OXIDATION STATE OF IRON IN THE JUPITER-FAMILY COMET WILD2. Andrew J. Westphal1, Donald E. Brownlee2, Anna L. Butterworth1, Sirine Fakra2, Zack Gainsforth2, David Joswiak2, Matthew A. Marcus3, C. J. Snead4, Ryan C. Ogliore1, David R. Gaffey5, Sirine Fakra2, Zack Gainsforth2, Matthew A. Marcus3, C. J. Snead4, Ryan C. Ogliore1, David R. Gaffey5. 1Space Sciences Laboratory, U. C. Berkeley, Berkeley CA 94720, USA. 2Astronomy Department, University of Washington, Seattle, WA 98195, USA. 3Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. 4Department of Earth Sciences, UCLA, Los Angeles, CA 90095-1567, USA.

Introduction: More than fifty years ago, Urey and Craig[1] recognized that the oxidation state of Fe varies systematically between meteorite families and groups, and indeed can be used to classify meteorites. Until now, no sample of a comet has been available in the laboratory for measurement of the bulk oxidation state of Fe for comparison with known meteorite groups. Here we report synchrotron-based x-ray microprobe measurements of the relative concentrations of reduced and oxidized iron in the first bona fide sample of a comet, the Jupiter-family comet Wild2. These samples were returned to earth by the Stardust spacecraft in January 2006.

Methods: Using robotically controlled micromanipulators and pulled glass microneedles, we extracted 11 tracks of varying sizes from cometary Stardust aerogel tiles in “keystones” — tiny wedge-shaped pieces of aerogel that completely contain the impact track[2]. The tracks were chosen randomly from a population of tracks at nearly normal incidence to the collector[3]. The keystones were mounted either on silicon “microfork” fixtures or sandwiched between 6-µm thick polypropylene films.

We analyzed the keystones by microbeam XRF and microbeam x-ray absorption near-edge structure (µXANES) spectroscopy on beamline 10.3.2 at the Advanced Light Source at LBNL[4]. For multivalent elements such as Fe, the position of the absorption edge, where the absorbance changes very rapidly, depends on the oxidation state: atoms in reduced environments start to absorb strongly several eV below where atoms in an oxidized environment do. The edge is well-determined, and alone can distinguish between oxidation states. Because of this, XANES is a particularly powerful and sensitive technique in determining oxidation state[5]. By comparing the spectrum of an unknown to a library of well-characterized standards, minerals can be identified, although identifications are not always unique. Identification of mineral groups is more reliable, since many minerals within a given group (e.g., sulfides) have similar XANES spectra. We computed the molar ratio $\xi$ of iron reduced (metals, carbides, silicides and sulfides) to oxidized Fe. We found that $\xi = 2.34^{+1.2}_{-1.0}$ (stat., 2σ).

In the Urey-Craig plot of concentration of metal + sulfides versus concentration of oxidized iron (Fe$^{2+}$ and Fe$^{3+}$), both normalized to Si, meteorite groups fall into distinct, mostly non-overlapping regions (Fig. 1). The carbonaceous chondrites (CR, CO, CV, CM, CI, CK) are oxidized to various degrees, with the CI group extensively oxidized by aqueous alteration. The enstatite chondrite groups EH and EL contain essentially no oxidized Fe. The ordinary chondrites and the K group (Kakangari) are intermediate in oxidation state.

Because the cometary particles were captured in silica aerogel, we could not measure their Si content. Thus our measurement appears as a band in Fig. 1. The allowed region includes the ordinary chondrite group H and the unclassified group K, and is marginally consistent ($\sim 2\sigma$) with the ordinary group L and the carbonaceous group CR. On the assumption that all of the carbide components are the result of smelting of oxides, the results are marginally consistent with the CV and CO groups. However, the relative fractions of metal and sulfide (Fig. 2) in Wild2 are inconsistent at the $\sim 2\sigma$ level with any recognized meteorite group. The combined measurements appear to have the closest affinity to the K group.

For comparison with Wild2, we measured the oxidation state of two chondritic porous (CP) IDPs, W7110A-2E (2 spots) and U2-20-GCA-7-2005 (fig. 2). The very limited statistics of these measurements do not yet allow us to compare the bulk composition of CP IDPs with Wild2.

Fig. 1: Urey-Craig plot: Fe in Fe$^{0}$ + sulfides vs. oxidized (Fe$^{2+}$ and Fe$^{3+}$), normalized to Si for carbonaceous (CI, CM, CO, ...), ordinary (H, L, LL) and enstatite (EH, EL) chondrite groups [6, 10, 7, 9, 8] and comet Wild2. The dark blue region is the 2-dimensional $2\sigma$ allowed region in the mean values for the ensemble of 11 tracks that we analyzed. The dashed region shows the effect of assuming that all carbide components originated as oxides.

Capture effects: Capture effects on the oxidation state of cometary material are a significant concern. Using microbeam Fe XANES and TEM, we have observed systematic reduction of Fe during hypervelocity capture of basalt glass projectiles into aerogel at 6 km sec$^{-1}$ [11]. This reduction results in iron carbide (Fe$_3$C), not iron metal, and is suggestive of smelting — that is, reduction of Fe oxide by reaction with residual
carbon in the aerogel. Carbide is $\sim 15\%$ of Fe$^{0}$ in our fits. We conclude that smelting is unlikely to have played a major role in the capture of Stardust samples, but is nevertheless a source of systematic uncertainty, and lowers the $2\sigma$ lower limit on $\xi$ from 0.78 to 0.67. Our results including this systematic error are shown as the dashed regions in Figs. 1 and 2. Sulfides can be converted to metal through loss of S by heating. This has been observed in TEM observations in Stardust samples. Any conversion of sulfides to metals would imply that Wild2 is even more sulfide-rich than our measured value (Fig. 2), which is already more sulfide-rich than any other meteorite group except K.

Conclusion: Relative concentrations of metals, sulfides and oxidized iron in Wild2 are inconsistent with any group of chondrites. Of the recognized meteorite groups, the oxidation state of Fe in Wild2 appears to be most similar to that of the rare K (Kakangari) chondrite grouplet. Like Kakangari, Wild2 is rich in sulfides. We find that, in contrast with previously reported measurements[15], S is not significantly depleted in Wild2 as compared with CI meteorites.

Acknowledgments: This work was supported at SSL by NASA grants NNG05GR30G, NNG04G127G, and NNG05GM01G. The LBNL is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

References