

OXIDATION STATE OF IRON IN THE JUPITER-FAMILY COMET WILD2. Andrew J. Westphal¹, Donald E. Brownlee², Anna L. Butterworth¹, Sirine Fakra³, Zack Gainsforth¹, David Joswiak², Matthew A. Marcus³, C. J. Snead⁴, Ryan C. Oglione¹, 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 ξ of reduced iron (metals, carbides, silicides and sulfides) to oxidized Fe. We found that $\xi = 2.34^{+1.77}_{-1.56}(\text{stat.}, 2\sigma)$.

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 grouplet.

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.

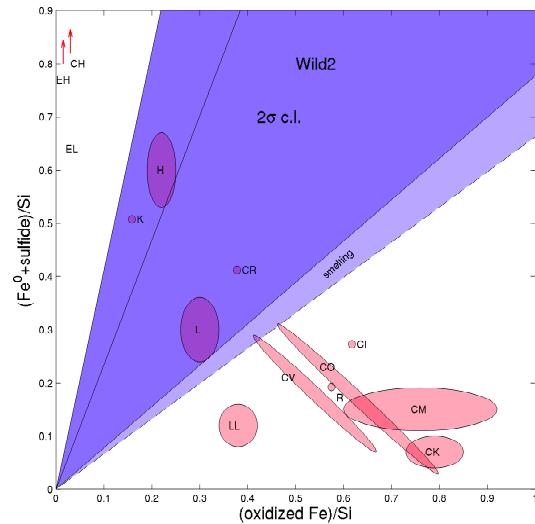


Fig. 1: Urey-Craig plot: Fe in Fe^0 + sulfides vs. oxidized (Fe^{2+} and Fe^{3+}), normalized to Si for carbonaceous (CI, CM, CO, ...), ordinary (H, L, LL) and enstatite (EH, EL) chondrite groups [6, 10, 7, 9, 8] and comet Wild2. The dark blue region is the 2-dimensional 2σ allowed region in the mean 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_3C), 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 2σ lower limit on ξ 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.

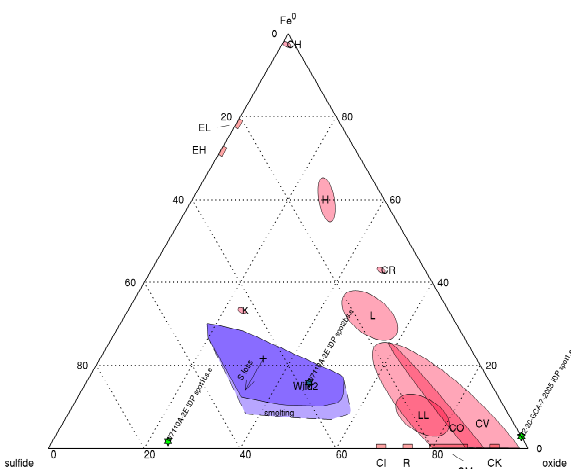


Fig. 2: Ternary plot of fraction of Fe^0 vs. sulfides vs. oxides for various meteorite groups. We also show measurements (green stars) of two IDPs (W7110A-2E, 2 spots, and U2-20-GCA-7-2005) for comparison.

Discussion: Although the Fe oxidation state clearly has fundamental significance, an underlying physical mechanism that leads to systematic differences in oxidation state remains elusive. The meteorite collection spans an enormous range of oxidation states, from orders of magnitude more reduced (E chondrites) to orders of magnitude more oxidized (CI chondrites) than a cooling gas of solar composition[12]. From thermodynamic considerations, Rubin and Wasson[13] have suggested that oxidation state is a reflection of heliocentric distance at the time of meteorite parent-body formation, with oxidation increasing with heliocentric distance. The oxidized carbonaceous chondrites would have formed at the greatest heliocentric distance, and the reduced E chondrites at the smallest, with the ordinary chondrites intermediate. If this were to hold uniformly, comets, which formed far from the Sun, would then be expected to be highly oxidized like the carbonaceous chondrites. Our observation that Wild2 is reduced compared to the carbonaceous chondrites at the very least implies that the situation must have been considerably more complex.

Our observations are most consistent with the unequilibrium K meteorites. The enigmatic K grouplet of chondrites consists of only two (or perhaps three) meteorites, with a total mass of less than 500g [14]. K meteorites are similar to ordinary chondrites in their abundances of volatile siderophile elements, and are similar to ordinary chondrites and enstatite

class in being somewhat depleted relative to CI in volatile lithophiles. The K group has properties (O isotopic composition, refractory lithophile abundances, chondrule volume fraction, and others) shared by both carbonaceous chondrites and enstatite chondrites[14]. Thus, the K chondrites are also an exception to the smooth dependence of meteorite properties on heliocentric distance suggested by Rubin and Wasson[13].

Flynn *et al.*[15] reported synchrotron x-ray fluorescence measurements of abundances of elements from S through Se in Stardust cometary samples. They reported that S was significantly underabundant ($\text{S/Fe} \sim 0.2 \times \text{CI}$), but that the moderately volatile chalcophile elements Cu, Zn and Ga were significantly ($\sim 2\sigma$) overabundant as compared with CI values. Our measurement of the abundance of FeS with respect to Fe (Fig. 2), gives a lower limit on S/Fe (our measurement is blind to volatilized S or S in non-Fe-bearing phases.) We find that $\text{S/Fe} > 0.63 \times \text{CI}$ (2σ), and is consistent with the overabundance of volatile chalcophile elements. We hypothesize that S was underestimated in the fluorescence measurements because of the short attenuation length of S $\text{K}\alpha$ x-rays in large sulfide grains.

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

- [1] H. C. Urey, H. Craig, *GCA* **4**, 36 (1953).
- [2] A. J. Westphal *et al.*, *MAPS* **39** 1375 (2004).
- [3] A. J. Westphal *et al.*, *MAPS* (in press) (2007).
- [4] A. Manceau *et al.*, in *Appl. of Synch. Rad. in Low-Temp. Geochem. Environ.* **49**, 341 (2002).
- [5] M. Wilke *et al.*, *Am. Mineralogist* **86**, 714 (2001).
- [6] E. Jarosewich, *Meteoritics* **25**, 323 (1990).
- [7] B. Mason, H. B. Wiik, *Am. Mus. Nov.* **2272** 1 (1966).
- [8] B. Mason, H. B. Wiik, *Am. Mus. Nov.* **2106** 1 (1962).
- [9] B. Mason, H. B. Wiik, *Am. Mus. Nov.* **2115** 1 (1962).
- [10] K. Yanai *Proc. 23 Lun. Planet. Sci. Conf.* 1559 (1992).
- [11] M. A. Marcus *et al.*, *Meteoritics Plan. Sci.* (in press).
- [12] A. N. Krot *et al.* in *Protostars and Planets IV*, 1019; D. S. Ebel & L. Grossman, *GCA* **64**, 339 (2000).
- [13] A. E. Rubin, J. T. Wasson, *30th Met. Soc.* 569 (1995).
- [14] M. K. Weisberg *et al.* *GCA* **60**, 4253 (1996).
- [15] G. F. Flynn *et al.* *Science* **314**, 1731 (2006).