

LOW TEMPERATURE SULFIDES IN CI CHONDRITES & STARDUST. E. L. Berger¹, L. P. Keller², D. J. Joswiak³, and D. S. Lauretta¹. ¹Lunar and Planetary Laboratory, University of Arizona, Tucson AZ 85721, USA. ²Robert M. Walker Laboratory for Space Science, ARES, NASA Johnson Space Center, Houston TX 77573, USA. ³Department of Astronomy, University of Washington, Seattle WA 98195, USA. (elberger@lpl.arizona.edu).

Introduction: The strongest evidence from Comet Wild 2 for preservation of grains that experienced aqueous alteration at some point in their history may be low-temperature sulfide minerals similar to those in the CI chondrites such as cubanite, pentlandite, and pyrrhotite [1, 2]. Unraveling the mechanisms and conditions of sulfide formation – through detailed characterization of cometary and meteoritic samples, thermodynamic modeling, and experimentation – has implications about large-scale mixing of low-temperature assemblages in the early Solar System. Here we present preliminary results of our investigation of such sulfides from Stardust tracks and compare them to analogous phases in CI chondrites.

Cubanite: Prior to the Stardust Mission, extraterrestrial CuFe_2S_3 had only been found in CI chondrites [3]. It is believed to be a hydrothermal alteration product [2]. The discovery of this mineral in the Stardust population has implications for the low-temperature history of Comet Wild 2.

CI chondrites: We have characterized cubanite grains from Alais and Orgueil on the Cameca SX50 electron microprobe at LPL. The composition of the cubanite is near stoichiometric CuFe_2S_3 with trace amounts of Ni. It occurs in association with pyrrhotite and as isolated grains. In two cases cubanite grains appear to have overgrown pyrrhotite (Figure 1).

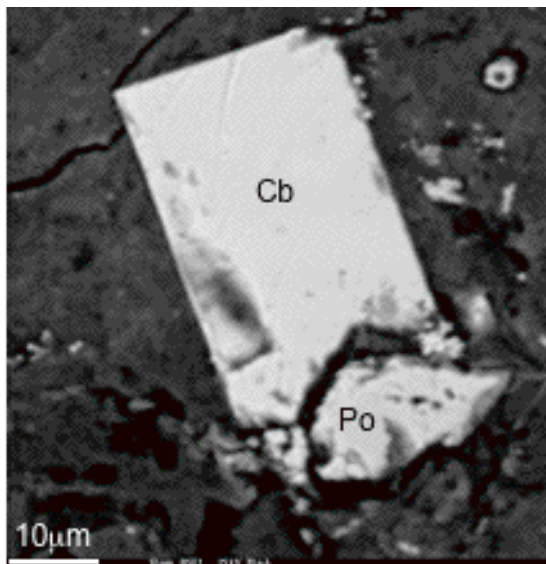


Fig. 1. BSE of cubanite (Cb)/Pyrrhotite (Po) assemblage (Orgueil, USNM TS 234-3)

Stardust: Track 26 (C2054, 5, 26, 1, 16) contains a cubanite grain located near the exterior of a terminal particle. Initial TEM analysis of the grain was done at the University of Washington. Further analysis was done on the JEOL 2000FX STEM, and the JEOL 2500SE 200keV FE-STEM at JSC. EDX of the particle and aerogel host yields the following composition: 46.2 at.% O, 17.2 at.% Si, 18.2 at.% S, 12.8 at.% Fe, and 5.6 at.% Cu (Figures 2, 3), consistent with stoichiometric CuFe_2S_3 embedded in aerogel. SAED patterns in three orientations are consistent with low-temperature orthorhombic cubanite [4] (e.g., Figure 4). The d-spacings are not consistent with isocubanite or any other known copper-iron sulfide [5].

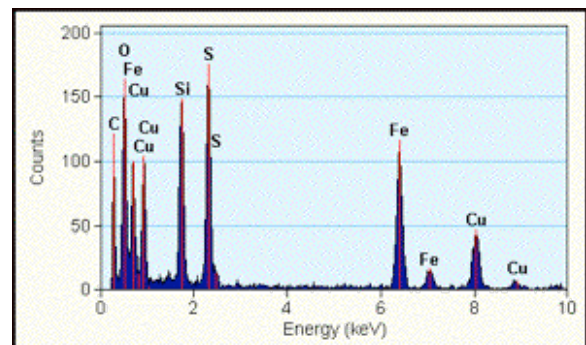


Fig. 2. EDX of cubanite (C2054, 5, 26, 1, 16)

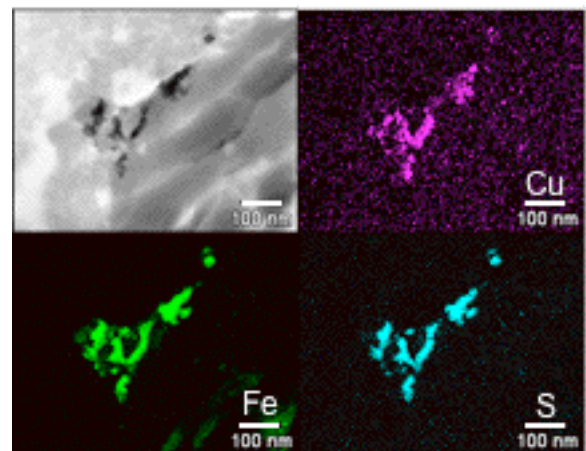


Fig. 3. X-ray maps of cubanite (C2054, 5, 26, 1, 16)

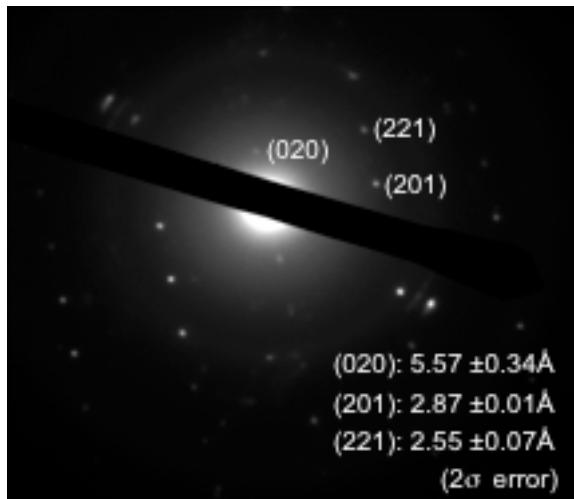


Fig. 4. SAED for the [20-4] zone of cubanite (C2054, 5, 26, 1, 16)

Discussion: The crystal structure of this Cu-Fe sulfide places a constraint on the maximum temperature of alteration. CuFe_2S_3 has two polymorphs: a low-temperature orthorhombic form (cubanite) and a high-temperature cubic form (isocubanite). CuFe_2S_3 undergoes an irreversible phase transition as the temperature increases to 210°C : cubanite \rightarrow isocubanite [6]. Upon cooling below 210°C isocubanite does not revert to orthorhombic cubanite, but rather exsolves chalcopyrite and pyrrhotite [7-9].

The presence of orthorhombic cubanite in Stardust samples has three implications: 1) the particle formed at low temperature; 2) the particle did not experience temperatures above 210°C during its residence on Wild 2; and 3) the particle was not significantly heated during capture into the aerogel.

We predict that the CI-chondrite cubanite, like that of Stardust, is the low temperature orthorhombic form. This structure would be consistent with the petrologic evidence suggesting that CI-chondrite cubanite formed at a later stage than pyrrhotite by precipitating from an aqueous fluid as the parent body cooled [2]. SAED studies are needed to confirm this prediction.

Other sulfides: Pentlandite $[(\text{Fe},\text{Ni})_9\text{S}_8]$ and pyrrhotite $[(\text{Fe},\text{Ni})_{1-x}\text{S}]$ are ubiquitous in both Stardust particles and CI chondrites.

CI chondrites: Bullock et al. (2005) [2] characterized pentlandite and pyrrhotite in the CI-chondrite suite; average Ni values are 0.8 ± 0.3 at.% in pyrrhotite and 25.1 ± 3.2 at.% in pentlandite (2σ error).

Stardust: Initial analyses of pyrrhotite and pentlandite grains from C2054, 5, 27, 1, 1 show compositions of 53.0 at.% S, 46.5 at.% Fe, 0.5 at.% Ni and 49.0 at.% S, 23.5 at.% Fe, 27.5 at.% Ni, respectively.

Discussion: Based on Fe-Ni-S phase diagrams [10] pyrrhotite/pentlandite assemblages on CI chondrites

equilibrated at $100\text{-}135^\circ\text{C}$ [2]. This temperature is consistent with other estimates of alteration conditions on the CI-chondrite parent body. Data from oxygen isotopes suggest an alteration temperature of $\sim 150^\circ\text{C}$ [11]; modeling of hydrous asteroids (CM- and CI-like) predicts temperatures of $50\text{-}150^\circ\text{C}$ [12].

The Ni contents of the Stardust pyrrhotite and pentlandite grains fall, within error, in the ranges reported for the CI chondrites, raising the possibility that these grains formed by a similar process. However, these two phases have not been observed in direct contact in the Stardust collection. Such a relationship is needed to determine if they formed concurrently.

Planned trace element measurements and continued compositional and crystal structure analyses of Stardust and chondrite sulfides will better constrain how similar the CI-chondrite sulfides are to Stardust sulfides.

Outlook: Thermodynamic modeling predicts the fluid from which the cubanite precipitates has a pH between 7-10 over the temperature range $10\text{-}300^\circ\text{C}$ and that the major aqueous sulfur species is HS^- . Hydrothermal re-crystallization experiments, to model parent-body precipitation processes, are being conducted over the predicted parameter space by controlling pH, T, and oxygen fugacity. Low-temperature gas-solid reactions are planned to model cubanite formation via nebular corrosion processes. The successful synthesis of orthorhombic cubanite (which has not been achieved by any lab, to date) will constrain the formation environment (nebular corrosion/parent-body precipitation) and source material for cubanite.

Conclusion: Compositions of sulfides from Wild 2 are similar in many respects to those in the CI chondrites, suggesting a possible relationship between the two types of materials. The presence of low temperature orthorhombic cubanite in the Stardust collection suggests that during its formation, residence in Wild 2, and during collection to the aerogel, this grain remained at temperatures below 210°C .

References: [1] Zolensky M. et al. (2006) *Science* 314, 1735. [2] Bullock E.S. et al. (2005) *Geochim Cosmochim Acta* 69, 2687. [3] Kerridge J. F. et al. (1979) *Earth Planet Sc Lett* 43, 359. [4] Fleet M. E. (1971) *Z Kristallogr* 132, 276. [5] Downs R. T. and Hall-Wallace M. (2003) *Am Mineral* 88, 247. [6] Caye et al. (1988) *Mineral Mag* 52, 509. [7] Miyamoto et al. (1988) *Mater Res Bul* 15, 907. [8] Pruseth et al. (1999) *Eur J Mineral* 11, 471. [9] Putnis (1977) *Phys Chem Miner* 1, 335. [10] Naldrett (1989) *Magmatic Sulfide Deposits*. Oxford University Press: New York, 186p. [11] Clayton R. N. and Mayeda T. K. (1999) *LPS XXX*, Abstract#1795. [12] Zolensky, M. E. et al. (1989) *Icarus* 78, 411.

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