# MINERALOGICAL IDENTIFICATION OF STARDUST PARTICLES BY XANES AT THE ADVANCED LIGHT SOURCE.

Zack Gainsforth[1], Anna Butterworth[1], Sirine Fakra[2], Matthew Marcus[2], Christopher Snead[1], Andrew J. Westphal[1] , [1] *Space Sciences Laboratory, University of California at Berkeley, Berkeley CA 94720, USA,* [2] *Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720-8225, USA* .

## Introduction

The Stardust cometary samples are the most technically challenging returned extraterrestrial materials to date. Friable cometary particles generally disintegrated upon impact with the aerogel and are distributed along tracks that are two to three orders of magnitude larger than the typical particle size. As a result, tracks contain up to hundreds of particles that are buried deep in the aerogel tiles and are intimately mixed with aerogel. A method for doing mineralogical surveys of these particles is urgently needed. As a first step in their analysis, entire tracks can be extracted in aerogel keystones [3] or quickstones [4]. Individual particles can then be laboriously extracted, but it is impractical to do this for more than a few particles per track. Here we describe a method for doing mineralogical analysis of particles within aerogel keystones using a combination of synchrotron x-ray fluorescence at the micron scale ($\mu$XRF), x-ray near edge structure spectroscopy ($\mu$XANES) and x-ray diffraction ($\mu$XRD). This should facilitate mineralogical surveys and efficient searches for rare minerals, such as Ca, Ti-rich CAI-like materials.

We performed our analysis of Stardust particles using keystones at beam line 10.3.2 of the Advanced Light Source at Lawrence Berkeley National Lab.[1] The $\mu$XANES capability of the beam line provides an excellent keystone survey technique to spot potentially interesting particles from the diverse material typically present in a keystone because it is able to rapidly identify minerals based on their chemical environment. Individual sub-micron particles such as those found in comet Wild 2 do not always yield useful diffraction data due to random crystal orientation and their small size. Furthermore, while electron microscopy can extract diffraction data from even the finest of minerals, it cannot do so rapidly (dozens of grains/day) as the preparation techniques are the rate limiting step. Therefore, when dealing with Wild 2 samples, XANES provides the powerful combination of mineralogical identification as well as high counting statistics and is very useful as a tool for comparing Wild-2 mineralogy against meteorite classes.

## Methods

Each Stardust XANES spectrum was compared against a linear superposition of XANES spectra from known mineralogical standards. A fit therefore yields a percentage composition of several known minerals to achieve a minimum $\chi^2$ fit. To obtain valid results it is necessary to have a library of XANES spectra on hand for every mineral suspected to exist in the sample. With a large standards database it is possible to make very exact mineralogical identifications in a very short time. By measuring spots in the keystone near the track, it is also possible to remove the XANES contribution from contaminants in the aerogel.

Many minerals require several XANES spectra to describe them as a consequence of optical anisotropy arising from the point group of the crystal. For example, diopside can have different signatures depending on the physical orientation of the crystal. See figure 1. Luckily, any crystal can be described using a linear superposition of at most 6 basis XANES spectra. [2]

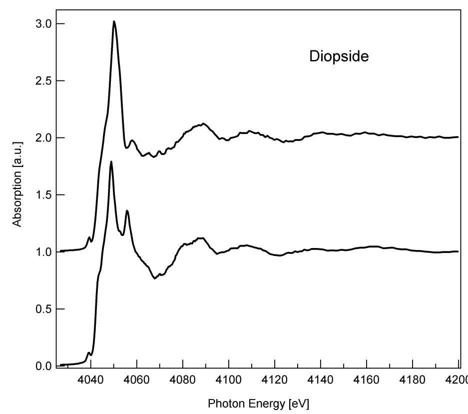


Figure 1: Two XANES spectra of Diopside with varied crystal orientation taken at the Ca K-edge. Notice that the spectroscopic signatures are strikingly different.

## Characterization of olivines

XANES has the ability to differentiate between members of the olivine family and can be used to constrain fayalite/forsterite abundances for comparison against meteorite classes. Because Fe and Mg have distinct electron potentials, the Fe-XANES probe can easily spot Fe concentration variations with high accuracy for a survey technique ($\approx$ 10%). Beam line 10.3.2 is not sensitive to Mg, and so Mg concentrations are inferred. See figure 2.

In combination with multi-channel fluorescence spectra which yield the elemental abundances of a given spot, it is also possible to detect Mn and Cr substitutions in olivines. This has potential for further classifying Wild 2 samples with respect to known meteorite classes.

## Searching for CAI-like material

Calcium aluminum rich inclusions (CAIs) are generally thought to originate near the center of the solar system during its early formation. This allows them to be used as a tracer in many theories of solar mixing and their presence and concentration in comet Wild 2 can be used to set parameters on the formation dynamics of our solar system. Such material is usually rich in calcium, aluminum and titanium. Both calcium and titanium can be detected at beam line 10.3.2. It is possible, therefore, to survey for CAI like minerals by using XRF to

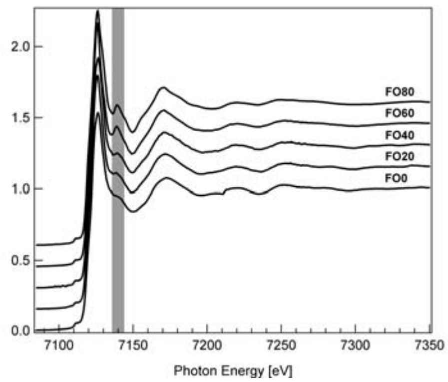


Figure 2: XANES spectra of Fo0 to Fo80[7] taken at the Fe K-edge. Continuous variation in the peak amplitudes signals the drop in iron concentration as Fo0 → Fo80. Note especially the highlighted peak near 7140 eV.[6]

identify all Ca + Ti rich spots in a keystone, and then perform a XANES scan of each point in series. Using this technique, we identified the presence of diopside and possibly anorthite (not yet confirmed by TEM), both minerals commonly found in CAI's, within track 77 extracted from tile 9. See figure 3.

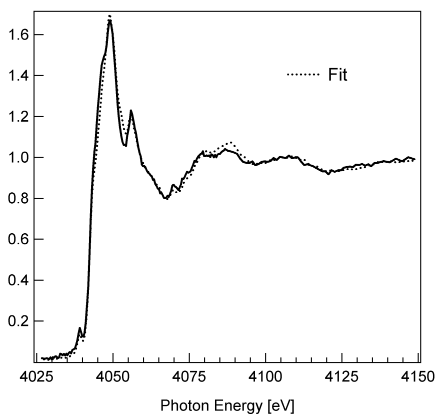


Figure 3: Ca K-edge XANES fit on a particle in Stardust sample c2009,20,77 (keystone) gives a match for 20% aerogel background and 80% diopside. Diopside was subsequently identified in the same track by electron diffraction. [5]

**Acknowledgments**

The Space Sciences Lab effort was supported by a NASA Stardust Participating Scientist grant. The ALS-LBNL is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy, under Contract No. DOE-AC03-76SF00098.

**References**

[1] Marcus, M. A., MacDowell, A. A., Celestre, R., Manceau, A., Miller, T., Padmore, H. A., Sublett, R. E. 2004, J. Synchrotron Radiation, 11, 239-247.

[2] Heald S. M. and Stern E. A. 1977, Anisotropic X-ray absorption in layered compounds. Phys. Rev. B16, 5549-5559.

[3] Westphal, A. J., et al. 2004, Meteoritics and Planetary Science, 39, 1375

[4] Ishii, H. A., Graham, G. A., Kearsley, A. T., Grant, P. G., Snead, C. J., & Bradley, J. P. 2005, Meteoritics and Planetary Science, 40, 1741

[5] Brownlee, D., Graciela M., 2006, personal communication.

[6] S. Fakra, M.A. Marcus, Z. Gainsforth, C. Snead, A. Butterworth, A. Westphal (in prep for MAPS)

[7] We gratefully acknowledge the Natural History Museum, London for providing olivine standards of known elemental abundance.