

**IRON- AND IRON-NICKEL SULFIDES IN CHONDRITIC INTERPLANETARY DUST PARTICLES**

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**MINI-ABSTRACT:** All examined IDPs contain much more pyrrhotite than troilite, suggesting that the former was a common nebular condensate phase. Hydrous IDPs contain pentlandite which is probably of secondary origin.

The bulk of theoretical and experimental investigations indicate that the first sulfur-containing mineral to form in the early solar nebula should have been stoichiometric FeS (troilite) [1]. Troilite is hexagonal, and crystallizes in a distorted NiAs type structure. However, primitive carbonaceous chondrites are generally found to contain pyrrhotite ( $Fe_{1-x}S$ ) instead of troilite. Pyrrhotite is based upon the troilite structure, but with ordered Fe omissions yielding a host of hexagonal to monoclinic structures, also generally exhibiting a debilitating variety of polytypism and twinning [2]. We are aware of only one report of experimental pyrrhotite formation as a condensation smoke [3]. Can the pyrrhotite in the carbonaceous chondrites be the result of post-nebular metamorphic reactions, or are our models of sulfide growth in the nebula merely simplistic? We have initiated a comprehensive electron beam determination of the compositions of sulfides in the most primitive extraterrestrial material currently available: cometary and asteroidal particles called chondritic interplanetary dust particles (IDPs). Fortunately, sulfides are generally abundant in IDPs, and are in fact probably the only major minerals found in practically all IDPs. Few previous studies have addressed this subject [4].

The IDPs were embedded in EMBED-812 low-viscosity epoxy and ultramicrotomed. The slicing was halted approximately half-way through each particle to yield a "potted butt" useful for backscattered electron imaging at 13kV. We have found that this procedure permits unparalleled petrographic examination in the SEM at high magnification. The ultramicrotomed slices were then used for determination of mineralogy and mineral chemistry by standard TEM techniques. We have obtained 186 EDX analyses of iron- and iron-nickel sulfides in 32 different chondritic interplanetary dust particles using a JEOL 2000 STEM, equipped with a light element LINK detector. The small grain size of these sulfides (generally 15-50 nm across) made matrix generation of spurious X-rays a problem in some cases. However, duplicate analyses of sulfide standards showed that analytical precision was a gratifying 1%, relative, where matrix effects were not a factor.

We show in Figures 1&2 the results separately for hydrous and anhydrous chondritic IDPs (a hydrous particle may contain any quantity of hydrous phases - an anhydrous particle contains none). The different types reflect significantly different physico-chemical histories. Put rather simply, the anhydrous IDPs include cometary particles as well as particles that have been subsequently geologically processed on anhydrous regions of asteroids. The hydrous IDPs must have been resident on a hydrous asteroid, since hydration reactions in the nebula or on a cometary body are considered unlikely [5]. We should expect to see mineralogical differences between sulfides from anhydrous and hydrous IDPs, since some of the former should contain only nebular and presolar materials.

Figure 1 shows the analytical results projected onto Fe-Ni-S atomic % ternary diagrams. No sulfides with more than 2 atomic % Ni were found in any anhydrous IDP, in marked contrast to the hydrous IDPs which displayed a wide range of Ni compositions in the sulfides. However, before discussing the Ni-rich compositions let us concentrate on the Ni-poor ones. Figure 2 shows the compositional range of Ni-poor sulfides (those with  $\leq 5$  atomic % Ni), projected onto the S-Fe binary join. The iron sulfide compositional distribution of the chondritic IDPs is essentially identical for both hydrous and anhydrous types. While troilite (FeS) is present among both types pyrrhotite ( $Fe_{75}S$  -  $Fe_{96}S$ ) clearly predominates. For the anhydrous IDPs, which should include the most primitive grains, the predominance of pyrrhotite over troilite implies that the former should have formed in the nebula. This result is therefore counter to our expectations based upon theoretical as well as experimental considerations [1], which are that for as long as metal is present troilite should be the stable sulfide phase.

Could the observation of pyrrhotite predominance be due to some selection bias or terrestrial contamination effect? We do not believe so for the following reasons: (1) Only chondritic particles were chosen for study, which should not have introduced a significant bias according to our present understanding; (2) All sulfides found in each thin section were analyzed, precluding selection bias; (3) Atmospheric entry heating would have served to produce troilite from pyrrhotite, rather than the opposite reaction, since sulfur is more volatile than iron under atmospheric conditions; (4) Contamination by a sulfur-containing aerosol in the stratosphere should not have penetrated deeply into a particle; (5) Oxygen was determined in the course of each analysis, and the lack of any in these analyses indicates that terrestrial oxidation is not a factor. Finally, we note that pyrrhotite has been previously described from both hydrous and anhydrous IDPs by independent investigators [6&7].

## SULFIDES IN IDPS: Zolensky M.E. and Thomas K.

Experimental studies performed by Lauretta and Fegley [1] showed that troilite forms at the expense of metal during sulfidation, and that the initial troilite rim about a metal grain consists of small randomly oriented, separated crystals. In our study only one unambiguous example of sulfide rimming a Fe-Ni metal grain was encountered. We suggest that this initial troilite can easily exfoliate from the metal core in the nebula. At this point the troilite is subject to further sulfidation, and pyrrhotite is thereby produced since metal is no longer in direct chemical communication. We therefore propose that pyrrhotite is a common nebular solid, and might predominate over troilite. An exception to this would be where sulfidizing metal grains become trapped within growing olivine or pyroxene crystals (or other material), preventing the spalling process and maintaining equilibrium between metal and troilite.

We observe that pyrrhotite also predominates among iron sulfides in hydrous IDPs. These sulfides could be remnant nebular sulfides, or represent a portion of a second sulfide generation formed during the parent body alteration episode. Crystallographic or sulfur isotope analyses might reveal the correct paragenesis.

In contrast to the situation for the anhydrous IDPs, Ni-rich sulfides are abundant in the hydrous IDPs, as shown in Figure 1. Their compositions extend between the Fe-S join and the pentlandite compositional range (the latter is shown as a line in Figure 1), as reported by previous workers. These compositions are thus basically intermediate between pyrrhotite and pentlandite [8] (following the trend of the high-temperature monosulfide  $[(\text{Fe}, \text{Ni})_{1-x}\text{S}]$  solid solution [2]), and could represent fine intergrowths of these two minerals. Since the majority of these grains measure less than 50nm, this intergrowth would be on the scale of nanometers. Alternatively, it is possible that these represent minerals truly intermediate in composition between pyrrhotite and pentlandite; for example  $\text{Fe}_9\text{S}_8$  with the pentlandite structure has been synthesized [9]. However, our electron diffraction data for these intermediate sulfides indicate structural similarities to pyrrhotite rather than pentlandite. It is well known that pentlandite forms during alteration at relatively high oxygen fugacities (above the  $\text{Fe}/\text{FeO}$  buffer), and so the observation of pentlandite (or at least Ni-rich sulfides) in hydrous IDPs is consistent with formation during aqueous alteration on (in) a hydrous asteroid. Future work will concentrate on the evolution of oxygen and sulfur fugacities in the nebula and asteroids implied by our results.

- [1] Lauretta D.S. and Fegley B. (1994) *Meteoritics* 29, 490; [2] Vaughn D.J. and Craig J.R. (1978) *Mineral Chemistry of Metal Sulfides*. Cambridge University Press, p. 305-308; [3] Osaka T. et al. (1976) *Journal of Crystal Growth* 34, 92-102; [4] Keller L.P. et al. (1993) *Lunar Planetary Science Conf. XXIV*, 785-786; [5] Zolensky M.E. and Barrett R.A. (1994) *Meteoritics* 29, 616-620; [6] Tomeoka K. and Buseck P. (1984) *Earth and Planetary Science Letters* 69, 243-254; [7] Bradley J.P. (1994) *Geochimica et Cosmochimica Acta* 58, 2123-2134; [8] Cambel B and Jarkovsky J. (1969) *Geochemistry of Pyrrhotite of Various Genetic Types*. Komenský University Press, p.164-171; [9] Nakazawa H. et al. (1973) *Nature Physical Science* 242, 13-14.

Figure 1

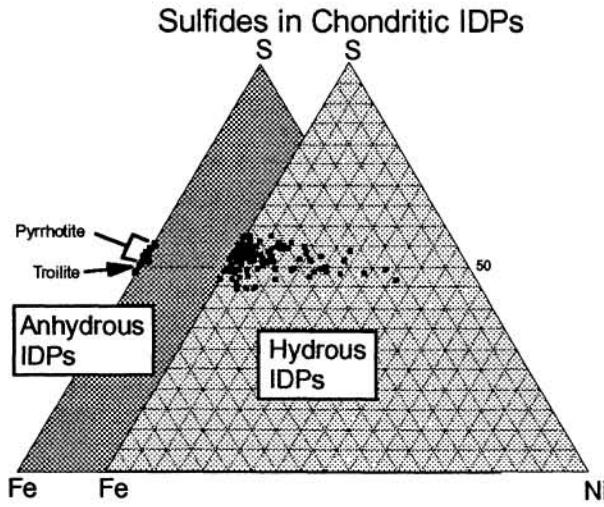


Figure 2

