PYRRHOTITE AND PENTLANDITE IN LL3 TO LL6 CHONDRITES: DETERMINING COMPOSITIONAL AND MICROSTRUCTURAL INDICATORS OF FORMATION CONDITIONS. D. L. Schrader1 and T. J. Zega2, 1Center for Meteorite Studies, School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-1404, USA (devin.schrader@asu.edu), 2Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona 85721, USA (tzega@lpl.arizona.edu).

Introduction: The compositions, textures, and crystal structures of sulfides can be used to constrain oxygen fugacity, aqueous, thermal, and cooling history [e.g., 1–5]. The most abundant sulfides in extraterrestrial samples are the pyrrhotite group [(Fe,Ni,Co,Cr)$_s$S], which can occur with pentlandite [(Fe,Ni,Co,Cr)$_s$S$_3$]. The pyrrhotite group sulfides are largely nonstoichiometric and have a range of compositions (0<s<0.125) and distinct crystal structures (polytypes). The stoichiometric end members are 2C (trollite; FeS, hexagonal) and 4C (Fe$_s$S$_3$, monoclinic) pyrrhotite. There are also non-integral NC-pyrrhotites with intermediate compositions with 0<s<0.125 (all hexagonal); which includes the integral 5C (Fe$_s$S$_{10}$), 6C (Fe$_s$S$_{12}$), and 11C (Fe$_s$S$_{11}$) pyrrhotites [e.g., 6–8]. Intergrowths of NC-pyrrhotites with 2C or 4C pyrrhotite are common in terrestrial assemblages [6].

Geothermometry of pyrrhotite-pentlandite intergrowths in meteorites shows that most formed via primary cooling from high temperature or thermal metamorphism [e.g., 9–11]. Sulfides in the LL4 to LL6 chondrites equilibrated between 600 and 500°C, consistent with formation during cooling after thermal metamorphism [11]. Moreover, because sulfides are present in both asteroids and meteorites, their comparison could yield valuable insights. Analyses of Hayabusa particles have identified asteroid 25143 Itokawa as LL5–6 chondrite material [e.g., 12,13], thermally metamorphosed between ~780 and 840°C [12]. Sulfides were observed in Hayabusa particles [12], and may record additional information on the formation conditions of asteroid Itokawa.

Our goal is to determine the origins and formation conditions of sulfides in LL3 to LL6 chondrites, so that we can compare them with Hayabusa sulfides and understand their origins in future studies.

Samples and Analytical Procedures: Sulfides consisting of pyrrhotite and pentlandite in Semarkona USNM1805-17 (LL3.00), Soko-Banja USNM3078-1 (LL4), Siena USNM3070-3 (LL5), and Saint-Sévérin USNM2608-3 (LL6) were selected for analysis. Their chemical compositions were studied with the Smithsonian Institution JEOL 8900 Superprobe electron probe microanalyzer (EPMA, [11]) and the University of Arizona (UAz) Cameca SX-100 EPMA. X-ray element maps and high-resolution images of a sulfide assemblage from each meteorite was obtained with the FEI Helios NanoLab 660 focused-ion-beam scanning-electron microscope (FIB-SEM) at UAz and the JEOL JXA-8530F Hyperprobe EPMA at Arizona State University (ASU). The FIB-SEM was also used to extract ~10 × 5 µm sections transecting the pyrrhotite-pentlandite interfaces within sulfide grains from each meteorite, which were thinned to electron transparency (<100 nm) using methods of [14]. FIB sections were then analyzed using the 200 keV aberration-corrected Hitachi HF5000 scanning transmission electron microscope (TEM) at UAz.

**Figure 1.** FeSnI (RGB composite) X-ray map of Semarkona (LL3.00) FIB section showing pyrrhotite (po) pentlandite (pn) intergrowth.

**Results:** EPMA analyses: The compositions of pyrrhotite and pentlandite vary with petrographic type. In pentlandite, the Ni (17.5±0.6 to 20±1.4 wt.%; LL3 to LL6; mean±1σ) and Co (0.39±0.17 to 0.77±0.63 wt.%) contents increase and the Cr content decreases (0.04±0.05 wt.% to below detection limit [<0.02 wt.% wt.%]), between LL3 and LL6 chondrites. In pyrrhotite, no Co was detected (detection limit <0.09 wt.%) and while Cr is present in pyrrhotites in LL3 to LL5 chondrites (mean ~0.03 wt.%), it is below the detection limit (detection limit <0.02 wt.%) in the LL6 chondrite.

EPMA analyses of pyrrhotite in Semarkona (LL3.00; 0<x<0.065; n = 64), Soko-Banja (LL4; 0.005<x<0.052; n = 54), and Saint-Sévérin (LL6; 0<x<0.077; n = 51) indicate it is dominantly the 2C polytype, but that some 6C pyrrhotite is present. Pyrrhotite in Siena (LL5; 0<x<0.060; n = 40) mostly contains 2C pyrrhotite, but appears to contain more 6C pyrrhotite than the other LL chondrites studied.
The morphology of pentlandite-pyrrhotite intergrowths in the meteorites varies: lamellae of pentlandite occur within pyrrhotite in Semarkona (LL3.00); blebs of pentlandite with islands of pyrrhotite occur in Sokobanja (LL4) and Siena (LL5); and blocky pentlandite in pyrrhotite occurs in Saint-Séverin (LL6).

**TEM results:** The FIB section of sulfide from Semarkona (LL3.00) was selected to preferentially sample pentlandite, and consists of pentlandite intergrown with pyrrhotite (Fig. 1). Selected-area electron-diffraction (SAED) patterns index to 2C and 6C pyrrhotite and pentlandite.

The FIB section of sulfide from Sokobanja (LL4) contains a grain of pentlandite with laths of pyrrhotite, all within pyrrhotite. The host pyrrhotite is polycrystalline, although SAED patterns show that the distinct grains are all closely oriented. SAED patterns of distinct pyrrhotite grains index to 2C and 4C pyrrhotite on one side of the pentlandite grain, and 6C pyrrhotite on the other. Constraining the polytype of the pyrrhotite laths within the pentlandite grain is tentative (SAED patterns indicate 2C, 4C, 5C, or 6C; 2C is the best fit), indicating it may be a non-integer NC-pyrrhotite.

The sulfide in Siena (LL5) contains a grain of pentlandite (with sub-µm pentlandite lamellae around the margin of the grain; Fig. 2) within pyrrhotite. Pyrrhotite consists of multiple domains with similar orientation, but additional SAED patterns are required to determine polytype(s). SAED patterns index to pentlandite with multiple, closely oriented domains, indicating it is likely a single crystal.

The sulfide in Saint-Séverin (LL6) contains blocky pentlandite in pyrrhotite [15]. SAED patterns index to 2C pyrrhotite and pentlandite [15].

**Figure 2. Ni X-ray map of Siena (LL5) FIB section.**

**Discussion:** The major and minor element compositions of pyrrhotite and pentlandite trend with the degree of thermal metamorphism. Therefore, chemical analyses of sulfides could potentially be used to determine the metamorphic type of the host LL chondrite.

In rare cases troilite (2C pyrrhotite; x = 0) was identified via EPMA. However, nearly all pyrrhotites in LL chondrites are non-stoichiometric, with some pyrrhotite compositions indicating 6C pyrrhotite; no 4C pyrrhotite was identified via EPMA.

TEM analyses of pyrrhotite in Semarkona (LL3.00) and Saint-Séverin (LL6) are consistent with those of their EPMA analyses. In contrast, TEM analyses of pyrrhotite in Sokobanja (LL4) and Siena (LL5) are more complex than inferred from EPMA analyses. Sokobanja (LL4) contains polycrystalline pyrrhotite potentially consisting of 2C, 4C, 5C, and 6C pyrrhotite. The pyrrhotite in Siena (LL5) may be non-stoichiometric non-integral pyrrhotite. Additional analyses are planned to confirm this result.

TEM reveals complexities in pyrrhotite not observable via EPMA (e.g., polycrystalline pyrrhotite and sub-µm pentlandite lamellae; Fig. 2). Since the interaction volume of the electron beam during EPMA analyses is significantly larger than SAED patterns in TEM, EPMA analyses provide average compositional analyses of structurally complex and compositionally heterogeneous pyrrhotites.

Additional FIB sections and TEM analyses of sulfides are underway to investigate microstructural trends with metamorphic grade and shock metamorphism on the compositions and microstructure of the sulfides. Analyses of sulfide bearing Hayabusa samples, courtesy of JAXA, are planned for comparison.


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