

IDENTIFICATION OF STARDUST ANALOGS IN AEROGEL USING RAMAN SPECTROSCOPY.

K. V. Fendrich¹ and D. S. Ebel^{1,2}. ¹Dept. of Earth and Planetary Sciences, American Museum of Natural History, Central Park West at 79th St, New York, NY 10024, ²Dept. of Earth and Environmental Sciences, Columbia University, New York (kfendrich@amnh.org)

Introduction: In 2006, NASA's *Stardust* mission returned a capsule to Earth with particles collected from the coma of comet 81P/Wild 2. Cometary particles were collected by impact into low-density silica aerogel at a relative velocity of 6.1 km/s [1]. Upon impacting the aerogel, particles left behind tracks of melted and compressed aerogel and void space, shedding material along the way. In order to maximize the scientific return from these samples, it is imperative to record their initial character using a variety of non-destructive techniques while they remain embedded in the capture medium.

At the Microscopy and Imaging Facility at the American Museum of Natural History (AMNH), a Zeiss LSM710 Laser Scanning Confocal Microscope (LSCM) is used to perform 3-dimensional mapping of whole Stardust tracks at high resolution (<80 nm/pixel.) Typically, these results are complemented with chemical data acquired using the GSECARS X-ray microprobe on beamline 13-IDE at the Advanced Photon Source (APS) of Argonne National Laboratory. However, time at APS is limited and highly competitive, which has motivated us to develop a system with which we can characterize Stardust grain mineralogy relying solely on instruments at our disposal at AMNH.

Experimental Methods: Pioneering work [2] has demonstrated that Raman spectroscopy is a practical, effective method for mineralogical identification of grains trapped in aerogel. To employ this technique at AMNH, a Princeton Instruments IsoPlane SCT 320 imaging spectrograph paired with a Princeton Instruments PIXIS 100BR CCD camera was coupled to the Zeiss LSM710 (Fig.1). This LSCM is equipped with several lasers of differing wavelengths. This arrangement facilitates the high-resolution location of grains in situ, followed by the capability of switching to Raman spectroscopy immediately, without losing focus or disturbing the sample. This unique LSCM-Raman setup presents the ability to perform mineralogical identification experiments with superior spatial resolution.

There are many benefits of using Raman spectroscopy; for example, [3] reports the possibility of quantifying the relative abundance of Mg and Fe in olivine based on the position of major peaks in the Raman spectrum. In addition, Raman permits the identification of silicates, unlike synchrotron X-ray fluorescence mapping, which is incapable of distinguishing between silicon in cometary particles versus that of the aerogel

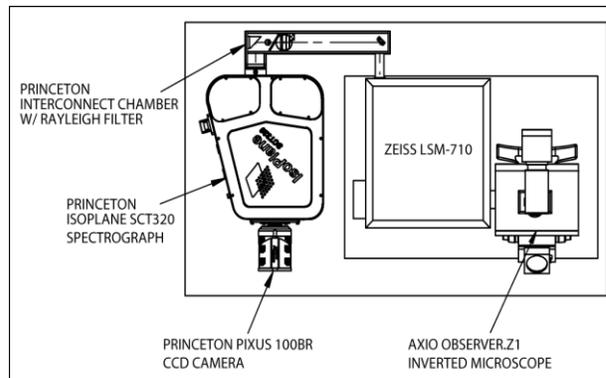


Figure 1: Schematic of LSCM-Raman system at AMNH

surrounding them [4]. The aerogel that contains the captured Wild 2 samples is known to fluoresce [5]. However, this effect is reduced by the small confocal aperture of the LSCM, which limits the excitation volume. During the experiments reported here, the confocal aperture was set to 1.2 μm .

To test the experimental setup, two mineral grains that were fired into Stardust-like aerogels at the University of Kent light gas gun facility were analyzed. In both cases, a 514 nm Ar-ion laser was used, generating ~3.5 mW of power at the sample through a 40x objective (measured using a power meter). This method differs from those of the British groups [2,6,7] in that they used 632.8 He-Ne lasers in their analyses, which in the case of [7], minimized fluorescence due to the presence of Kapton windows. Each of these studies reports ~3 mW of power at the sample, which is close to the value measured in this study. In the work done by [6], a range of power from 0.8 - 10 mW was utilized. While it is more difficult to attain a Raman signal with low power, it is necessary to minimize the power at the sample, as the aerogel and most importantly organic material potentially present are susceptible to heat-induced damage.

Results: A Raman spectrum of an aerogel-embedded grain of diopside ~18 μm in diameter was acquired with an integration time of 180 seconds, whereas a smaller olivine grain (~5 μm , Fig. 2) required an integration time of 240 seconds for improved signal-to-noise ratio. Spectra obtained from minerals in aerogel by [2] required up to 1000 seconds, while [6] tested the outcomes of integration times ranging from a few minutes to 20 hours. The two spectral analyses presented here were matched to those in the University

of Arizona's RRUFF database (rruff.info) to confirm the mineral identities (Fig. 3, 4).

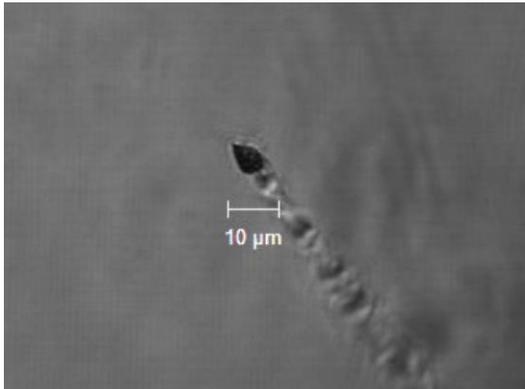


Figure 2: Olivine analyzed in this study. Note the track left behind as the grain tunneled through aerogel upon impact.

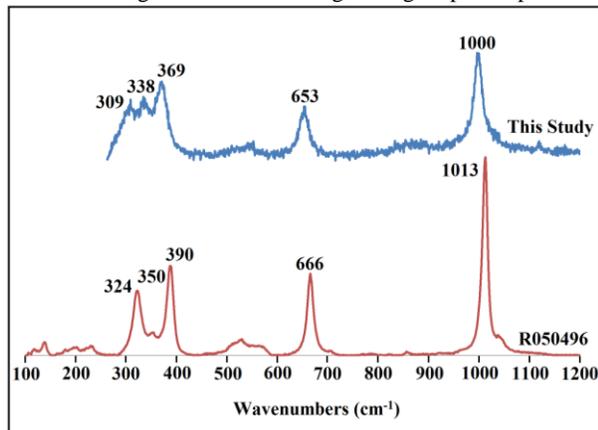


Figure 3: Diopside spectrum from the RRUFF database (below) overlain by the one acquired in this study (above). The intensity of the reported spectrum has been exaggerated by a factor of 10 for comparison.

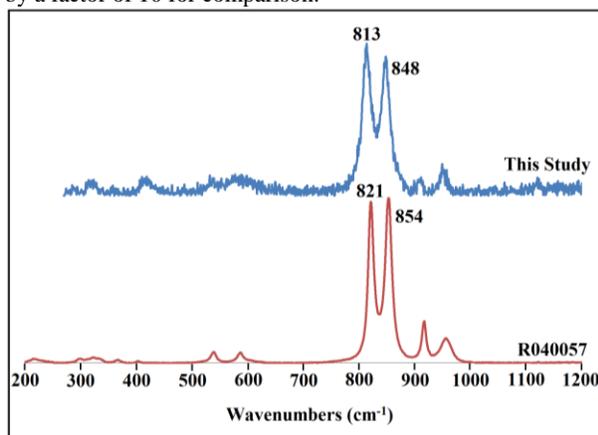


Figure 4: Olivine spectrum from the RRUFF database (below) overlain by the one acquired in this study (above). The intensity of the reported spectrum has been exaggerated by a factor of 10 for comparison.

Outlook: The primary goal of this project is to locate significant non-terminal grains in aerogel by high-resolution LSCM mapping, and then to use image-guided high spatial resolution Raman spectroscopy to efficiently characterize them in-house in order to identify grains that warrant possible extraction and further investigation. This method increases efficiency and by potentially obviating the need for the use of the beam-line facilities at the APS synchrotron, saves time and resources. While synchrotron mapping is always desirable, Raman spectroscopy can expedite the search for high-value cometary grains, particularly those rich in daughter products of extinct radionuclides.

Ultimately, our goal is that selected grains of interest would be harvested for investigation through collaboration with colleagues at the University of Chicago where the Chicago Instrument for Laser Ionization (CHILI) [8] would be used to perform detailed chemical analyses, providing in-depth information on the history of grains in comet 81P/Wild 2.

Conclusion: The LSCM-Raman system at AMNH is fully operational. This work demonstrates the successful identification of minerals at $<20 \mu\text{m}$ size in aerogel. Future work will rely on obtaining allocated Stardust tracks from CAPTEM for Raman investigation of cometary grains. Mineralogical and compositional data will provide information on the early stages of solar system formation and offer a glimpse into the origins of the earliest solids in the solar nebula.

References: [1] Brownlee D. (2014) *Annu. Rev. Earth Planet. Sci.*, 42, 179–205. [2] Burchell M. J. et al. (2006) *Meteoritics & Planet. Sci.*, 41.2, 217-232. [3] Foster N. J. et al. (2012) *GCA*, 121, 1-14. [4] Price M. C. et al. (2012) *EPSC*, EPSC2012-333. [5] Wopenka B. (2012) *Meteoritics & Planet. Sci.*, 47.4, 565-584. [6] Bridges J. C. et al. (2010) *Meteoritics & Planet. Sci.*, 45.1, 55-72. [7] Price M. C. et al. (2014) *LPS XLV*, Abstract #1252. [8] Stephan T. (2016) *International Journal of Mass. Spec.*, 407, 1-15.

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