

## A Sintered and Sulfidized Equilibrated Aggregate from an Interplanetary Dust Particle

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Heating processes in the early solar nebula are presumed to have melted precursor dust to create igneous objects called equilibrated aggregates (EAs). EAs range from  $< 1 \mu\text{m}$  up to  $\sim 100 \mu\text{m}$ , and show textures indicative of melting and formation of minerals under a variety of conditions ( $f\text{O}_2$ , T, P). In this work, we study an EA from an interplanetary dust particle (L2071 cluster 12, “Humpty and Dumpty”) captured by a stratospheric flight over North America in 2008. We prepared it using a Focused Ion Beam (FIB), and examined it using the TitanX Transmission Electron Microscope (TEM) at the Molecular Foundry in Berkeley, CA. Figure 1A shows the EA with a pyrrhotite/metal core which is Fe-rich on the left (red), and Ni-rich on the right (blue), and silicates (green). The small boxed area contains fine-grained silicates also shown in Figure 1B. Figure 1B is colored using Non-negative Matrix Factorization (NMF) of the EDS map. Olivine and kosmochloric [Joswiak] clinopyroxene (CPX) crystals are embedded in an Al-, Si-rich glass. The Mg# varies from 73 to 83 depending on the phase. See compositions in Table 1. Phase identifications are based on EDS with the exception of the large olivine and pyrrhotite which are confirmed by electron diffraction as well.

The Ni-rich side of the sulfide has Ni/Fe = 0.3 by at%, 2 wt% Co and no Mn. The Ni-poor side of the sulfide has Ni/Fe = 0.03 by at%, 1 wt% Co, and no Mn. On average Ni/Fe = 0.12 by at%. Figure 2A shows that diffraction of the sulfide matches pyrrhotite 4C zone 110. The FWHM of the superlattice reflections ( $0.44 \text{ nm}^{-1}$ ) is much wider than the lattice reflections ( $0.22 \text{ nm}^{-1}$ ) which indicates that the sulfide is far out of equilibrium. Using the method of [Gainsforth] we find that the degree of equilibration matches sulfides grown by reaction of  $\text{H}_2\text{S}$  gas with metal at about  $500^\circ\text{C}$ . Faint reflections at  $2 \text{ \AA}$  coupled with a deficit of S by EDS likely indicate the presence of metal as well.

Brightfield imaging of the olivine (Figure 1A, “Ol”) shows that it has a 50 nm damage rim where many defects are present. In addition, the neighboring sulfide contains a metal-rich rim of similar thickness.

[Jilly-Rehak] previously measured O isotopes and found that the silicates had a  $\Delta^{18}\text{O} = 0\text{‰}$ . This is consistent with many silicates found in comets [Ogliore, Westphal], as well as FeO-rich silicates in type II chondrules [Schrader]. These observations are consistent with the silicates being formed or altered within our Solar System (i.e., not pre-solar).

Using the glass thermometer from [Putirka, Helz] we found a glass equilibration temperature between  $920 - 1015^\circ\text{C}$ . As glass and sulfide are the most rapidly equilibrating phases in our aggregate, they should best constrain the final conditions of formation or alteration.

We also modeled the phases via MELTS [Smith, Ghiorso, Asimow] using the bulk composition of the fine silicates (Figure 1B) with added Fe+Ni in the ratio found in the sulfide (Figure 1A). It was not possible to correctly model the higher temperature phases: olivine and pyroxene. At  $f\text{O}_2 < \text{IW}-3$ , modeling predicts LIME olivine with MnO between 10-20 wt%, and FeO  $< 1 \text{ wt } \%$ . At  $f\text{O}_2 > \text{IW}-3$  and  $T > 1300$

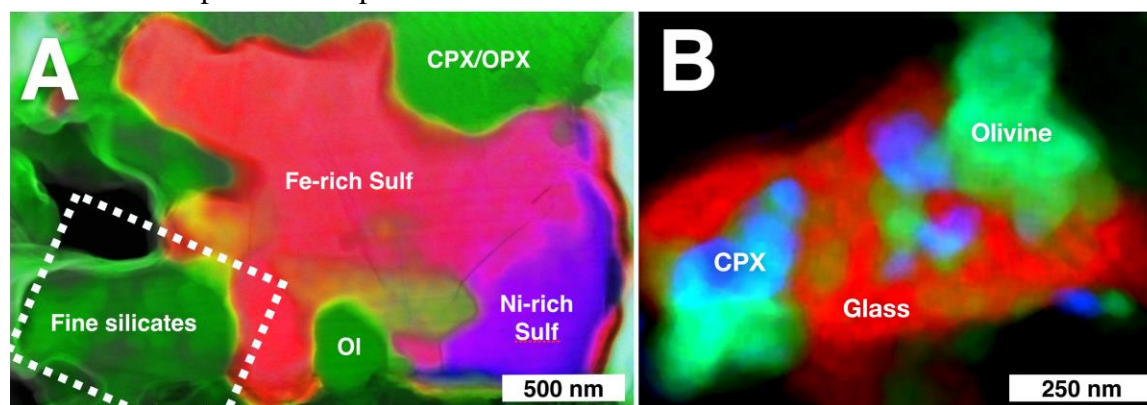
C we could produce MnO near the experimental value of 0.8 wt % but the olivine was too Fe-rich. Similarly, it was not possible to simultaneously match Al<sub>2</sub>O<sub>3</sub>, FeO and CaO in the CPX. Both of these phases are clearly out of equilibrium. We could model approximately the correct glass compositions at nearly any fO<sub>2</sub> only if T < 1000 °C. If the sulfide formed by sulfidation of metal, then the metal could only be modeled with the correct bulk Fe/Ni ratio near fO<sub>2</sub> = IW-1.

Therefore we suggest the aggregate originally formed near IW-1 by sintering of relict silicates and metal near 1000 °C. It later partially sulfidized at T ≈ 500-1000 °C. The second step could have occurred later in the same event or during a subsequent sulfidizing event.

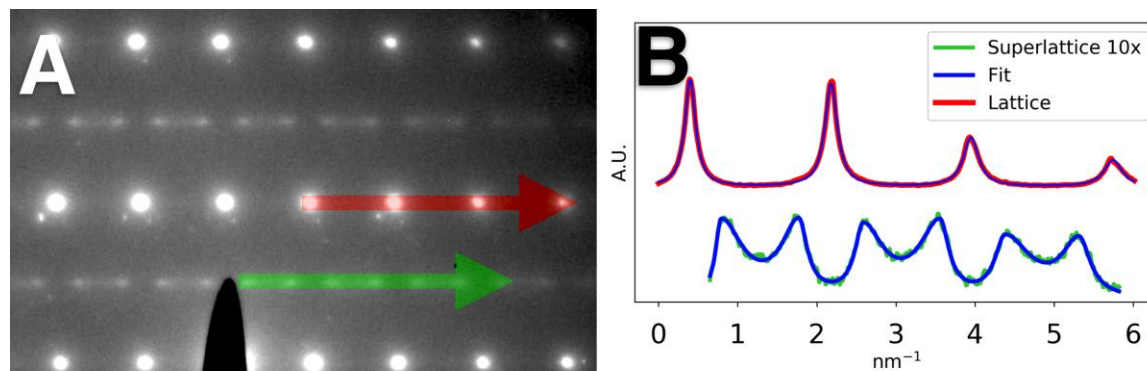
[Joswiak] recently studied fine-grained kosmochloric pyroxenes associated with olivine, glass and sulfides from comet Wild 2. Preferential partitioning of Al, Ti to pyroxene and Mn to olivine indicated cogenetic formation. In our EA, Al and Ti do partition to pyroxene, but Mn behaves less predictably. Texturally, our fine-grained silicate region resembles Wild 2 material such as Arinna-A-1 [Joswiak, Fig 3] which suggests a relationship to other cometary material. [Schrader] examined agglomeratic olivine chondrules in CR meteorites and made a case that Wild 2 and AO chondrules both formed from AOA-like precursors. The low T formation of this aggregate fits with the idea that fine grained aggregates were formed and then lightly heated by a gentle chondrule formation process. In this case, the heating should have been ≤ 1000 °C while still holding a high fO<sub>2</sub> and/or fS<sub>2</sub>.

Phase	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	MgO	FeO	CaO	MnO	Na <sub>2</sub> O	K <sub>2</sub> O	Mg#
Coarse Olivine	36.84				39.82	22.11		1.23			76
Fine Olivine	44.65		0.26		39.04	15.25		0.80			82
Coarse CPX	49.12	0.95		6.57	13.80	7.69	20.90	0.97			76
Fine CPX	56.30	0.33	5.05	4.31	13.49	4.12	14.14		2.27		83
Coarse OPX	45.07			1.79	27.38	17.47	7.00	1.29			74
Fine Glass	78.20		20.02		0.85	0.57				0.38	73

Table 1. Compositions of phases in Oxide Wt %.



**Figure 1.** A) STEM/EDS view of a FIBed equilibrated aggregate (EA). Image is an LRGB with HAADF (luminance), Fe (red), Mg (green), and Ni (blue). Ol=Olivine, Sulf=sulfide, CPX=clinopyroxene. B) Zoomin on fine grained silicates in the EA. The phases are colored using NMF (see text): Glass (red), Olivine (green), CPX (blue).



**Figure 2.** SAED down zone 110 of pyrrhotite 4C. The red arrow shows a trace across four lattice reflections while the green arrow shows a trace across 6 superlattice reflections. The traces are shown in B. B) Lattice (red) and superlattice (green) peak shapes with fits (blue) using split-Lorentzian peaks and after removal of a linear background. The amplitude of the superlattice reflections has been multiplied by 10. The FWHM of the superlattice reflections is about double that of the primary reflections indicating formation out of equilibrium (see text).

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