Measurement of the Oxidation State of Fe in the ISM Using X-Ray Absorption Spectroscopy

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Abstract

The relative fractions of Fe in metal, sulfide, or oxide—the Fe oxidation state—in the interstellar medium (ISM) can provide constraints on the processes that operated on material in the protosolar disk. We used synchrotron-based X-ray absorption spectra of three mineral standards and two kinds of primitive extraterrestrial materials to constrain the oxidation state and mineralogy of the host phase of ISM Fe as measured by X-ray observations of Fe-L ISM absorption from the Chandra X-ray Observatory. Oxidation of cometary material appears to have taken place in the nebula, before incorporation into cometary nuclei, although the mechanism is unknown. We also test the hypothesis of Ishii et al. that ISM solids consist largely of Glass with Embedded Metals and Sulfides (GEMS), enigmatic components of primitive interplanetary dust particles. The hypothesis is not consistent with observations. Using Fe L-edge absorption spectra of comet 81P/Wild 2 samples returned by the Stardust mission, we also find that Chandra observations are inconsistent with the hypothesis the cometary fine-grained material consists of unaltered interstellar dust.

Key words: dust, extinction

1. Introduction

The most primitive materials in the solar system reside in comets. The size distribution of minerals in even the finest-grained components of cometary dust particles, however, is inconsistent with the size distribution of interstellar medium (ISM) dust as inferred from astronomical observations (Draine 2009; Gainsforth et al. 2017). This simple observation implies that some processing of material must have occurred in the protosolar disk, even in the outer comet-forming region, in the epoch before comets formed. The nature of that processing is unknown, but the oxidation state of Fe can provide important constraints. Processes and environments that modify materials in the nebula can either oxidize Fe, for example, by heating in the presence of water vapor (Grossman et al. 2012), or reduce it, for example through ion bombardment (Carrez et al. 2002). The oxidation state of Fe varies widely among solar system materials. Indeed, the Fe oxidation state was used by Urey & Craig (1953) to define the first rigorous, quantitative classification scheme for meteorites. So the oxidation state of Fe in the ISM is an important piece of the puzzle, because it defines the starting chemical state of the protosolar cloud that eventually formed the solar system.

Fe also 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 ISM in the gas phase (Dwek 2016). The astronomical observation that >90% of Fe is depleted from the gas phase in the ISM (Jenkins 2009) leads to the conclusion that Fe must condense in the ISM. The condensation mechanism and host phase(s) are unknown. Circumstantial evidence, however, points away from condensation of Fe with Mg and Si, pointing toward a nonsilicate host for Fe in the solid phase (Dwek 2016).

Here, we have combined synchrotron-based X-ray absorption spectra of three mineral standards and two kinds of primitive extraterrestrial materials with X-ray observations of Fe-L ISM absorption observations from the Chandra X-ray Observatory (Weisskopf et al. 2002) to constrain the mineralogy of the host phase and oxidation state of ISM Fe, and to explore the relationship, if any, between interstellar dust and the most primitive solar system materials.

2. ISM Observations

We combined six Chandra observations (Table 1) of the X-ray binary Cyg X-1, with a total exposure time of 92.8 ks. We used observations for which the X-ray source was to the side of its binary companion so as to avoid any possible contamination within the Fe spectrum from the stellar wind, and the orbital phases of Cyg X-1 during the observations are provided in Table 1. The observations were made with the High Energy Transmission Grating (Canizares et al. 2005), and we used the data from the Medium Energy Grating (MEG), downloading the spectra from the TGCat website (Huenemoerder et al. 2011) and processing with the Sherpa software package (Freeman et al. 2001). Final spectra combine the MEG+1 and MEG-1 diffraction orders. The data include the K absorption edge of singly ionized Ne, nominally at 848.6 eV. We rebinned the data by a factor of four.

3. Acquisition of Absorption Spectra

We used an ultramicrotome to cut ~100 nm thick sections of samples onto Cu transmission electron microscope (TEM) grids, or using an FEI DualBeam focused ion beam (FIB) at the Molecular Foundry (MF) at Lawrence Berkeley National Laboratory (LBNL). We identified phases and determined their crystalline/amorphous character using an FEI Titan TEM at the MF at LBL (Figure 1). From our library of Fe-bearing materials, representing various oxidation states, formation processes, and Fe site symmetries, we selected Fe metal, troilite, and amorphous...
silicate glass (reticulite, a natural volcanic glass) to determine the oxidation state of Fe in the ISM. We set upper limits of 1% and 6% on the oxidation (that is, O/Fe) of the metal and sulfide samples, respectively, by measuring the O K-edge spectra on the same spots where we acquired the Fe L-edge spectra at ALS STXM Beamline 5.3.2.2. For comparison with Glass with Metals and Sulfides (GEMS), we used absorption spectra of two GEMS in an interplanetary dust particle (RB-12A31-2), and for comparison with fine-grained primitive silicates, we used absorption spectra of fine-grained material (FGM) associated with a large sulfide recently identified in the Stardust collection from comet Wild 2 (Butterworth et al. 2010; Stodolna et al. 2013; Gainsforth et al. 2015). We acquired GEMS spectra from 680 eV to 735 eV and Wild 2 FGM from 680 to 740 eV. This material may be representative of the least-processed material surviving in the solar system. The elemental composition of the reticulite, GEMS, and Wild 2 FGM are given in Table 2.

We collected high spatial resolution (50 nm) X-ray absorption stacks at beamline 11.0.2.2 at the Advanced Light Source at LBL. Stacks were acquired as images at successive energies across the Fe L23-edges. The highest energy resolution was 100 meV. We converted stack data to Optical Density (OD) XANES spectra by aligning the images and normalizing counts to the incident beam intensity using aXis2000 software. We converted OD to cross-section spectra in MATLAB by first subtracting the background using a linear fit to the pre-edge and scaling so that the post-edge and L-edge absorption lengths were equal to that provided by the Center for X-ray Optics at ~735 eV.

Spectra that we used for this study are shown in Figure 2. For fitting astronomical data, we used three standards: metal, troilite (FeS), and, because infrared observations of the ISM indicate that >97% of ISM silicates are amorphous (Kemper et al. 2005), we used Fe-bearing volcanic reticulite glass, an amorphous silicate. Although the spectral shapes are similar, the absorption strengths of the resonant peaks relative to the tail of the normalized spectra are highly variable. The gas spectrum was taken from tabls (Wilms et al. 2000) on the XSPEC library (Arnaud 1996).

4. Analysis

4.1. Derivation of Extinction Spectra

Our astronomical X-ray observations consist of extinction spectra, the result of absorption and scattering. As pointed out by Corrales et al. (2016), astronomical X-ray Mie scattering

### Table 1

| ObsID   | T0 | Orbital Phase (°) | Δφ | Exposure (ks) |
|---------|----|------------------|----|---------------|
| 107     | 51470.80 | 0.741 | 0.034 | 11.398 |
| 1511    | 51555.30 | 0.836 | 0.030 | 12.624 |
| 2741    | 52302.20 | 0.204 | 0.014 | 2.731 |
| 2743    | 52377.87 | 0.711 | 0.014 | 3.023 |
| 3815    | 52702.66 | 0.765 | 0.124 | 56.837 |
| 13219   | 55597.27 | 0.635 | 0.030 | 6.211 |

Notes:
- a Modified Julian date at the beginning of the observation.
- b Orbital phase of Cyg X-1 at the midpoint of the observation (phase zero corresponds to the black hole being behind the supergiant companion).
- c Change in orbital phase from the start to the end of the observation (in units of 5.599829 terrestrial days).

### Table 2

| Element | Reticulite Composition | GEMS1 Composition | GEMS2 Composition | Wild 2 FGM Composition |
|---------|------------------------|-------------------|-------------------|-----------------------|
| O       | 60.8                   | 56.1              | 59.2              | 52.9                  |
| Na      | 1.2                    | BDL\(^b\)         | BDL\(^b\)         | 0.27                  |
| Mg      | 3.8                    | 13.9              | 5.8               | 1.33                  |
| Al      | 5.9                    | 0.78              | 1.4               | 0.25                  |
| Si      | 19.3                   | 15.3              | 21.1              | 17.39                 |
| S       | 5.2                    | 4.0               | 3.4               | 11.6                  |
| Ca      | 5.2                    | 0.50              | 0.16              | 0.57                  |
| Fe      | 3.8                    | 8.4               | 8.3               | 15.2                  |
| Ni      | BDL\(^b\)              | 0.28              | 0.27              | 0.14                  |

Notes:
- a Atom percent.
- b Below the detection limit.

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Figure 1. Sample selections for acquiring Fe L-edge spectra from Fe-bearing amorphous silicate and GEMS. (A) TEM HAADF image of a 300 nm thick section of reticulite glass without inclusions, prepared by Focused Ion Beam (FIB). STXM line spectra were acquired at the position shown by the dashed red line. Inset, TEM electron diffraction of FIB section. The lack of diffraction spots confirmed that the glass was amorphous. (B) Ultra-microtomed section of a chondritic-porous interplanetary dust particle with GEMS (red outlines). The TEM HAADF image overlaid with the STXM Fe map (yellow) extracted from a stack of 120 images at energies across the Fe L-edge (680–735 eV). Spectra were integrated within each dashed red region, above the background threshold. (C) TEM bright field image of selected GEMS, showing low density amorphous mass with dark Fe metal and sulfide nanometer-sized inclusions.
Figure 2. Fe L-edge absorption spectra used for this analysis. Each absorption spectrum is normalized to $1.8 \times 10^4$ (g/cm$^2$)$^{-1}$, the amplitude of the absorption step at $\sim$750 eV.

cross-sections, and therefore extinction spectra, are sensitive to the particle size distribution. The size distribution of the Fe-bearing phases within interstellar dust particles is not known, but is constrained by microwave and infrared emission, and optical and ultraviolet extinction. We used the Weingartner & Draine (2001; WD01) dust size distribution, which is consistent with and is derived from these observations. However, we introduced an upper size cutoff ($a_{\text{cutoff}}$) to the WD01 distribution as an additional free parameter. The reason is as follows. At ultraviolet and longer wavelengths, randomly distributed, fractal-like aggregates composed of small ($\ll 100$ nm) monomers would be indistinguishable from particles of the same size composed of larger monomers. However, the extinction of X-rays with wavelengths near the Fe L-edge ($\lambda = 1.7$ nm) would be quite different. (Fe-bearing monomers assembled in fractals would be indistinguishable in X-ray observations from the same monomers dispersed in the ISM as physically separated objects.) To calculate scattering cross-sections, we followed Draine (2003) and Corrales et al. (2016). We first calculated optical constants from synchrotron absorption data using the Kramers–Kronig relation implemented in kkcalc (v0.7.3), a Python package written and made publicly available by Ben Watts and Dan Lauk. We then calculated the total scattering spectrum by integrating over the Draine WD01 (Weingartner & Draine 2001) interstellar dust size spectrum, with an upper size cutoff left as a free parameter. As a check, we reproduced the published extinction spectra in Corrales et al. (2016) in their published test case.

4.2. Spectral Fitting to Expected Phases

We fit the astronomical data against derived extinction spectra from metal, sulfide, and amorphous silicate using an eight parameter least-squares fit: we used a cubic continuum (four parameters), metal, sulfide, and silicate basis spectra (three parameters), and the truncation parameter discussed above (one parameter, $a_{\text{cutoff}}$). Regardless of the value of $a_{\text{cutoff}}$, we normalized the extinction spectra to the step height before fitting. We show the best fit in Figure 3. $\chi^2$ was 316.5 with 293 degrees of freedom. Here we used statistical errors only. The excess in $\chi^2$ may be due to uncertainties in the instrumental response matrix. We found only a lower limit on the truncation parameter: the fit using the full WD01 size distribution was as good as any with $a_{\text{cutoff}} > 245$ nm (2$\sigma$). This is consistent with the conclusion of Zeegers et al. (2017), who inferred that a significant population of large dust particles exists in the ISM from observations of ISM extinction at the Si K-edge. In Figure 4 we show the best fits for each of the basis spectra.

Although most Fe is condensed in the ISM, a significant fraction may be in the gas phase. Based on their $XMM$ observations of 4U 1820-30, Costantini et al. (2012) derived a gas-phase Fe fraction of 0.13 ± 0.14. To account for this possibility, we repeated our analysis assuming that 30% of the Fe is in the gas. Including gas changes the shape of the confidence region slightly, without changing the silicate fraction significantly (Figure 5).

4.3. GEMS and Cometary FGM

Glass with Embedded Metals and Sulphides (GEMS) constitute a major but enigmatic component of chondritic porous interplanetary dust particles (Bradley 1994). They show anhedral morphology, and consist of nanophase metal inclusions in an amorphous silicate matrix, with iron sulfides either decorating the surfaces or, rarely, inside the particles. They show a restricted size range, between 100 and 500 nm in the largest dimension. GEMS have been variously proposed to have a solar system (Keller & Messenger 2011) or interstellar (Ishii et al. 2018b, 2008a) origin. Along with equilibrated aggregates, GEMS dominate the silicate fraction of CP-IDPs. Here we test the hypothesis that interstellar silicates consist of GEMS as seen in CP-IDPs. We took three approaches to this
test, using three different assumptions about the particle size distribution. We used the measured GEMS absorption spectra, and computed the extinction spectrum using the method described in Section 3.

In the first approach, we tested the hypothesis that interstellar silicates consist of GEMS-like material, but with the WD01 size distribution, in contrast with GEMS as observed in CP-IDPs. The approach was thus identical with that of the previous section, but using a GEMS spectrum instead of amorphous reticulite. The resulting fit and corresponding composition are shown in Figure 6. As compared with solar abundances (Fe/Si = 0.88), GEMS are deficient in Fe with respect to Si, with Fe/Si = 0.44–0.56 (Keller & Messenger 2011).

If interstellar silicates are GEMS-like, then the remaining 36%–50% of the Fe must be in some other phases. Assuming that these are either metal or sulfide, this leads to a compositional constraint on the oxidation state of Fe. The observed composition is strongly inconsistent with this hypothesis (Figure 6).

In the second approach, we tested the hypothesis that interstellar silicates are GEMS-like both in composition and in particle size distribution, as observed in CP-IDPs. We summed over the observed sizes reported by Keller & Messenger (2011) in analyses of 44 GEMS, but assumed that the metals and sulfides followed the WD01 distribution with a upper cutoff, as in analyses described above. Because the Keller & Messenger size distribution is dominated by large particles, overabsorption is more significant. The unconstrained fit to the data is good ($\chi^2 = 313$), but the fit in the region of the ternary allowed by the composition is poor ($\chi^2 > 342$) (Figure 7).

Based on detailed TEM observations of GEMS and the observation of C-rich rims within GEMS, Ishii et al. (2018b) have recently suggested that GEMS are aggregates of smaller components. In the absence of a particle size distribution, this hypothesis is difficult to evaluate here, but it should lie between the first and second approaches above.

Finally, in the third approach, we test the hypothesis that interstellar dust consists of silicates containing nanophase metal and sulfides that have been oxidized and are now observed as GEMS in CP-IDPs. The GEMS Fe L-edge absorption spectrum (Figure 2) shows an enhanced resonance consistent with a major fraction of Fe in the silicate phase, about 50% of the Fe. In principle, oxidation of Fe could occur at any time between residence in the ISM and analysis in the laboratory—in the solar nebula, during atmospheric entry, or due to exposure to terrestrial oxygen (Figure 8).

To test the hypothesis that GEMS are just oxidized interstellar dust, we generated a synthetic spectrum of an unoxidized GEMS. To do this, we measured the size distribution of metals and sulfides in a GEMS and used the observed size distribution to compute the expected extinction spectrum. Unoxidized GEMS should have a mix of metal and sulfide with a particle size distribution similar to that seen in present GEMS. Because the Fe metal grains in the GEMS were typically on the order of 10 nm in diameter, the synthetic extinction spectrum did not exhibit a significant pre-edge scattering feature—the turn-up in the data below 680 eV and 705 eV in Figure 4—so the fit to the Chandra data was poor, with $\chi^2 = 515$, indicating that GEMS in which Fe is entirely sequestered in metal and sulfides are an unlikely candidate for interstellar silicates.

It is possible that the oxidation process could change the size distribution of the metal and sulfide inclusions within a GEMS. Typically, oxidation would require heating, and the particles could
Figure 4. Best fit to Cyg X-1 absorption data using metal, sulfide, and silicate (293 d.o.f., 82% metal, 18% silicate, no sulfide), and the best fits using only single components (metal, sulfide, and silicate, 295 d.o.f.). The green curves are the continuum components of each fit.

Figure 5. (Left) Oxidation state of condensed ISM Fe assuming that 30% of the Fe is in neutral gas. (Right) Best fit to Chandra observations.
either grow through Ostwald ripening, or could shrink as Fe is consumed into the silicate. In the first case, the original metal grains in the unoxidized GEMS would have been even smaller than those we observe in IDPs, which is inconsistent with an interstellar origin. In the second case, the original Fe grains could have started as larger grains and shrunk as Fe oxidized and moved into the silicate. However, since only about 50% of the Fe in the IDP RB-12A31-2 GEMS is oxidized, the metal grains could not

Figure 6. Test of hypothesis that interstellar silicates have a GEMS-like composition but a WD01 particle size distribution. (Left) Measurement of the composition of ISM Fe using metal, troilite, and GEMS as end-members. The gray shaded area is the allowed region based on GEMS composition, under the assumption that interstellar silicates are GEMS-like and the overall composition is protosolar. (Right) The fit to the data within the region of the compositional constraint is significantly worse ($\chi^2 > 357.7$) than the best fit to the data with no compositional constraint ($\chi^2 = 316$).

Figure 7. Test of hypothesis that interstellar silicates have a GEMS-like composition and the size distribution observed in real GEMS in CP-IDPs. (Left) Measurement of the composition of ISM Fe using metal, troilite, and GEMS as end-members. The gray shaded area is the expected composition if interstellar silicates are GEMS-like. (Right) The fit to the data within the region of the compositional constraint is significantly worse ($\chi^2 > 342.9$) than the best fit to the data with no compositional constraint ($\chi^2 = 313$).
be greater than $2^{1/3} = 1.25$ times larger in radius than observed in GEMS in the laboratory. Since the size distribution necessary to produce the turn up between 680 and 705 eV is about 100 nm, this is also inconsistent with ISM dust.

Finally, we tested the hypothesis that unaltered interstellar solids are preserved in cometary material. We compared the Chandra data extinction spectra derived from analyses of FGM from a particle (“Andromeda,” Gainsforth et al. 2016) collected and returned by the Stardust spacecraft from the coma of comet Wild 2. We used the truncated WD01 particle size distribution. If interstellar solids were identical to the Andromeda FGM, we would expect a measurement with little or no additional metal or sulfide. Instead, the measurement (Figure 9) is dominated by metal, so is inconsistent with this hypothesis.
5. Discussion

In a pioneering techniques paper, Lee (2009) proposed using Fe L-edge XANES data to interpret L-edge extinction spectra in astronomical X-ray observations. They did not attempt to assess the oxidation state of Fe in the ISM. They also used absorption spectra only, without addressing the need to derive extinction spectra from absorption spectra, which requires a model of the dust size distribution, as we describe above.

Our measurement of the Fe oxidation state of the ISM is inconsistent with a major component of Fe in silicate, and is broadly consistent with the lack of correlation of Fe with Mg and Si reported by Dwek (2016). The best fit to the data indicate that no more than 38.5% (2σ) of Fe in the ISM, at least in this line of sight, resides in silicate. Whether this is consistent with the gas-phase depletions reported by Dwek (2016) is an open question.

Iron in the ISM is strongly reduced by comparison with most, but not all, materials from small bodies in the solar system (Figure 3). The oxidation state observed in laboratory analyses was determined by the oxygen fugacity in the formation region of these materials, and by oxidation, usually due to aqueous chemistry, after incorporation into parent bodies. Carbonaceous chondrites (CI, CM, CK, CV, CO, and CR) are generally the most oxidized (Westphal et al. 2009 and references therein). No cometary samples measured so far lie within the ISM confidence region (Westphal et al. 2009, 2017; Ogliore et al. 2010). It is intriguing that the CH carbonaceous chondrites, the H ordinary chondrites, and the EL and EH enstatite chondrites lie within the 2σ ISM confidence region. Because they are depleted in siderophile and chalcophile volatile elements (e.g., Zn), these groups are thought to represent inner solar system objects that formed from materials that were processed in the hot solar nebula Brearley et al. (1998). (CH chondrites are also strongly depleted in lithophile volatile elements, but H, EH, and EL are not.) Nevertheless, our results raise the intriguing possibility that their Fe oxidation states were inherited from the ISM.

Constantini et al. (2012) studied the Fe-L, Mg-K, and O-K edges of the X-ray binary 4U 1820-30, and found conclusions compatible with those presented here. The abundance of Fe in the gas phase was low, but not insignificant (13%), the Fe could not be detected in silicate, and the Fe-L edge was dominated by Fe metal. They noted that they had large residuals on the long wavelength side of the spectrum—i.e., they did not fit a complete extinction spectrum but only an absorption spectrum. Because of this it was not possible to evaluate whether the Fe metal grain sizes were compatible with GEMS. They also did not have the ability to fit Fe sulfide.

5.1. Oxidation in the Early Solar System

This paper does not address the complexity of processes that converted presumably well-mixed, homogeneous ISM material into the diversity of small bodies in the early solar system. We observe only the initial and final states. However, it is clear that net oxidation was required in a variety of degrees to arrive at the remarkable diversity of oxidation states shown in Figure 3.

A hot gas with cosmic abundances is highly reducing because of the extreme excess of H. ISM dust evaporated and recondensed in such a gas would be expected to have an oxidation state indicated by the star shown in Figure 3. In a cooling gas, S does not go into solids until quite late, when S sulfidizes Fe metal at ~700 K, so if gas is lost from the system, for example, by stellar outflows or out-of-plane outward transport from the inner solar system, it preferentially removes S. As a consequence, less FeS is eventually produced. Similarly, FeS might be lost through relatively mild heating and conversion of FeS to Fe metal, with loss of S from the large-scale transport.

The S/Fe ratio in the solar system is ~0.5 (Lodders & Fegley 1998). If Fe and S are entirely condensed into Fe metal and FeS, then Fe should be equally partitioned into metal and sulfide. This value would be expected in a high-temperature condensation sequence, in which Fe metal condenses first at ~1350 K, followed by sulfidation of approximately half of the Fe metal at ~700 K (Ebel & Grossman 2000). This point is marked with the red star in Figure 3. Sulfidation of Fe would place an additional constraint on the oxidation state of Fe: the region of oxidation state to the left of the S/Fe = 0.5 is excluded. To the extent that sulfide is pyrrhotite (Fe1−xS, x < 0.2), or that sulfur condenses in significant quantities in other phases—H2S or polycyclic aromatic hydrocarbons—this boundary will shift away from sulfide-rich composition in Figure 3.

The net pathway for carbonaceous chondrites and ordinary chondrites, except perhaps for H chondrites, may have been oxidation of metal. The most likely candidate for these processes is in an aqueous environment in a wet parent body. This may be consistent with the proposed origin of the carbonaceous chondrites at or just beyond the snowline in the early solar system (Scott et al. 2018).

The Fe oxidation state in the ISM and that of cometary material is disjoint. The path from the ISM to cometary materials remains unclear, since comets were probably too cold to have ever hosted liquid water.

An unsolved problem in meteoritics is an understanding of the origin of Fe-rich olivine (FeMg2−xSiO4) and low-Ca pyroxene Fe2Mg1−xSiO3, which are unexpected to condense from a gas cooling from high temperature (Grossman et al. 2012). The Fe content of these minerals is an increasing function of oxidation state. Even in an oxygen-rich condensing gas, these minerals are expected to be very Fe-poor, with fayalitic contents (≈Fe/(Fe+Mg)) of no more than 4% (Grossman et al. 2012). Before the return of samples from comet Wild 2, it was thought that oxidation of crystalline silicates might have occurred within the parent bodies of meteorites, during aqueous alteration or thermal metamorphism. However, olivines returned from comet Wild 2 show a very broad and nearly flat distribution in fayalitic content from 0 to ~40%, and a range of fayalitic content from 0% to 97% (Frank et al. 2014), so the oxidation appears to have taken place in a nebular environment, through an unknown mechanism.

We note that all three collections of cometary materials have the potential to have suffered oxidation state change, or the appearance of oxidation state change through sample bias, between release from the parent body and analysis in the laboratory. Samples from comet Wild 2 were captured in the coma at 6.1 km s−1, which may have led to reduction of Fe through smelting: the arrow in Figure 3 indicates that the original material may have been less reduced than observed in laboratory analyses. Cometary materials captured in the stratosphere may suffer from biases against metal-rich, high-density particles,
because of their shorter residence time. This is consistent with the metal-poor composition of individual small CP-IDPs, in contrast to the relatively metal-rich composition of particles from giant cluster IDPs. However, none of these capture or sample bias effects go in a direction to reconcile cometary oxidation state with that of the ISM.

5.2. Summary

A comparison of Fe L-edge absorption spectrum of continuum X-rays from Cygnus X-1 with extinction spectra derived from synchrotron X-ray microprobe analyses of mineral standards leads to the following conclusions:

1. Observations are consistent with the hypothesis that Fe is sequestered principally in metals, at least in this line of sight. The data are marginally consistent with Fe evenly divided between sulfide and metal, a composition that would be expected if Fe and S reside entirely in metal and sulfide, e.g., in a high-temperature condensation sequence. Less than 38.5% (2σ) of Fe resides in amorphous silicates.

2. The observations are inconsistent with the hypothesis of Ishii et al. (2018b) that interstellar silicates consist of GEMS or their subcomponents as found in chondritic-porous IDPs. This conclusion is robust even if some Fe is oxidized between residence in the ISM and observation in the laboratory.

3. Fine-grained cometary material, as represented by FGM returned by the Stardust mission from comet 81P/Wild 2, with a WD01 size distribution predicts an extinction spectrum that is inconsistent with Chandra observations.

4. Our conclusions are consistent with the independent analysis of Zhukovska et al. (2018), who concluded, based on astronomical observations of dust depletions and modeling of dust evolution, that 70% of interstellar Fe resides in metallic nanoparticles, either in silicates (their preferred site) or as independent particles.

The same methodology may be applied to explore the oxidation state of ISM Fe in other lines of sight, toward other X-ray binaries.

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