HYDROGEN AND HELIUM IN VESICLES IN IDP GRAINS ANALYZED WITH SCANNING TRANSMISSION ELECTRON MICROSCOPY. K. D. Burgess[1], R. M. Stroud[1], D. Joswiak[2], and D. E. Brownlee[2]; [1]U.S. Naval Research Laboratory, Washington, DC 20375; [2]Dept. of Astronomy, University of Washington, Seattle WA, 98195. (kate.burgess@nrl.navy.mil)

Introduction: Anhydrous interplanetary dust particles (IDPs) may contain volatiles from pre-accretionary processes, interactions with parent body ices, or exposure to the solar wind while on the parent body or in transit to Earth. Vesicles formed in the space weathered rims of grains are thought to be filled with hydrogen or helium. Heating, such as from atmospheric entry, may be required for the formation of vesicles in some materials or could alter contents of vesicles already present. Solar wind hydrogen has been identified in vesicles in the space weathered rim of a pyroxene grain [1], while helium was suggested as the likely source of bubbles formed in a pyrrhotite grain [2]. The shape, size, and contents of vesicles are key to understanding the source(s) of volatiles and can be analyzed using (scanning) transmission electron microscopy (S/TEM) with energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS).

Methods: Stratospheric IDPs from collection plate U2012, flown on NASA Ames Research Center U2 aircraft in March 1993, were washed and embedded in epoxy, then microtomed and placed on grids for STEM analysis. The samples were baked at 140°C for six hours to drive off adsorbed water before insertion in the UHV system. The EELS and EDS data were collected with the NION UltraSTEM200-X at the U.S. Naval Research Laboratory, which is equipped with a Gatan Enfinium ER EEL spectrometer and a Bruker SDD-EDS detector. The STEM was operated at 60 kV or 200 kV, with a ~0.1 nm probe. Spectra were collected as spectrum images (SI), with a spectrum collected for each pixel, allowing for mapping of variations in thickness and composition.

Results and Discussion: Sample U2012A-2J is a pyrrhotite grain with a nominally continuous space weathered rim full of subhedral to euhedral vesicles. The voids range in size from a few nanometers to ~30 nm. Brownlee et al. [2] suggested that these voids formed due to helium implantation, but were unable to confirm the presence of helium in specific voids. EELS mapping of the rim reveals a small peak at ~22 eV associated with individual vesicles, indicating they are filled with helium from the solar wind (Figure 1).

The concentration of helium in the individual vesicles can be calculated from the size of the vesicle and intensity of the peak (Figure 2). In comparison with helium-filled vesicles in a lunar ilmenite grain [3], the vesicles in the pyrrhotite contain relatively low amounts of helium. This could be due to loss during atmospheric entry heating or differences in material properties such as yield strength of the sulfide grain or He diffusion rate.

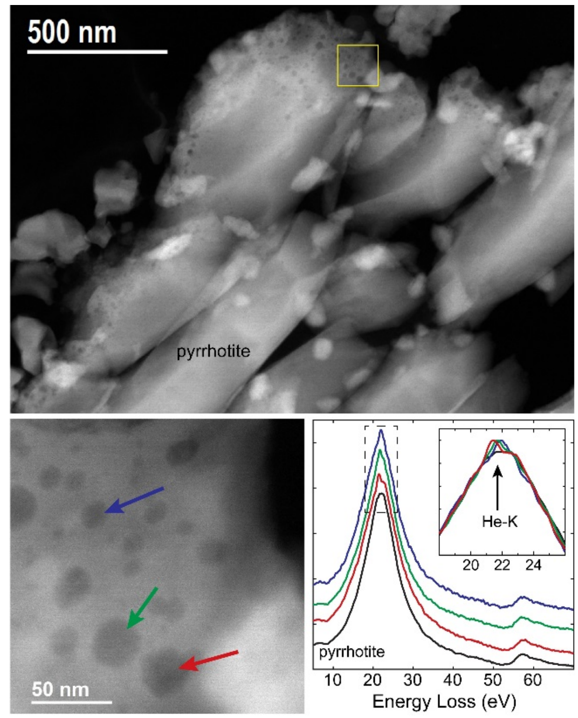

Figure 1. The HAADF images show a section of the pyrrhotite IDP grain and close-up of vesicles. EELS data from three He-filled vesicles noted by arrows compared with surrounding pyrrhotite (black) shows the small peak at ~22 eV.

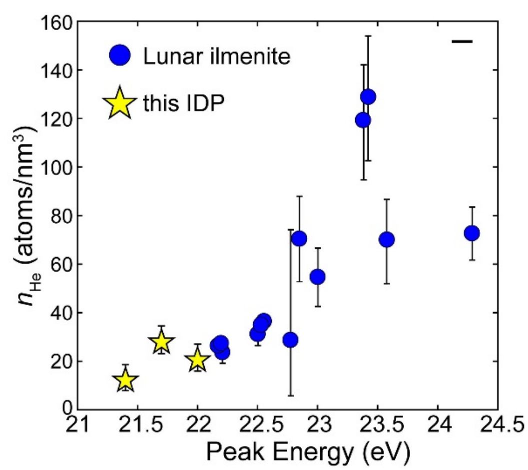

Figure 2. The helium concentration in IDP pyrrhotite vesicles is relatively low and falls on the trend previously established for lunar ilmenite with He-filled vesicles [3].

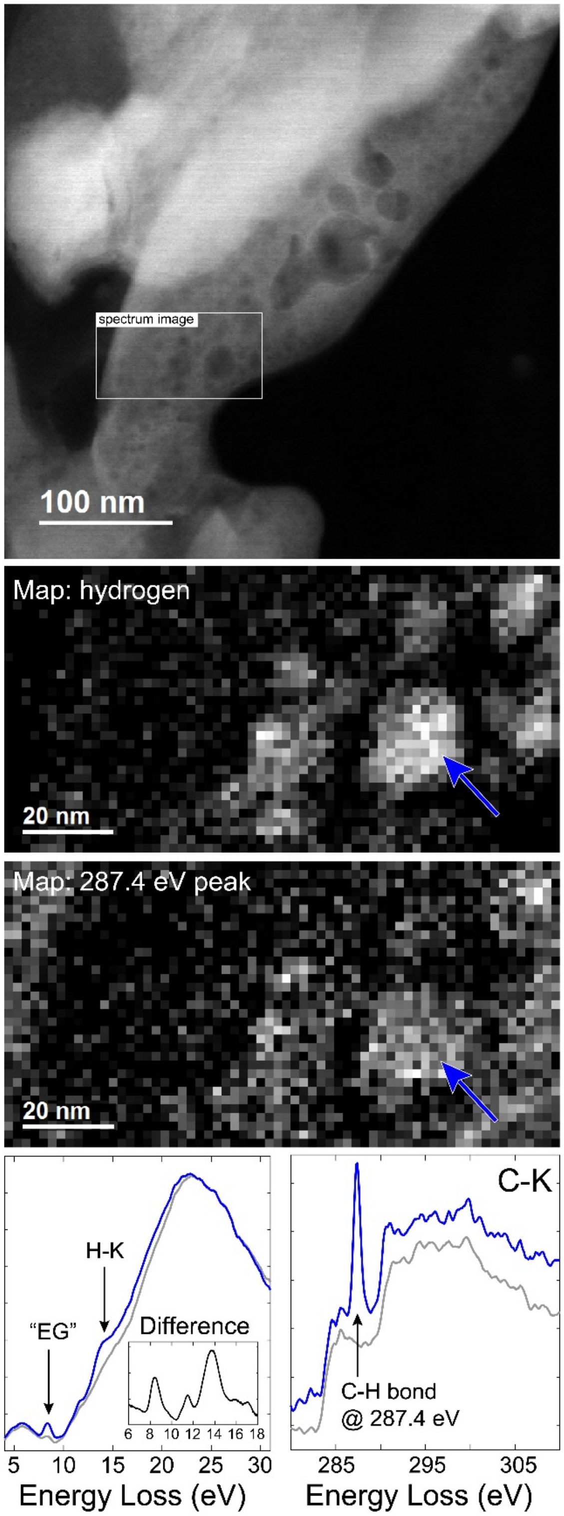

Figure 3. HAADF image of vesicular grain in an IDP. From EELS SIs vesicular region, we can map out the presence of hydrogen and carbon in C-H bonds in the vesicles. Spectra from an individual vesicle (blue) show distinct peaks. Gray spectra are from vesicle-free material.

A vesicular grain observed in sample U2012A-3C is enigmatic and not clearly related to space weathering processes (Figure 3). The grain itself is in the midst of other vesicle-free grains, rather than near an edge. The core of the grain is iron sulfide and it is surrounded by an amorphous, highly vesicular, oxygen-rich shell. EDS data show the rim material contains significant O, Fe and S, along with several at% Mg. Small amounts of Si (~0.5 at%) are present over both the core and rim of the grain. EELS data from the vesicles show small peaks at 8.5 eV and ~13 eV, both associated with hydrogen [1]. Additionally, the carbon K-edge in spectra from the same vesicles shows a distinct peak at 287.4 eV due to the presence of C-H bonds. Attribution of this peak to a specific compound is ambiguous due to the ubiquity of these types of bonds in natural materials as well as laboratory sources. A sharp peak at the same energy is seen in hexamethyldisiloxane [4], a compound related to the silicone oil in which the IDPs were collected, and hexane [5], used to wash the IDPs, both possible sources of contamination. However, the peak is associated only with this particle and clearly tied to the individual vesicles, suggesting it is indigenous. No evidence of contamination is seen elsewhere on the sample.

The helium- and hydrogen-filled bubbles have very different morphologies, and it is unlikely the hydrogen filled vesicles formed solely due to the influence of the solar wind. The cores of both grains are predominantly iron sulfide. However, while the helium vesicles are euhedral and in material that otherwise very closely resembles vesicle-free portions of the grain, the hydrogen vesicles are in a highly porous rim that is rich in oxygen relative to the core of the grain and also has other minor and trace elements (e.g., Mg, Si) not present in the core. Solar wind helium-filled vesicles in lunar ilmenite are not euhedral [3], indicating that both host mineral composition and heating could play a role in vesicle formation and shape.

Conclusion: With the ability to identify and map the volatile contents of very small vesicles in IDPs and other extraterrestrial materials, we can better understand the timing of alteration and source of volatiles, whether from pre-accretionary processes, implantation by the solar wind, or contamination during collection and laboratory preparation procedures. This technique is applicable to samples collected from many airless bodies including current and future collections from the Moon, Itokawa, Bennu, and Ryugu.

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References: [1] Bradley, J.P., et al. (2014) *PNAS, 111*, 1732. [2] Brownlee, D., et al. (1998) *LPSC, 29*, #1869. [3] Burgess, K. and R. Stroud (2018) *GCA, in press*. [4] Urquhart, S.G., et al. (1997) *Organometallics, 16*, 2080. [5] Hitchcock, A.P., and I. Ishii (1987) *J Electron Spectrosc, 42*, 11.