SULFUR ISOTOPE MEASUREMENTS OF A STARDUST FRAGMENT R. C. Ogliore[1], A. L. Butterworth[2], Z. Gainsforth[2], G. R. Huss[1], K. Nagashima[1], J. Stodolna[2], A. J. Westphal[2], [1]Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Mānoa, Honolulu, HI 96822, USA, [2]Space Sciences Laboratory, University of California Berkeley, Berkeley, CA 94720, USA.

Introduction

Stardust samples from the Jupiter-family comet Wild 2 show a larger fraction of Fe bonded as iron sulfide compared to most meteorite classes [1]. Berger *et al.* [2] investigated sulfide assemblages from Stardust and concluded that their composition and structure is evidence of low-temperature hydrothermal processing, similar to CI chondrites. Iron-sulfide grains are present in protoplanetary disks [3]. Experiments by Keller & Rahman [4] showed that iron-sulfide grains are sputtered away in the interstellar medium faster than crystalline silicates, but they estimate that surviving presolar sulfides should still be present in meteoritic materials (e.g., in isotopically primitive IDPs at the $\sim$100 ppm level). Aqueous alteration on the chondrite parent body can form sulfates from sulfides in a mass-dependent process that concentrates light S in the sulfates, leaving the remaining sulfides isotopically heavy in S [5]. High-precision ion probe measurements of S in Stardust iron sulfides can provide further clues to aqueous processing of cometary material. Addtionally, presolar sulfides would be identifiable by large isotopic anomalies, particularly in ^{36}S [6], though so far none have been discovered. We present results of our ion-probe measurements of an individual Stardust iron-sulfide grain captured in the aerogel collector.

Methods

We identified a $\sim$4-μm iron-sulfide grain (named Gigan) in Stardust track C2052,2,74 by synchrotron X-ray absorption near-edge spectroscopy at the Fe K-edge. After extracting Gigan and embedding it in an epoxy bullet, we microtomed $\sim$100-nm-thick slices for TEM analysis (Figure 1). The electron-diffraction pattern of Gigan closely matches pyrrhotite. Synchrotron X-ray fluorescence measurements of the potted butt yield the following elemental ratios: Ni/Fe $\approx$ 0.02, Zn/Fe $\approx$ 0.008, Se/Fe $\approx$ 0.001. STEM/EDS measurements in Gigan TEM slices are also consistent with a pyrrhotite composition close to troilite.

The leftover Gigan potted butt was prepared for isotope analysis using a specially designed holder [7]. We measured four S isotopes on Gigan using the University of Hawaii Cameca ims 1280 ion microprobe: ^{33}S, ^{34}S, and ^{36}S were measured simultaneously on electron multipliers (^{34}S on monocollector EM) followed by peak-jumping to ^{32}S (measured on the monocollector EM, due to insufficient count rate to be measured on a Faraday cup). A Cs^+ primary ion beam of $\sim$3 pA was focused to $\sim$1 μm and rastered over a 2$\times$2 μm area on the sample to suppress instrumental fractionation during the measurement. The mass-resolving power of $\sim$4800 was sufficient to resolve hydride interferences and $^{12}C_3$ from ^{36}S.

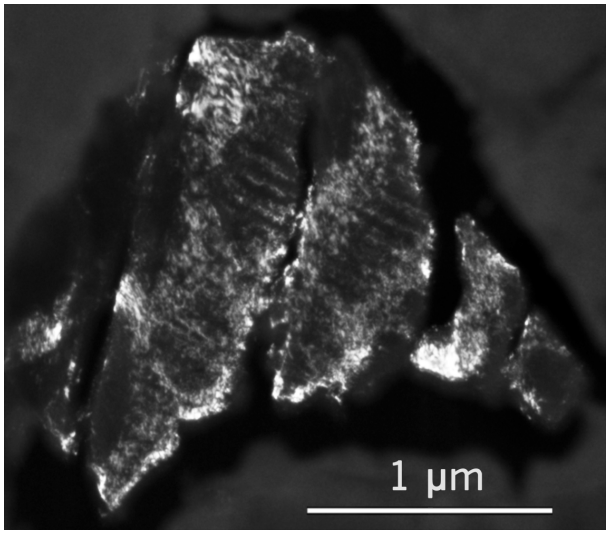

Figure 1: Dark-field TEM image of a Gigan microtomed slice. Defects in the crystal lattice of pyrrhotite are clearly visible.

For a S isotopic composition standard, we used troilite from the Canyon Diablo iron meteorite prepared in a normal ion probe mount and in an epoxy bullet and holder analogous to Gigan. The epoxy bullet contained numerous grains a few microns in size that we used to confirm our capability of measuring the S isotopic composition of Gigan-sized grains embedded in epoxy.

Results

Measurements of the Canyon Diablo standard had a typical 2σ statistical uncertainty of 1‰ in δ^{33}S, 0.6‰ in δ^{34}S, and 7‰ in δ^{36}S. The standards showed a spread in mass-dependent instrumental fractionation of $\sim$3‰ in δ^{33}S over several measurements in a given mount, sufficient to resolve the several per mil mass-dependent fractionation effects seen in small, aqueously altered sulfide grains from CM and CI chondrites measured by ion probe [5].

Unfortunately Gigan experienced a significant loss of

S while it was embedded in its epoxy bullet. This could be due to chemical interaction between Gigan and Cl in the epoxy embedding medium, or damage from an incident electron or X-ray beam. The S isotopic composition of Gigan was measured to be δ^{33}S = -7.7‰ ± 27.5‰, δ^{34}S = -20.7‰ ± 17.5‰, and δ^{36}S = -0.7‰ ± 179.8‰ (δ^{x}S is defined as the per mil deviation of ^{x}S/^{32}S from the Canyon Diablo troilite ratio), where the quoted total uncertainties are 2σ and are dominated by counting statistics due to the very low S signal from Gigan.

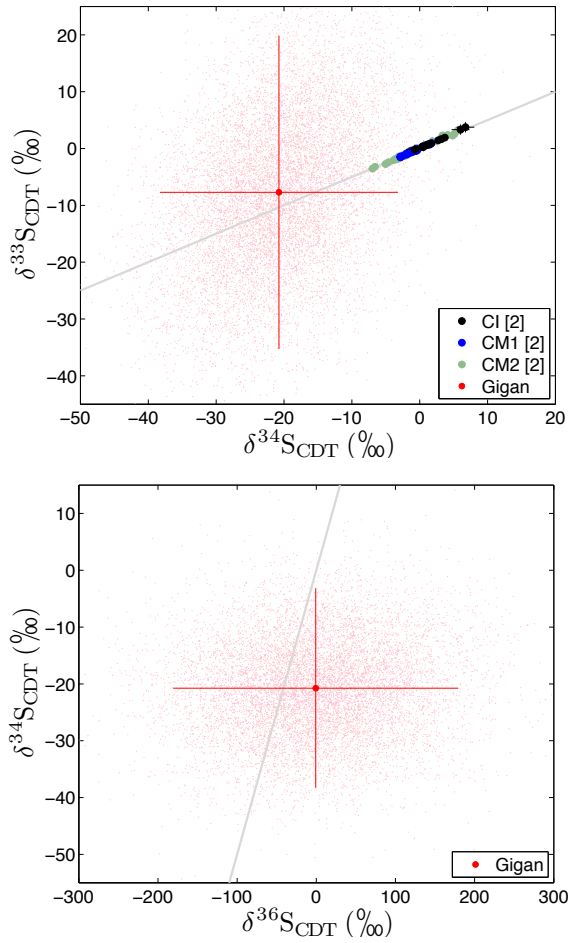

Figure 2: The S isotopic composition of Gigan (red circles) compared with ion probe measurements of CI (black circles), CM1 (blue circles), and CM2 (green circles) sulfides. [5] did not measure ^{36}S. All uncertainties are 2σ; measurement uncertainties from [5] are mostly smaller than the symbols. Small red dots are Monte Carlo simulations of the Gigan measurement to account for statistical uncertainty and observed instrumental mass fractionation in the standards. The terrestrial mass fractionation line (slope=1/2) is shown in grey.

Gigan does not appear to have large isotope anomalies characteristic of presolar grains, consistent with previous measurements of S isotopes of S-rich cometary impacts into the Stardust Al foils [8].

Conclusions

We have successfully developed a sample preparation technique and instrumental protocol to measure S isotopes in aerogel-collected Stardust sulfide grains a few microns in size. This will help determine the level of aqueous alteration of iron sulfides in comet Wild 2, or identify presolar iron-sulfides captured by Stardust. We have measured one pyrrhotite grain from Stardust (a small, non-terminal fragment) that experienced S loss in its embedding medium resulting in large statistical uncertainties.

The S isotopic composition of Gigan indicates that it formed in the solar system. Even with these large uncertainties, Gigan does not appear to be enriched in the heavier isotopes of S. This implies that Gigan was not formed in an aqueous-alteration process that produced isotopically light sulfates and heavy sulfides as described in [5]. However, this conclusion is somewhat uncertain because the S isotopic composition of Gigan could have been affected during the reaction that caused a loss of S in the particle.

We are developing sample preparation techniques to minimize S loss before future isotope measurements of other Stardust sulfide gains.

Acknowledgements

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