FIB-TEM INVESTIGATIONS OF Fe-Ni-SULFIDES IN THE CI CHONDRITES ALAIS AND ORGUEIL.

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Introduction: The CI chondrites are primitive meteorites with bulk compositions matching the solar photosphere for all but the lightest elements [1]. They have been extensively aqueously altered, and are composed primarily of fine-grained phyllosilicate matrix material which is host to carbonates, sulfates, sulfides, and minor amounts of olivine and pyroxene [2, and ref. therein]. The alteration, while extensive, is heterogeneous. For example, CI-chondrite cubanite [3] and carbonate grains [4] differ on mm to sub-mm scales, demonstrating multiple aqueous episodes. CI-chondrite variability is also evidenced by degree of brecciation, abundance and size of coarse-grained phyllosilicates, olivine and pyroxene abundance [4], as well as Ni-content and size of sulfide grains [4,5].

Our previous work [6] revealed Orgueil sulfide grains with variable Ni-contents, metal:S ratios, crystal structures and textures. We continue to explore the variability of CI-chondrite pyrrhotite (Po, $(FeNi)_{1-x}S$) and pentlandite (Pn, $(Fe,Ni)_9S_8$) grains. We investigate the microstructure of sulfides within and among CI-chondrite meteorites in order to place constraints on the conditions under which they formed.

Samples & Techniques: Samples of Orgueil and Alais were provided by the Vatican Observatory and the Smithsonian Institution, respectively. EMPA was done on the Cameca SX-100 (JSC). Electron transparent thin sections were prepared and analyzed on the Quanta 3D FIB-SEM and JEOL 2500 SE STEM (JSC).

Results: The bulk of the investigated Fe-Ni sulfide grains (n=107) in Orgueil have <1.0 at.% Ni and metal:S ratios consistent with 4C monoclinic Po, $(FeNi)_7S_8$. However, EDX mapping of 64 grains reveals that ~50% have areas of increased Ni-content, which trends with an increase in the metal:S ratio (see table 1, figs. 1-6). TEM analyses of 9 nine grains show that the textures of the Ni-enriched regions coarsen with increasing Ni-content and metal:S ratios. Low-Ni grains are structurally consistent with 4C monoclinic Po. The microstructures of those with higher Ni-contents vary and include lenses of Ni-rich 4C Po, regions of Ni-rich 4C Po, intergrowths of 4C Po and 6C monoclinic Po/Pn, and discrete Pn and Po crystals.

Seven of 15 EDX-mapped Alais sulfide grains contain areas of enriched Ni-content. To date, FIB-TEM analyses have been done on 2 of the grains, one of which showed minor Ni-enrichment in thin section. The first grain is 4C monoclinic Po, the second is an assemblage of discrete Pn and 4C Po crystals.

Discussion: Plotting the compositional data on the 100-135°C Fe-Ni-S ternary [7] reveals that the Ni-rich material in Orgueil is distinct from the Ni-rich material in Alais [5]. While the Alais compositional data fits the 100-135°C ternary [5], the Orgueil Fe-Ni-sulfide compositions show a better correspondence to phase relations in the 25°C Fe-Ni-S ternary [8]. We propose that higher metal:S ratios and Ni-contents in Orgueil Po grains result from a low-T process in which Ni fills vacancies (□) in the crystal structure and preferentially replaces Fe^{3+}, as ferric ions are more easily disrupted from the crystal structure relative to ferrous ones [9].

$$Fe_5^{2+}Fe_2^{3+}\square\, S_8^{2-} \xrightarrow[+Ni^{2+}]{-\square,\,-Fe^{3+}} Fe_5^{2+}Ni_3^{2+}S_8^{2-}$$

The Ni-rich, vacancy-poor end member ($Fe_5Ni_3S_8$) has a metal:S ratio of 1 and contains 18.75 at. % Ni. Higher Ni contents are accommodated by the pentlandite structure. This low-temperature process could account for the variety of Fe-Ni-sulfides we see in Orgueil. The microstructures of the Alais grains are similar to the Orgueil end-members (4C Po, and an assemblage of discrete 4C Po and Pn crystals); none of the intermediary textures or structures (e.g., lenses, intergrowths) have been found. This may reflect higher processing temperatures for Alais, consistent with the better fit of its compositional data to the 100-135°C ternary.

Conclusion: Data suggest that Alais sulfide grains experienced higher temperatures than those in Orgueil (100-135°C vs. 25°C). We propose that in many cases the formation of Pn was kinetically prohibited in Orgueil. We predict that future FIB sections of Ni-enriched sulfides in Alais will contain discrete Po and Pn crystals, and should not exhibit the microstructural variety seen in the Orgueil sulfides. EELS work will be done to test the hypothesis that ferric iron is being preferentially replaced by Ni in the Orgueil sulfides.

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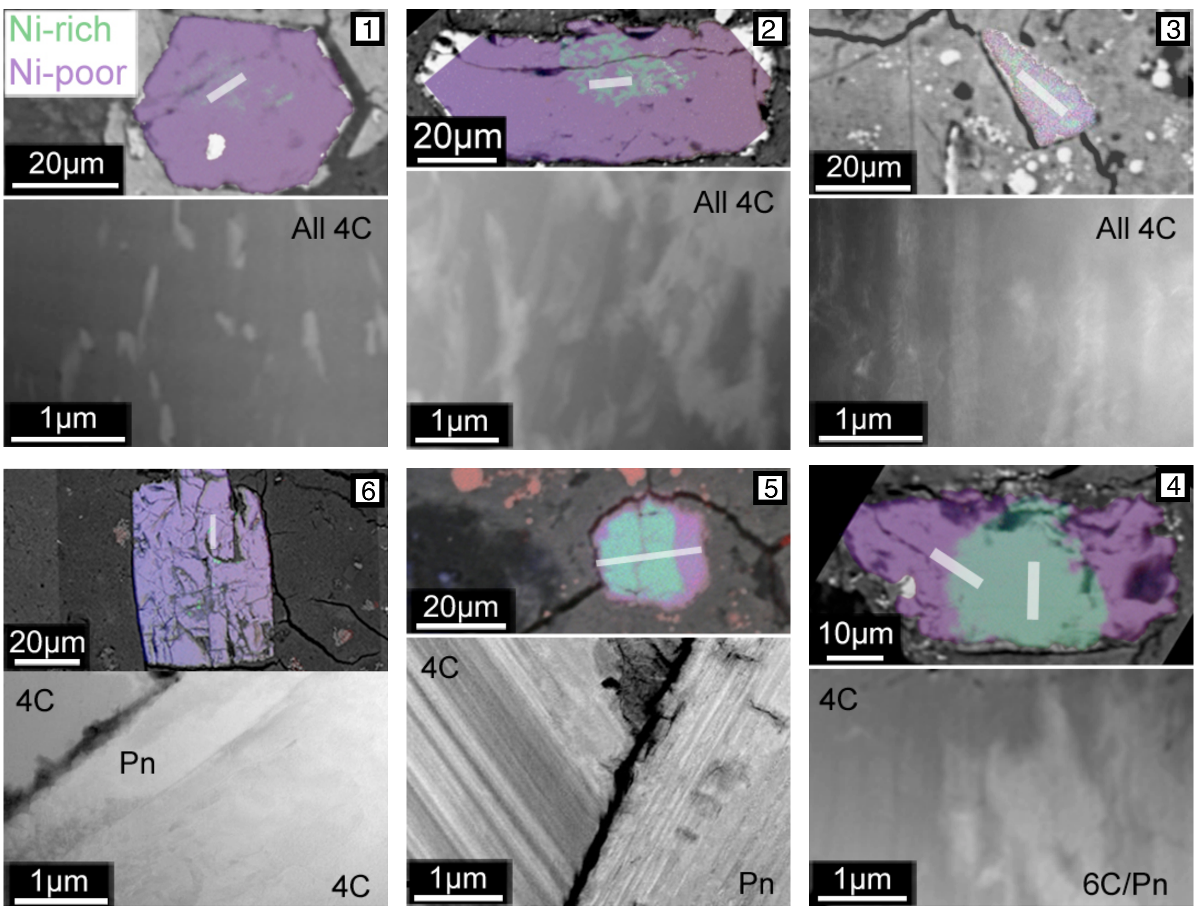
Acknowledgements: Special thanks to the Vatican Observatory and the Smithsonian Institution for providing samples. This work was supported by the NASA Postdoctoral Program (elb) and the NASA Cosmochemistry program (lpk).

Table 1. Compositional (EMPA), microtextural (TEM) and structural (TEM) data from Alais and Orgueil sulfide grains.

Fe (at.%)	Ni (at.%)	Co (at.%)	S (at.%)	metal:S	Sample	Microtextures and crystal structures
45.8±0.6	0.8±0.2	0.0	53.4±0.6	0.87	Orgueil low-Ni*	Chemically homogeneous 4C Po
44.0	2.5	n.d.	53.5	0.87	Orgueil H4 (*figure 1*)	Lenses of Ni-rich material within a Ni-poor matrix, all 4C Po
45.9	0.7	n.d.	53.4	0.87		
34.2	15.1	n.d.	50.7	0.97	Orgueil Z1 (*figure 2*)	Mottled areas of Ni-rich material intergrown with Ni-poor material, all 4C Po
35.6	13.3	n.d.	51.1	0.96		
46.2	0.6	n.d.	53.2	0.88		
37.6	10.3	0.4	51.7	0.93	Orgueil K1 (*figure 3*)	Diffuse columns of Ni-rich material intergrown with Ni-poor material, all 4C Po
40.1	7.2	b.d.l.	52.7	0.90		
41.4	5.6	0.4	52.6	0.90		
41.0	5.9	b.d.l.	53.1	0.88		
26.9	24.3	n.d.	48.8	1.05	Orgueil H3 (*figure 4*)	Ni-poor 4C Po intergrown with a high-Ni phase which is structurally intermediate to 6C Po and Pn
33.2	15.8	n.d.	51.0	0.96		
45.4	0.9	n.d.	53.7	0.86		
24.9	26.9	1.0	47.2	1.12	Orgueil G5 (*figure 5*)	Discrete 4C Po and Pn crystals The 4C Po has distinct Ni-rich and Ni-poor stripes
24.0	27.7	1.0	47.3	1.11		
24.0	27.3	0.9	47.8	1.09		
24.8	26.5	0.9	47.8	1.09		
37.0	8.7	1.0	53.2	0.88		
36.5	18.5	0.5	44.5	1.25	Orgueil K9	Pn crystals with lamellar features
27.5	24.2	0.7	47.6	1.10		
45.6	0.8	0.0	53.6	0.87	Alais 6695-7-G1	Chemically homogeneous 4C Po
46.1	0.6	0.0	53.3	0.88		
24.3	25.2	0.9	49.6	1.02§	Alais 6695-7-G2 (*figure 6*)	4C Po crystal crosscut by a Pn crystal
46.3	0.6	b.d.l.	53.1	0.88		

*EMPA data is the average composition ±2σ of Orgueil Fe-Ni-sulfide grains with <1.0 at.% Ni. Three FIB sections were made from grains in this population.
§weight percent total for this datapoint is 98.1, all others are between 98.5 and 101.5.



Figures 1-5 (Orgueil) and figure 6 (Alais) correspond to a subset of the grains listed in Table 1. For each, there is: 1) a BSE image of the sulfide with x-ray maps superimposed (Fe= red, S= blue, Ni= green) and FIB-section locations noted (white rectangles); and 2) HAADF images from the corresponding FIB sections. In the HAADF images, brighter material is more Ni-rich; 4C= 4C pyrrhotite, 6C = 6C pyrrhotite, Pn = pentlandite. As the Ni-content in the Orgueil sulfides increases (fig. 1→fig. 5), the Ni-rich areas have coarsening textures and increasing metal:S ratios.