetration depth of SW for this particle was approximately 50 nm, with a linear attenuation profile (Fig. 3). This finding is broadly consistent with Monte Carlo simulations of space weathering implanted H⁺ ions [3]. Measured abundances of He and Ne for other Itokawa grains with space-weathered rims are above the detection limits of APM [4, 7]. The absence of He and Ne within these rims therefore indicates that our Itokawa grain was

not exposed for as long as the grains studied by Nagao et al., [4], in agreement with our interpretation that this is an immature space weathered rim.

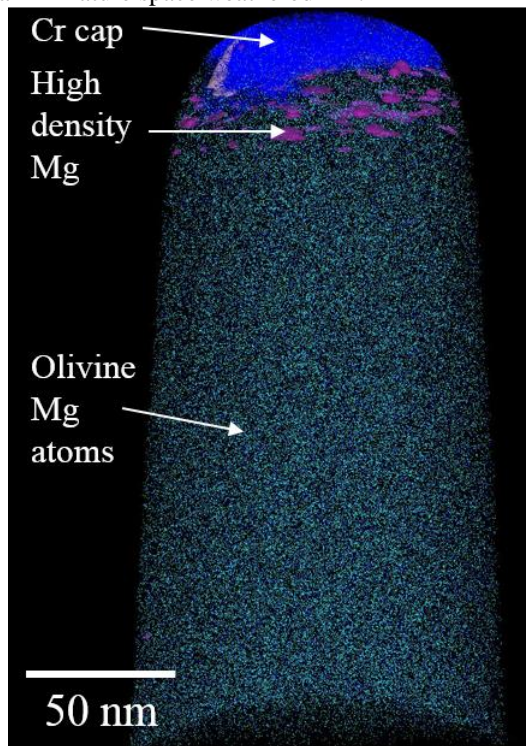


Figure 2: Atom probe specimen of a space weathered rim of Itokawa. The blue and teal dots represent individual atoms of Cr and Mg, respectively. The protective Cr cap is clearly visible where the blue atoms are concentrated at the top of the needle. Pink isosurfaces depict Mg-rich, high-density regions close to the surface of the olivine grain.

Despite minimal exposure to the SW we still observe a rimwards enrichment in OH and H₂O, up to 1.2 at.% (Fig. 3). This finding indicates that even brief SW exposure results in a substantial implantation of H, which bonds with O to produce OH and H₂O [5]. Here, an enrichment of ~1 at. % water across a 50 nm depth in a 100 μ m diameter grain would result in a 0.1 at% enrichment in water for the whole grain. For smaller grains, this effect would be magnified substantially.

Our work has important implications for understanding the origin of water in the inner solar system. It has been suggested that solar, comets or carbonaceous chondrites could be the source of Earth's water [8, 9]. However, the D/H ratio of Earth's water is too heavy compared to that of the Sun, while it is too light to be derived from the majority of known cometary material [8]. Carbonaceous chondrites could be a source, as their D/H ratios are indistinguishable from terrestrial ratios

[9]. However, several isotope systems, particularly Ru, are inconsistent with such a suggestion [10].

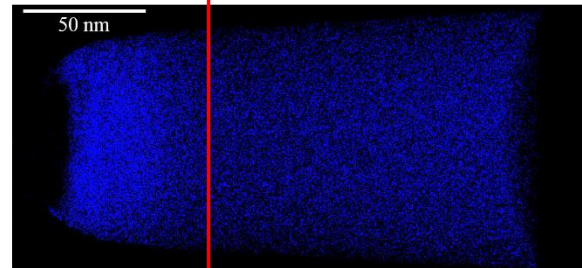
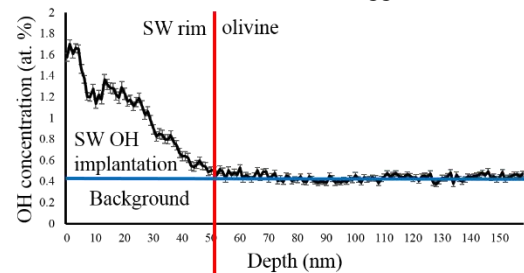


Figure 3 Atom probe specimen of a space weathered rim of Itokawa. The blue dots represent OH ions, which are enriched up to 1.6 at. % in the outer 50 nm of the particle (left hand side).

In addition, as shown here, small grains exposed to the SW can be infused with large amounts of water. Therefore, small grains may represent an extra reservoir of water that could contribute somewhat to the terrestrial water abundance and D/H ratios we observe via the accretion of small SW irradiated particles.

Conclusion: Space weathering of Itokawa grains has been evaluated by atom probe for the first time. Density variations within the rim, and a lack of detectable noble gasses (He and Ne), suggest that this grain was only briefly exposed to the SW. However, we still observe a rimward enrichment in OH and H₂O extending to 50 nm depth. The implantation of volatiles such as O and H, as well as their combination to produce OH and water molecules, indicates that SW implantation may be a further mechanism to seed planetesimals with water.

References: [1] Chapman C.R., (2004) *Ann. Rev. of Earth & Planet. Sci.*, 32, 539-567. [2] Noguchi T., et al., (2011), *Science*, 333, 6046, 1121-1125. [3] Noguchi T. et al., (2014) *MAPS*, 49, 2, 188-214. [4] Nagao K., et al., (2011) *Science*, 333, 6046, 1128-1131. [5] Bradley J.P., et al., (2014) *PNAS*, 111, 5, 1732-1735. [6] Thompson M. S. et al., (2014) *Earth, Planets & Space*, 66, 89. [7] Edmondson P.D. (2011) *Scripta Mat.*, 65, 731-734 [8] Robert F., (2001) *Science*, 293, 5532, 1056-1058. [9] Robert F., (2006), *Meteorites & the Early Solar System II*, Eds: Laruetta D.S., & McSween Jr. H.J. [10] Fischer-Gödde M., & Kleine T., (2017) *Nature*, 541, 525-527.

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