

**OXIDATION STATE OF FE IN THE INTERSTELLAR MEDIUM** A. J. Westphal<sup>1</sup>, A. L. Butterworth<sup>1</sup>, J. A. Tomsick<sup>1</sup>, <sup>1</sup> Space Sciences Laboratory, University of California at Berkeley, Berkeley CA 94720, USA

**Introduction:** Fe plays a special role in probing the relative rates of dust destruction and formation in the ISM. While other major rock-forming refractory elements (Mg, Si) are synthesized principally in stars with dust-forming stellar outflows, Fe is synthesized mostly in Type Ia supernovae, which do not produce dust-forming outflows. At least 70% of freshly-synthesized Fe is injected into the interstellar medium in the gas phase[1]. The astronomical observation that >90% of Fe is depleted from the gas-phase in the ISM leads to the conclusion that Fe must condense in the ISM. The condensation mechanism and host phase(s) are unknown. Circumstantial evidence points away from co-condensation of Fe with Mg and Si, pointing toward a non-silicate host for Fe in the solid phase[1]. Here, we combine synchrotron-based X-ray absorption spectra of several mineral standards and two kinds of primitive extraterrestrial materials with X-ray observations of Fe-L ISM absorption with the *Chandra X-ray Observatory* [2] to constrain the mineralogy of the host-phase of ISM Fe.

**Methods:**

**ISM observations:** We used a 51-ksec *Chandra* exposure of an outburst of the X-ray binary XTE J1817–330. The observation was made with the High Energy Transmission Grating, and we used the data from the Medium Energy Grating (MEG), downloading the spectra from the TGCAT website and combining the MEG+1 and MEG-1 spectra. The data include the K absorption edge of singly-ionized Ne, nominally at 848.6 eV. The position of the Ne absorption line is consistent with a energy blueshift of  $0.2 \pm 0.1$  eV.

**Synchrotron observations:** We acquired high resolution library of Fe L-edge X-ray Absorption Near Edges Structure (XANES) spectra at the Advanced Light Source Beamline 11.0.2 Scanning Transmission X-ray Microscope (STXM). The undulator source was calibrated at Ne 867.3eV. Samples included previously characterized metal, troilite, Fe<sub>68</sub> olivine [3,4], spinel (1.46 wt% Fe natural spinel from Natural History Museum, London), and synthetic glasses [5]. We collected data in stack mode, comprising of high spatial resolution (50 nm) X-ray absorption images taken at successive energies across the Fe L23-edges. The highest energy resolution 100 meV. We processed stack data using aXis2000 software [6], converting to Optical Density (OD) XANES spectra by normalizing counts to the incident beam intensity.

Using a linear fit to the pre-edge spectrum, we first subtracted the background, then calculated the cross-section as a function of energy by scaling the OD spectrum so that the L-edge cross section at  $\sim 730$  eV was

equal to that provided by the Center for X-ray Optics (CXRO),  $1.81 \times 10^4$  (g cm<sup>-2</sup>)<sup>-1</sup>. The resulting library of L-edge spectra is shown in Fig. 1. Although the spectral shapes are similar, the absorption strengths are highly variable. Metal shows the smallest amplitude, and crystalline silicates show strong resonances.

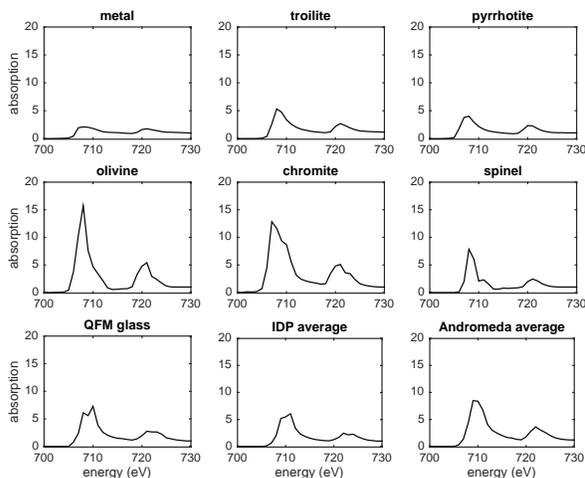


Fig. 1: Library of L-edge spectra from mineral standards. Each absorption spectrum is normalized to  $1.8 \times 10^4$ (g/cm)<sup>-1</sup>, the amplitude of the absorption step at  $\sim 730$  eV.

**Analysis:** We took two independent approaches to the data analysis. In the first, we initially rebinned the data by a factor of four. We then used a quadratic with a step to fit the background in the pre-edge (<705 eV) and post-edge (>730 eV) regions, and subtracted the quadratic portion only. In Fig. 2, we show the resulting ISM absorption spectrum overlaid with absorption spectra of kamacite, pyrrhotite, QFM glass, and olivine, one of the crystalline silicates. All crystalline silicates in our library show very large amplitudes in the XANES region as compared with the ISM absorption spectrum. This is consistent with infrared observations of the ISM, which indicate that >97% of ISM silicates are amorphous[7]. We focused on three standards that are likely to be the closest analogs to the host phases for Fe in the ISM: kamacite, pyrrhotite, and QFM glass. In Fig. 3, we show the  $\Delta\chi^2 = 1$  ( $1\sigma$ ) and  $\Delta\chi^2 = 4$  ( $2\sigma$ ) contours over the space of metal and sulfide fractions. Projections of these contours onto the two axes give confidence intervals of the parameters.

Our second approach was to fit the 0.6-0.9 keV portion of the *Chandra* spectrum directly with the XSPEC software package with a model consisting of a continuum component and various combinations of dust absorption components. We modeled the continuum with a broad

Gaussian component. While this provides a good fit to the continuum, the reduced- $\chi^2$  is  $\chi^2_\nu = 2.32$  for 341 degrees of freedom (dof) due to narrow absorption lines in the 0.65-0.66 and 0.84-0.86 keV ranges and broader absorption features in the Fe L energy range (0.70-0.74 keV). For the fitting, we removed the energy regions with narrow lines, and modeled the Fe L region. The Fe L modeling was done by converting three of the profiles shown in Figure 1 (a sulfide, a metal, and an oxide) into XSPEC table models.

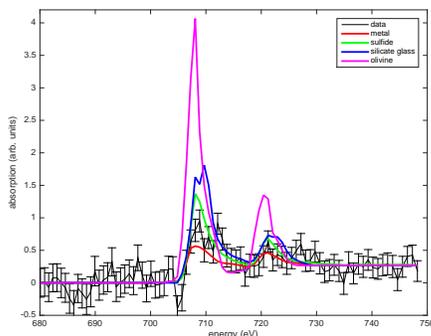


Fig. 2: *Chandra* absorption Fe L-edge absorption data, with metal, sulfide, silicate glass and olivine standards.

With the narrow line regions removed, the Gaussian continuum model gives  $\chi^2_\nu = 1.84$  (307 dof), but the fits are significantly improved to  $\chi^2_\nu = 1.23$ , 1.24, and 1.31 (306 dof) for sulfide, metal, and oxide, respectively. A combination of sulfide and metal provides a small improvement in the fit from  $\chi^2_\nu = 377.4/306$  to  $\chi^2_\nu = 372.1/305$ , which, based on an F-test, indicates a significance for the second component of  $\sim 2.1\sigma$ . The addition of a third dust component (oxide) does not improve the fit at all. Based on the fit parameters, we conclude that the fractions of sulfide, metal, and oxide that contribute to the Fe L absorption are:  $0.38 \pm 0.17$ ,  $0.63 \pm 0.27$ , and  $<0.08$ , respectively ( $1\sigma$  errors are given).

**Discussion:** The *Chandra* data are inconsistent with a large fraction of Fe in the silicate phase. We place a  $2\sigma$  upper limit on the fraction of Fe in silicate of 0.22.

The S/Fe ratio in the solar system is  $\sim 0.5$ . If Fe and S are entirely condensed into Fe metal and FeS, then Fe should be approximately equally partitioned into metal and sulfide, the blue dot in Fig. 3. This value would be expected in a high-temperature condensation sequence, in which Fe metal condenses first at  $\sim 1350\text{K}$ , followed by sulfidation of approximately half of the Fe metal at  $\sim 600\text{K}$ . If, however, Fe and S both condense at low temperature, it is unlikely that the Fe would sulfidize. The condensation value is near the center of the confidence regions for both methods, but Method 2 is more conservative, and gives an acceptable fit for almost any mixture of metal and sulfide except nearly pure sulfide.

We also compared the *Chandra* data to average Fe L-edge spectra taken from a chondritic-porous interplanetary dust particle, thought to originate in a comet, and from fine-grained material from a particle (“Andromeda”) collected by the Stardust spacecraft from the coma of comet Wild 2. These are thought to be among the most primitive solar system materials known in extraterrestrial collections. The match is poor, confirming that these materials have experienced significant processing in the protosolar nebula before incorporation into comets.

We plan to explore further lines of sight in *Chandra* data to reduce the statistical errors, and to explore the variability of Fe-bearing mineralogy in the ISM.

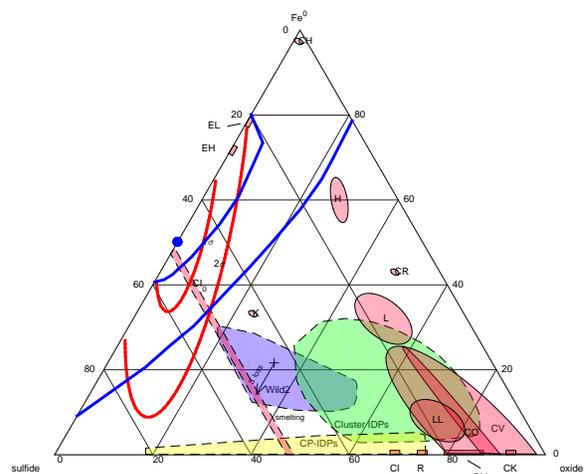


Fig. 3: Oxidation state of Fe in extraterrestrial materials. ISM values derived by the two analytical methods described in the text are shown as red (method 1) and blue (method 2) confidence regions. The expectation value of a high-temperature condensation sequence with solar abundances is shown by the blue dot. Oxidation state of meteorite families and cometary materials (Wild 2, CP-IDPs[8], cluster IDPs[9]) are also shown.

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**References:** [1] Dwek E. (2016) *ApJ* 825, 136 [2] Weisskopf M.C. et al. (2002) *PASP*, 114, 1 [3] Butterworth A. L., et al. (2010) *LPSC XVI*, 2446. [4] Gainsforth Z. et al. (2015) *MAPS*, 50, 976. [5] Stodolna J. et al. (2013) *GCA*, 122, 1. [6] <http://unicorn.mcmaster.ca/aXis2000.html> [7] Kemper F. et al. (2005) *ApJ* 633, 534 [8] Ogliore R. et al. (2010) *EPSL* 296, 278 [9] Westphal A. et al. (2017) *LPSC XLVIII*.