Widespread evidence for high-temperature formation of pentlandite in chondrites

Devin L. Schrader^{1*†}, Jemma Davidson², and Timothy J. McCoy¹

¹Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, 10th & Constitution Avenue NW, Washington, D.C. 20560-0119, USA

²Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Road NW, Washington, DC 20015-1305, USA

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*Corresponding author: Devin L. Schrader

†Present Address:

Phone: 480-965-0720

Email: schraderd@asu.edu

Center for Meteorite Studies

School of Earth and Space Exploration

Arizona State University

P.O. Box 871404

Tempe AZ 85287, USA

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ABSTRACT

By investigating the compositional and textural evolution of sulfides within a wide range of relatively pristine, aqueously altered, and thermally metamorphosed chondrites we constrain the equilibration temperatures of sulfide minerals and compare them to the metamorphic history of their host meteorite. Sulfides in Mighei-like carbonaceous chondrites are complex as they equilibrated mostly between 100 and 135°C, but some may have equilibrated at temperatures up to 600°C. This is consistent with some CM chondrite sulfides forming at high temperature during chondrule cooling and others during low-temperature aqueous alteration and/or annealing. Karoonda-like carbonaceous chondrite sulfides equilibrated between 500 and 230°C, which is consistent with formation during cooling and annealing after thermal metamorphism. Sulfides in the LL chondrites equilibrated between 600 and 230°C, and are consistent with formation during chondrule cooling for Semarkona (LL3.00) and during cooling after thermal metamorphism for the equilibrated samples (types 4–6). Sulfides in the Rumuruti-like (R) chondrites equilibrated between 600 and 500°C, and are consistent with formation after thermal metamorphism. The sulfides within the brachinite equilibrated between 600 and 400°C, consistent with formation during cooling after thermal metamorphism.

Contrary to the assertion that pentlandite is solely the product of low-temperature aqueous alteration in many chondrite groups, this study suggests that most sulfides in chondrites are formed at or upon cooling from high-temperature. The evaluation of a single mineral system within samples that retain petrographic context is vital to the interpretation of formation and alteration processes recorded by small extraterrestrial samples, such as those that have been returned by the spacecraft missions Stardust and Hayabusa and will be returned by OSIRIS-REx and Hayabusa2.

1. INTRODUCTION

As the 10th most abundant element in the Solar System, sulfur is a major rock-forming element in terrestrial and early Solar System materials (e.g., Brearley, 2006; Vaughan, 2006; Lodders et al., 2009; Dare et al., 2010; Schrader et al., 2015a). Sulfur is a volatile element that exhibits chalcophile behavior. Sulfides are present in returned samples and a wide range of meteorites with varied metamorphic histories. These include pristine material nearly unaltered since asteroid accretion (e.g., Davidson et al., 2014a; Schrader et al., 2015a), aqueously altered and thermally metamorphosed extraterrestrial materials (e.g., Geiger and Bischoff, 1995; Zolensky and Thomas, 1995; Bullock et al., 2005; Rubin, 2006; Richter and Neff, 2007; Zolensky et al., 2008; Kimura et al., 2011; Harries and Langenhorst, 2013), and partially and fully differentiated meteorites (e.g., McCoy et al., 2006; Schrader et al., 2010a; Gardner-Vandy et al., 2013). Sulfides have been identified in both Stardust and Hayabusa returned samples (e.g., Zolensky et al., 2008; Berger et al., 2011; Nakamura et al., 2011). The most abundant sulfides in extraterrestrial samples are the pyrrhotite group sulfides troilite [FeS] and pyrrhotite [(Fe,Ni,Co,Cr)_{1-x}S], which can occur in combination with other sulfides, such as pentlandite [(Fe,Ni,Co,Cr)_{9-x}S₈], pyrite [FeS₂], and chalcopyrite [CuFeS₂].

Pyrrhotite and pentlandite can form over a range of conditions, via both high- and low-temperature processes, which are recorded by their compositions. Experimental petrologists have determined that the composition of pentlandite varies with equilibration temperature, and constructed equilibrium phase diagrams at a range of temperatures in the Fe-Ni-S system (e.g., Kullerud, 1963a; Kullerud et al., 1969; Misra and Fleet, 1973; Francis et al., 1976; Naldrett, 1989; Karup-Moeller and Makovicky, 1995; Sugaki and Kitakaze, 1998; Etschmann et al., 2004; Raghavan, 2004a). The composition of sulfides, in comparison to these diagrams, can be used to constrain equilibration temperatures. Pyrrhotite-pentlandite intergrowths can form via multiple mechanisms: (1) aqueous alteration (e.g., Brearley, 2006), (2) cooling of a primary high-temperature Ni-rich Fe-Ni-S melt with crystallization of monosulfide solid solution (mss) at ~950°C (Fe,Ni-FeS eutectic; Kullerud, 1963b; McCoy et al., 2006) followed by pentlandite exsolution starting at ~610°C, (3) thermal metamorphism of an Fe-Ni-S assemblage >610°C and

subsequent cooling, (4) annealing between ~600 and 200°C (e.g., Kullerud, 1963a; Misra and Fleet, 1973; Francis et al., 1976; Etschmann et al., 2004), and (5) gas-solid sulfurization (Lauretta et al., 1998). If the Ni content of a sulfide is too low, pentlandite does not form and instead Ni remains in pyrrhotite.

In extraterrestrial samples, pentlandite formation has been attributed to parent body low-temperature metamorphism and/or aqueous alteration, as suggested for the Ivuna-like (CI), Mighei-like (CM), Renazzo-like (CR), and Vigarano-like (CV) carbonaceous chondrites, the LL3.00 ordinary chondrite (OC) Semarkona, and returned samples from comet 81P/Wild 2 (e.g., Zolensky and Thomas, 1995; Bullock et al., 2005; Brearley, 2006; Rubin, 2006; Zolensky et al., 2008; Berger et al., 2011; Kimura et al., 2011; Harries and Langenhorst, 2013). The composition of pyrrhotite and pentlandite within the CI chondrites are consistent with formation during aqueous alteration between 100 and 135°C (Bullock et al., 2005). Furthermore, pentlandite is present in hydrous interplanetary dust particles (IDPs) but absent from anhydrous IDPs, which contain troilite and pyrrhotite, suggesting that pentlandite was an aqueous-alteration product (Zolensky and Thomas, 1995).

In contrast, experimental petrologists have shown that pentlandite can form through alternative pathways. The cooling of high-temperature Fe-Ni-S melts results in pentlandite formation via exsolution below 610°C during the breakdown of crystallized mss into pentlandite and pyrrhotite (e.g., Kullerud, 1963a; Francis et al., 1976; Kelly and Vaughn, 1983; Etschmann et al., 2004). When cooling from a melt, mss crystallizes at ~950°C and then pentlandite exsolution commences at ~610 to 550°C and completes at ~325 to 275°C (Kullerud, 1963a; Francis et al., 1976; Etschmann et al., 2004). Upon heating a solidified sulfide containing pentlandite and pyrrhotite, pentlandite dissolves back into mss above ~610°C and re-exsolves during cooling below 610°C. Annealing/quench experiments result in rapid (~1 hr) initial exsolution of pentlandite at 500 to 230°C (Misra and Fleet, 1973; Etschmann et al., 2004), however not all Ni partitioned into pentlandite and pyrrhotite remained Ni-rich (~17 at.% Ni) after months at constant temperature, indicating the formation of intergrowths of pentlandite and Ni-poor pyrrhotite by annealing requires much longer timescales (Etschmann et al., 2004). Alternatively, pentlandite has also been shown to form as a result of gas-solid kamacite

sulfurization experiments between ~285 and 370°C over one month duration (Lauretta et al., 1998).

The anhydrous formation mechanisms discussed above produce three general textures of pyrrhotite-pentlandite intergrowths (Figs. 1 and 2): (1) pentlandite rims around pyrrhotite; (2) blocky pentlandite, which sometimes contain ‘islands’ of pyrrhotite; and (3) blebs or ‘stringers’ (often termed flame or brush texture) of pentlandite within pyrrhotite (e.g., Newhouse, 1927; Hewitt, 1938; Hawley and Haw, 1957; Francis et al., 1976; Etschmann et al., 2004; Dare et al., 2010). Rapid cooling (quench) results in randomly oriented pentlandite blebs in pyrrhotite, while slower cooling results in oriented blebs and pentlandite lamellae (Francis et al., 1976; Etschmann et al., 2004). In terrestrial magmatic sulfide ore deposits, pyrrhotite and pentlandite are often associated with chalcopyrite and pyrite (Naldrett et al., 1967; Keays et al., 1981; Dare et al., 2010) and sometimes with Co-rich pentlandite (Merkle and Gruenewaldt, 1986).

Recent studies of sulfides in chondrites indicate that not all pentlandite formed via aqueous alteration. Observations of pyrrhotite-pentlandite intergrowths in the CR and CM chondrites suggest that they are primary high-temperature products (pre-accretionary) that formed during crystallization and exsolution below silicate solidus temperatures (Schrader et al., 2010b; 2014; 2015a; 2015b; Singerling and Brearley, 2014; 2015). However, it has also been suggested that pentlandite in CM chondrites exsolved from mss after low- and high-temperature parent body thermal metamorphism (Brearley and Martinez, 2010; Kimura et al., 2011), and formed by gas-solid interactions prior to accretion (Harries and Langenhorst, 2013). In addition, blocky pentlandite in the LL-impact melt Northwest Africa 4859 is attributed to low-temperature annealing (<230°C) after impact heating (Jamsja and Ruzicka, 2010), while pentlandite in CV chondrite metamorphosed clasts were determined to have exsolved at high temperature (~600°C; Jogo et al., 2012).

To critically evaluate the formation conditions of pentlandite within meteorites, we investigated pentlandite and associated sulfides from meteorites covering a wide range of aqueous and thermal histories; including CM, Karoonda-like carbonaceous (CK), LL and Rumuruti-like (R) chondrites, and a brachinite. The evaluation of a single mineral system within samples that retain petrographic context is vital to interpreting formation and

alteration processes recorded by small extraterrestrial samples, such as those that have been returned by the spacecraft missions Stardust and Hayabusa and will be returned by OSIRIS-REx and Hayabusa2.

2. ANALYTICAL PROCEDURE

2.1. Mineralogy and Petrology

Sulfides and silicates in thin sections of 16 meteorites were studied: Mighei USNM3483-3 (CM2), Sutter's Mill (C, CM-like), ALH 85002,87 (CK4), Karoonda USNM2428-3 (CK4), LAR 06868 (CK5), and LEW 87009 (CK6), Semarkona USNM1805-17 (LL3.00), Soko-Banja USNM3078-1 (LL4), Siena USNM3070-3 (LL5), Saint-Séverin USNM2608-3 (LL6), MET 01149,27 (R3), LAP 03639,2 (R4), LAP 031275,2 (R5), LAP 04840,4 (R6), MIL 11207,2 (R6), and EET 99402,6 (brachinite) (Table 1). To minimize the effects of terrestrial weathering, falls and minimally weathered Antarctic meteorites were selected whenever possible. Thin sections were initially characterized using an optical microscope to identify sulfides. Backscatter electron (BSE) images and mineral identification via energy dispersive X-ray spectroscopy (EDS) were conducted on an FEI Nova NanoSEM 600 scanning electron microscope (SEM) at the Smithsonian Institution (SI) National Museum of Natural History, Department of Mineral Sciences.

The major element compositions of sulfides, metals, low-calcium pyroxene (LCP), and high-calcium pyroxene (HCP) were measured with a JEOL 8900 Superprobe electron probe microanalyzer (EPMA) at SI. Polished and carbon-coated thin sections were analyzed with a focused beam as individual points and line scans, with operating conditions of 15kV and 20 nA, and a ZAF correction method (a Phi-Rho-Z correction technique; Armstrong 1988); peak and background counting times were varied per element to optimize detection limits. Only sulfide and metal analyses with totals between 97.5–102.5 wt.%, and stoichiometric silicate analyses with totals between 98.0–102.0 wt.% were retained. Standards and detection limits are listed in Tables 2 and 3.

2.2. Closure temperatures and oxygen fugacities

Minimum temperatures of thermal metamorphism were previously estimated via diffusion-driven geothermometers (e.g., graphite ordering, and olivine-chromite and two-pyroxene equilibration) in the literature (Table 1) for many samples in this study. For those without prior temperatures constraints, and to enable direct comparison to literature data, closure temperatures were calculated for thermally metamorphosed and equilibrated samples using the two-pyroxene geothermometer when suitable mineral pairs were present (Tables 1 and 3). Two-pyroxene equilibration temperatures were determined using the compositions of co-existing LCP and HCP mineral pairs with the QUILF program (Anderson et al., 1993). Each temperature was determined at a pressure estimate of 1 bar; which is a reasonable approximation for an asteroid (e.g., Benedix et al., 2005; Gardner-Vandy et al., 2013). Proper pyroxene projections were computed using QUILF by considering both major and minor element compositions (e.g., Lindsley, 1983) for each pyroxene pair (i.e., coexisting LCP and HCP). Uncertainties on temperatures are determined for each mineral pair by QUILF for two-pyroxene temperatures (from $\pm 25^\circ\text{C}$ to $\pm 194^\circ\text{C}$, 1σ). Multiple mineral pairs (5 to 10) and corresponding temperatures were obtained per sample; suitable mineral pairs were obtained in both chondrules and matrix. Since individual two-pyroxene temperatures were within 2σ for each sample, weighted means using all calculated temperatures were determined to obtain a single temperature for each sample and minimize uncertainties (Table 1).

The corresponding oxygen fugacity ($f\text{O}_2$) for Siena and Saint-Séverin were calculated at the appropriate weighted mean two-pyroxene closure temperature because specific $f\text{O}_2$ values were not available. The $f\text{O}_2$ s were determined from the quartz-iron-ferrosilite buffer reaction (QIFs). The reaction equation is:

The $f\text{O}_2$ for each reaction is determined via the following equation (for simplicity, FeSiO_3 is expressed as Fs):

$$\log(f\text{O}_2)=2\log(a_{\text{Fs}}) - \log K - 2\log(a_{\text{Fe}}) - 2\log(a_{\text{SiO}_2}) \quad (2).$$

The online MELTS calculator (<http://melts.ofm-research.org/CalcForms/index.html>) was used to obtain the activity of ferrosilite (a_{Fs}) (Sack and Ghiorso, 1989; Hirschmann, 1991). The Fe content of Fe,Ni-metal was used to obtain the Fe activity (a_{Fe}) (Siena, $a_{\text{Fe}} = 0.47$; Saint-Séverin, $a_{\text{Fe}} = 0.72$). Following Benedix et al. (2005), we assume a silica activity (a_{SiO_2}) of 0.9 for the three-component system metal-olivine-LCP. The HSC 7.0 Chemistry Reaction Equation module was used to obtain the temperature dependent equilibrium constant (K) at 1 bar. Oxygen fugacities are then referenced to the iron-wüstite (IW) buffer, which was also determined using HSC Chemistry.

3. RESULTS

3.1. Sulfide composition, morphology, and associated minerals

Analyses of major and minor elements were performed on pyrrhotite/troilite/pyrite (495 analyses), pentlandite (439 analyses), Fe,Ni-metal (9 analyses), Co-rich pentlandite (7 analyses), chalcopyrite (5 analyses), and Cu-rich sulfide (1.7–9.7 wt.% Cu; 2 analyses) (Tables 2 and 4). While some analyses indicate the sulfides are troilite, they also contain minor elements (e.g., Ni, Co, Cr, and Cu). For ease of communication, pyrrhotite and troilite, both members of the pyrrhotite group of sulfides, will be collectively referred to as pyrrhotite. The vast majority of data was collected on phase pure grains. However, some of the nearly continuous range in Ni content between pyrrhotite and pentlandite is likely due to beam overlap; pentlandite is determined in Section 4.2 to have ≥ 16 wt.% Ni (Fig. 3, and Tables 2 and 4; Schrader et al., 2015a). Due to the presence of sub-micron size grains of pentlandite in pyrrhotite, sulfide analyses in the CM and R chondrites may include some analyses with beam overlaps. In contrast, beam overlaps in the brachinite, and the LL and CK chondrites are less likely as sulfide analyses were conducted on phase pure pentlandite grains larger than the interaction volume of the EPMA beam (Figs. 1 and 2, and Electronic Annex [EA]-1).

In thermally metamorphosed samples, analyses of LCP and HCP (Table 3) were obtained to facilitate two-pyroxene thermometry and $f\text{O}_2$ calculations.

3.1.1. CM chondrites

Pentlandite (22.2–34.0 wt.% Ni) is common in the CM chondrites and is present as blocky grains, lamellae, and oriented blebs (e.g., Fig. 1a and EA-1) within pyrrhotite (0.26–9.7 wt.% Ni; Fig. 3 and Table 4). Minerals associated with pyrrhotite and pentlandite include sporadic magnetite (Mighei and Sutter's Mill), phosphide around a sulfide grain in one instance (Mighei), and EDS suggests Ir-bearing and Y-bearing Ni-rich sulfides (Mighei; EA-2). The Ir-bearing sulfide may be similar to platinum-group-element bearing sulfides (e.g., $[\text{Os,Ru,Ir}]_2\text{S}_2$) observed by Geiger and Bischoff (1995) in the CK chondrites. In addition, Sutter's Mill also contains what appears to be a hydroxysulfide. Fe,Ni metal was observed in association with pyrrhotite and pentlandite in a single instance in Mighei. Mineral phases surrounding sulfides include olivine, pyroxene, plagioclase, and phyllosilicates.

3.1.2. CK chondrites

Pentlandite (17.3–41.8 wt.% Ni) is the most common sulfide in the CK chondrites and is associated with pyrrhotite and pyrite (Figs. 1b and 3, EA-1, and Table 4). Pentlandite is present as lamellae within pyrrhotite/pyrite and as blocky grains with islands of pyrrhotite/pyrite (Fig. 1b). Magnetite and ilmenite are ubiquitous accessory minerals, while chalcopyrite and Co-rich pentlandite are minor (in ALH 85002 and Karoonda; Figs. 2a, 3, EA-2, and Table 2), and a Y,Ru sulfide (in ALH 85002) and Ag-bearing sulfide (in Karoonda; EDS analyses suggest it is Ag_2S) are rare (EA-2). Rare Ru-bearing sulfides and Ag-bearing sulfides were also observed in the CK chondrites by Geiger and Bischoff (1995). Fe,Ni metal was not observed in association with sulfides. Pyrrhotite and pyrite are typically Ni-rich, containing 0.08–15.7 wt.% Ni (avg. 3.0 ± 4.5 wt.% [1σ]; Table 4). One analysis of Cu-rich pentlandite in ALH 85002 is not included in Table 4, but contains 28.4 wt.% Ni, 0.05 wt.% Cr, 9.7 wt.% Cu, and Co is below detection limit (bdl). Mineral phases surrounding sulfides include olivine, pyroxene, and plagioclase.

Pyroxene is compositionally homogeneous in LEW 87009 (CK6; $\text{Fs}_{25.6\pm0.5}\text{En}_{73.8\pm0.6}\text{Wo}_{0.7\pm0.1}$, N=7; ; $\text{Fs}_{11.3\pm0.9}\text{En}_{41.3\pm0.6}\text{Wo}_{47.4\pm0.8}$, N=8). In LAP 06868 (CK5) LCP is homogenous ($\text{Fs}_{24.8\pm0.4}\text{En}_{74.4\pm0.4}\text{Wo}_{0.8\pm0.2}$, N=14), however HCP is compositionally heterogeneous ($\text{Fs}_{11.3\pm3.8}\text{En}_{42.2\pm5.8}\text{Wo}_{46.5\pm2.4}$, N=11).

3.1.3. *LL chondrites*

While uncommon, pentlandite (16.0–23.7 wt.% Ni) was observed in all four LL chondrites studied, is present as all three textural types, and is associated with pyrrhotite (Figs. 1c, 2b, and 3, EA-1, and Table 4). However, pentlandite is only present as lamellae within pyrrhotite (bdl–15.3 wt.% Ni) in Semarkona. Pentlandite in Semarkona has a lower average Ni content than that in the LL4–6 chondrites (Table 4). Fe,Ni-metal (kamacite and taenite) and chromite are common accessory minerals, while molybdenite (associated with pyrrhotite and found only in Soko-Banja; Fig. 2b and EA-2), ilmenite (Siena), and Cu-rich sulfide (~1.7 wt.% Cu in Siena and ~15 wt.% Cu in Saint-Séverin) are rare. Fe,Ni metal was occasionally observed in association with sulfides. Mineral phases surrounding sulfides include olivine, pyroxene, and plagioclase; phyllosilicates were not observed. The vast majority of sulfides studied in Semarkona are in chondrules with clear glassy mesostasis. Magnetite, potentially an aqueous alteration product, was observed in the matrix of Semarkona.

Pyroxene is compositionally homogeneous in Siena (LL5; $\text{Fs}_{23.7\pm0.5}\text{En}_{74.9\pm0.5}\text{Wo}_{1.4\pm0.3}$, N=13; $\text{Fs}_{8.8\pm0.4}\text{En}_{46.8\pm0.3}\text{Wo}_{44.4\pm0.5}$, N=14) and Saint-Séverin (LL6; $\text{Fs}_{23.3\pm0.3}\text{En}_{75.1\pm0.3}\text{Wo}_{1.6\pm0.1}$, N=11; $\text{Fs}_{9.3\pm0.5}\text{En}_{47.1\pm0.4}\text{Wo}_{43.5\pm0.6}$, N=13).

3.1.4. *R chondrites*

Pentlandite (19.1–38.6 wt.% Ni) is common in the R chondrites, it is present as blocky grains, blebs, and lamellae in association with pyrrhotite (bdl–15.3 wt.% Ni) (e.g., Figs. 1d,e, and 3, EA-1, and Table 4). Chromite is a common accessory mineral, while chalcopyrite is uncommon (present in MET 01149, LAP 031275, and LAP 03639; e.g., Figs. 1d,e, and 2c), and magnetite is rare (MET 01149; EA-1). In some cases, the sulfides are polycrystalline (multiple crystals are discernable due to different orientations of pentlandite lamellae; MET 01149, MIL 11207, and LAP 04840; Fig. 1d). Fe,Ni metal

was not observed in association with pyrrhotite and pentlandite. Mineral phases surrounding sulfides include olivine, pyroxene, and plagioclase. Amphibole was observed in both LAP 04840 and MIL 11207.

While LAP 03639 is officially classified as an R4 and LAP 031275 as an R5 (Satterwhite and Righter, 2008), based on the unequilibrated nature of LAP 031275 (presence of FeO-poor chondrules) and relatively equilibrated nature of LAP 03639, we suggest that LAP 03639 is an R5 and LAP 031275 is an R4 (Table 1).

Pyroxene is compositionally homogeneous in MET 01149 (R3; $\text{Fs}_{28.4\pm1.4}\text{En}_{70.6\pm1.5}\text{Wo}_{1.1\pm0.2}$, N=9; $\text{Fs}_{9.7\pm0.7}\text{En}_{45.5\pm0.7}\text{Wo}_{44.8\pm1.0}$, N=9), LAP 031275 (R4; $\text{Fs}_{29.2\pm0.7}\text{En}_{69.5\pm1.0}\text{Wo}_{1.3\pm0.4}$, N=9; $\text{Fs}_{10.9\pm1.0}\text{En}_{44.9\pm0.7}\text{Wo}_{44.3\pm1.4}$, N=7), and LAP 03639 (R5; $\text{Fs}_{25.7\pm2.5}\text{En}_{75.2\pm3.2}\text{Wo}_{2.1\pm1.0}$, N=9; $\text{Fs}_{9.7\pm1.1}\text{En}_{45.6\pm1.1}\text{Wo}_{44.7\pm2.1}$, N=6).

3.1.5. *Brachinite*

Sulfides within EET 99402 are rare and typically pyrrhotite (bdl–11.6 wt.% Ni), with rare pentlandite (18.9–19.6 wt.% Ni; Fig. 3, and EA-1, and Table 4). Pentlandite is present as blebs and lamellae morphological types (e.g., Fig. 1f), and is associated with pyrrhotite. Rare Fe,Ni-metal and more abundant chromite are often associated with sulfides. However, Fe,Ni-metal and pentlandite are not observed associated together. Mineral phases observed in contact with sulfides include olivine, pyroxene, and plagioclase.

3.2. Closure temperatures and oxidation states

Two-pyroxene closure temperatures were determined for equilibrated samples with homogeneous LCP and HCP compositions. These temperatures vary between meteorite groups and agree with literature values (Tables 1 and 3). Although two-pyroxene literature values exist for Saint-Séverin, closure temperatures for Siena (LL5) and Saint-Séverin (LL6) were determined to verify the technique used here. The weighted mean temperatures, with two standard error of the mean (2SE) uncertainties, are $867\pm28^\circ\text{C}$ (10 pairs) for Siena and $899\pm70^\circ\text{C}$ (5 pairs) for Saint-Séverin; nearly identical to the Saint-Séverin value of Slater-Reynolds and McSween (2005) ($897\pm104^\circ\text{C}$; Table 1). Mineral

pairs from a chondrule in Siena and those in the matrix give the same temperatures within uncertainties, indicating thermal equilibration. Utilizing the QIFs buffer reaction at two-pyroxene temperatures, Eq. (1) and (2), the fO_2 s for Siena and Saint-Séverin are determined to be IW–2.2 and IW–1.9, respectively.

The weighted mean two-pyroxene temperature determined for the CK6 LEW 87009 is $740\pm 38^\circ\text{C}$ (5 pairs; Table 1). A temperature for LAR 06868 (CK5) was not determined because it contains compositionally heterogeneous HCP. However, LAR 06868 has recognizable relict chondrules unlike LEW 87009, suggesting either the peak temperature for LAR 06868 was lower or the duration of heating was shorter than that of LEW 87009. This temperature is similar to peak metamorphic temperatures estimated by Chaumard and Devouard (2016) using Fe/Mg interdiffusion: CK3 chondrites between 577°C and 647°C , and CK4–6 chondrites between 647°C and 867°C (Table 1).

The weighted mean temperature determined for LAP 03639 (R5) is $853\pm 62^\circ\text{C}$ (5 pairs) (Tables 1 and 3). Closure temperatures, within uncertainty, were the same between mineral pairs within chondrules, the matrix, and the R6 clast in LAP 03639. Although LCP and HCP are compositionally homogeneous in MET 01149 and LAP 031275, closure temperatures were not determined because both samples contain unequilibrated olivine. Closure temperatures were not determined for either R6 chondrite studied, LAP 04840 and MIL 11207, as HCP was not observed; it was probably replaced by amphiboles during aqueous alteration (McCanta et al., 2008; Gross et al., 2013; Rubin, 2014). However, FeNiS veins observed in MIL 11207 constrain the minimum metamorphic temperature of this sample to $\geq 950^\circ\text{C}$ (the Fe,Ni–FeS eutectic; Kullerud, 1963b; McCoy et al., 2006), consistent with its lack of recognizable relict chondrules.

4. DISCUSSION

4.1. Relationship of sulfide mineralogy with oxygen fugacity

While the presence of pentlandite alone does not indicate a particular formation mechanism, it does constrain a minimum fO_2 (in the presence of sufficient S). Comparison of pentlandite presence with the calculated fO_2 for each bulk sample for

equilibrated samples or host chondrule for unequilibrated samples shows that it is controlled primarily by the fO_2 of formation. In addition to the observations of meteoritic sulfides in this study, experimental petrologists have shown that the composition of Fe-S-O liquids at any temperature is a function of its fO_2 and fS_2 (Naldrett, 1969; 2004; Kress, 1997). In settings with sulfide droplets surrounded by silicates, as in the meteorites discussed here, Naldrett (1969) suggested that the sulfide droplets may have lost their O to the surrounding silicates at subsolidus temperatures. While we argue that the composition of the Fe-Ni-S liquid was determined by the surrounding fO_2 and fS_2 >950°C we cannot rule out local disequilibrium effects during cooling discussed by Jamsja and Ruzicka (2010).

While troilite (Ni-free, stoichiometric FeS) is known to form under reducing (i.e., low fO_2) conditions (e.g., Evans, 1970), pentlandite formation requires an oxidizing (i.e., high fO_2) environment because the incorporation of Fe into oxidized minerals (silicates/oxides/phyllsilicates) lowers its availability for sulfide formation. The scarcity of Fe,Ni-metal results in sulfides that are enriched in Ni. Furthermore, Schrader et al. (2015a) found that in high temperature (600–400°C) sulfides, only sulfide assemblages with bulk Ni contents >3 wt.% (~2.4 at.% Ni) contained pentlandite, indicating the minimum bulk Ni content for exsolution to occur.

Pentlandite was observed in all meteorites studied here, and always in association with FeO-rich minerals. Pentlandite was found distributed across FeO-rich samples, such as the brachinite EET 99402 (avg. $Fa_{35.8 \pm 0.2}$; Gardner-Vandy et al., 2013), and within FeO-rich chondrules ($Fa > 10$) of relatively less oxidized samples. Pentlandite was also found in the matrices and chondrules of the CK chondrites (highly-oxidized) and the CM chondrites (aqueously altered). Samples that formed under oxidizing conditions have less Fe,Ni-metal and, consequently, more pentlandite.

4.1.1. Bulk fO_2 and pentlandite in equilibrated chondrites

The CK (Fa_{29-33}) and R (Fa_{38-40}) chondrites are highly oxidized (more so than the LL chondrites) with fO_2 relative to the iron-wüstite (IW) buffer of IW+7.5 and IW to IW+3, respectively (Kallemeyn et al., 1991; Weisberg et al., 2006; Righter and Neff, 2007; Satterwhite and Righter, 2008). They also contain the most abundant pentlandite. As they

formed at higher fO_2 , the CK and R chondrites typically contain trace amounts of Fe,Ni-metal (Geiger and Bischoff, 1995; Weisberg et al., 2006) and have abundant pentlandite that is far more Ni-rich compared to that of LL chondrites (Fig. 3 and Table 4).

Equilibrated LL chondrites are the most oxidized OCs (Fa_{27–32}; Weisberg et al., 2006; IW–2.2 to –1.9), yet still contain ~2 vol.% Fe,Ni-metal (much of which is Ni-rich) which limits the amount of Ni for incorporation into sulfides; consistent with pentlandite being uncommon and low in Ni content.

While less abundant, pentlandite is also present in the brachinite (~IW–1.0 for brachinites; Gardner-Vandy et al., 2013).

4.1.2. Site-specific fO_2 and pentlandite in unequilibrated chondrites

The location of pentlandite in unequilibrated chondrites is typically restricted to FeO-rich chondrules, rare FeO-poor chondrules, and occasionally in the matrix. The following fO_2 values from the literature were determined for individual chondrules. Pentlandite is common in FeO-rich chondrules from the LL (IW–1.7 to –0.4; Zanda et al., 1994), CM, and CR (IW–1.6 to –0.6; Schrader et al., 2013) chondrites. However, pentlandite is nearly always absent from the more reduced FeO-poor chondrules from the CR (IW–4.0 to –2.3; Zanda et al., 1994; Schrader et al., 2013), CM (IW–4.0 to –3.4; Zanda et al., 1994), and LL chondrites (IW–4.2 to –2.5; Zanda et al., 1994). The most oxidized FeO-poor chondrules that are pentlandite-free (IW–2.3, Schrader et al., 2013) formed at nearly the same fO_2 under which LL chondrites were thermally metamorphosed (IW–2.2, this study), suggesting they formed in a S-poor gas and that the sulfur fugacity of a system is also a contributing factor for pentlandite formation. The only sulfides in IAB iron meteorite silicate clasts (IW–3.2 to –2.9, fO_2 at olivine-spinel temperatures) are Ni-poor pyrrhotite (Benedix et al., 2005). Therefore, while fO_2 is not the only factor, samples (whole-rocks or chondrules) that formed under conditions more reducing than ~IW–2.2 do not contain pentlandite. However, systems that were more oxidizing and had sufficient S contain more pentlandite. If pentlandite in aqueously altered chondrites was all formed via aqueous alteration, it would be present in both FeO-poor and FeO-rich chondrules. Therefore, this trend supports an fO_2 dependency for high-temperature pentlandite formation, instead of being solely a secondary aqueous alteration product.

4.2. Petrology, composition, and equilibration temperatures

The compositions of pyrrhotite and pentlandite vary with closure temperature. Through experimental petrology equilibrium phase diagrams at a range of temperatures in the Fe-Ni-S system have been developed (e.g., Kullerud, 1963a; Kullerud et al., 1969; Misra and Fleet, 1973; Francis et al., 1976; Naldrett, 1989; 2004; Karup-Moeller and Makovicky, 1995; Sugaki and Kitakaze, 1998; Etschmann et al., 2004; Raghavan, 2004a). The composition of pyrrhotite and pentlandite, in comparison to these diagrams, can be used to constrain their closure/equilibration temperature. To estimate the sulfide equilibration temperature for samples studied here, the compositions of sulfides from each meteorite are shown on Fe-Ni-S phase diagrams at 100 to 135°C, 230°C, 400°C, 500°C, 600°C, and 725°C in EA-3. With increasing equilibration temperature, pentlandite becomes richer in both S and Ni (EA-3). Representative phase diagrams that match the compositions of some sulfides in each group are shown in Figure 5. While the vast majority of analyzes were conducted on phase pure grains larger than the interaction volume of the EPMA, there were undoubtedly some beam overlaps between Ni-poor and Ni-rich sulfides. However, any overlaps would likely plot along mixing-lines on an Fe-Ni-S phase diagram, and would therefore plot along or near tie-lines.

The morphologies and compositions of sulfides vary between meteorite groups (Figs. 1 and 2, and EA-1), and between petrographic subtypes within groups. The textures and equilibration temperatures of sulfides, combined with the sample's thermal history, constrain their formation mechanism(s). None of the sulfides studied here have Fe-Ni-S compositions consistent with equilibrating above 600°C (EA-3), indicating that pentlandite studied here is not the high-temperature form of pentlandite that is stable up to 865°C (Sugaki and Kitakaze, 1998). This is in contrast to Chaumard and Devouard (2016), where the high-temperature form of pentlandite was considered to be present in CK chondrites based on estimated peak metamorphic temperatures.

The relationship of minor elements (e.g., Co, P, Cu, and Cr) with the Ni content of meteoritic sulfides is consistent with their behavior in terrestrial magmatic sulfide ore deposits (Dare et al. 2010; e.g., Fig. 3 and Tables 2 and 4). In sulfides from the Sudbury

igneous complex (an impact melt sheet) Co partitions into pentlandite and is depleted in pyrrhotite (Dare et al., 2010), consistent with melt partitioning experiments (Raghavan, 1998; 2004b; Soltanieh et al. 1999). This behavior is also consistent with sulfides studied here (Fig. 3), with the exception of some sulfides in the CK chondrites. The increase of Co with Ni abundance becomes clear at ~16 wt.% Ni (Fig. 3), indicating that this marks the compositional separation between pyrrhotite and pentlandite. Sulfides in samples of higher petrographic type typically have higher Co contents (Fig. 3). Pentlandite typically contains more Co than Ni-poor sulfides such as pyrrhotite; while the oxidized CK chondrites and the brachinite contain abundant Co in both Ni-poor and Ni-rich sulfides. Co may be incorporated into pyrrhotite and pentlandite in the most oxidized samples because at high fO_2 there is little to no Fe,Ni-metal and neither magnetite nor chromite contains Co (e.g., Davidson et al., 2014b), making Co available for incorporation into sulfides.

4.2.1. CM chondrites

The CM chondrites experienced extensive ‘low-temperature’ aqueous alteration (<220°C for Mighei [Busemann et al., 2007]; 150 to 500°C for Sutter’s Mill lithologies [Jenniskens et al., 2012]; Fig. 4 and Table 1). Aqueously altered minerals (i.e., phyllosilicates) were commonly, but not always, observed near sulfides. Although the composition of pyrrhotite and pentlandite are broadly consistent with a range of equilibration temperatures (EA-3), the composition of pyrrhotite is most consistent with equilibrating between 100 and 135°C (Fig. 5a). However, some pentlandite in Sutter’s Mill is relatively depleted in S and therefore we cannot rule out equilibration at temperatures up to 600°C (Fig. 5b and EA-3). This contradicts the common inference that pentlandite is solely an aqueous product in the CM chondrites (e.g., Zolensky and Le, 2003; Brearley, 2006). Furthermore, pentlandite abundance is independent of the degree of whole-rock aqueous alteration in the CM chondrites (Zolensky and Le, 2003), which we interpret as evidence that it did not form solely via aqueous alteration. Lamellar and oriented bleb morphologies of pentlandite are inconsistent with formation via aqueous alteration (Fig. 1a and EA-1), and their equilibration temperatures indicate formation during cooling from high temperature; perhaps during chondrule cooling. However, most

CM chondrite sulfides are consistent with equilibration temperatures of 100 to 135°C, and likely formed via aqueous alteration (Zolensky and Le, 2003; Brearley, 2006), and/or by low-temperature annealing or metamorphism (e.g., Brearley and Martinez, 2010; Kimura et al., 2011). Therefore, sulfides in the CM chondrites record a complex set of formation conditions.

4.2.2. CK chondrites

Pentlandite is the dominant sulfide in the CK chondrites, and is present as lamellae within pyrrhotite/pyrite and blocky grains containing islands of pyrrhotite/pyrite (Fig. 1b). Sulfides were not associated with aqueously altered minerals. The composition of pentlandite is broadly consistent with a range of equilibration temperatures (EA-3), however the composition of pyrite and pyrrhotite indicate that sulfides in the CK4 chondrites equilibrated at 230°C (Fig. 5c and EA-3). The compositions of pyrrhotite and pentlandite in the CK5–6 chondrites have S contents inconsistent with equilibration at 230°C. However, the presence of pyrite and the compositions of pyrrhotite and pentlandite are consistent with an equilibration temperature of 500°C (e.g., EA-3). CK chondrite sulfides are considered to have formed during cooling from peak thermal metamorphic temperatures of 550 to 950°C, mostly during annealing <300°C (Geiger and Bischoff, 1995). Recently Chaumard and Devouard (2016) estimated metamorphic temperatures of between 647°C and 867°C for the CK4–6 chondrites (Fig. 4 and Table 1). These previously determined metamorphic temperatures are consistent with that calculated here ($740 \pm 38^\circ\text{C}$ for the CK6; Table 1). The nearly equal abundance of pyrite and pyrrhotite (Fig. 5c) in the CK chondrites also indicates a history of annealing; Fe-Ni-S annealing experiments of crystallized mss show that pyrite-pentlandite assemblages form $\sim 212 \pm 13^\circ\text{C}$ (Craig, 1973), consistent with sulfide equilibration temperatures. These experiments also resulted in Ni-rich pyrrhotite and pyrite (Craig, 1973). Pyrite exsolution is a slow process (Kissin and Scott, 1982), suggesting formation of CK sulfides by prolonged annealing. Furthermore, high-temperature (i.e., $>200^\circ\text{C}$) formation of pentlandite-pyrite is consistent with the presence of chalcopyrite and Co-rich pentlandite (Figs. 2a and 3a), both of which are present in terrestrial magmatic sulfide ore deposits

(e.g., Naldrett et al., 1967; Keays et al., 1981; Merkle and Gruenewaldt, 1986; Dare et al., 2010). In pyrite-pentlandite annealing experiments between 400 and 200°C, chalcopyrite exsolved when 2 wt.% Cu was added to experimental Fe-Ni-S charges (Craig, 1973). Furthermore, laboratory experiments determined that Fe,Co-mss decomposes into Fe-rich and Co-rich pentlandite below 425°C (Farrell and Fleet, 2002). Due to the compositions of pyrrhotite and pentlandite, and the presence of pyrite among pyrrhotite-pentlandite intergrowths, we find that CK4 chondrite sulfides most likely equilibrated around 230°C while the CK5–6 chondrites equilibrated around 500°C (Fig. 5c and EA-3).

Magnetite within the CK chondrites is considered to have formed by oxidation during mild aqueous alteration (e.g., Huber et al., 2006; Davidson et al., 2014b). The presence of magnetite with sulfides may indicate that pentlandite was replaced by magnetite under highly oxidizing conditions during metamorphism (Geiger and Bischoff, 1995). However, magnetite is known to crystallize co-genetically with sulfides in terrestrial magmas in the Fe-Ni-S-O system (Naldrett, 1989), and CK chondrites contain rounded magnetite blebs surrounded by pyrrhotite and pentlandite (Fig. 1b) indicating that these magnetite blebs crystallized co-genetically with sulfides. In terrestrial magmas that formed around $fO_2 \sim 10^{-8}$ (IW+14.3 at ~677°C) magnetite crystallized before pyrrhotite (Doyle and Naldrett, 1986; Naldrett, 1989). Although these terrestrial magmas were thermally metamorphosed at more oxidizing conditions than CK chondrites, which were metamorphosed around $fO_2 \sim 10^{-14.7}$ (~677°C at IW+7.5 [fO_2 determined from magnetite-ilmenite pairs at 950K by Righter and Neff, 2007; Gardner-Vandy et al., 2013]), the CK chondrites formed at highly oxidizing conditions. Therefore, based on petrographic observations and fO_2 of formation, we conclude that magnetite-sulfide intergrowths are likely magmatic and formed co-genetically, but magnetite crystallized after pyrrhotite and pentlandite from immiscible melts. This statement only applies to magnetite-sulfide intergrowths, we do not rule out the possibility that some magnetite in the CK chondrites formed by oxidation during aqueous alteration (e.g., Huber et al., 2006; Davidson et al., 2014b).

4.2.3. LL chondrites

Pentlandite was observed in all LL chondrites studied here and is present as all three textural types (Fig. 1c and EA-1), but lamellae are only present in Semarkona. Aqueous

alteration products (i.e., phyllosilicates and carbonates) were not observed in association with sulfides, but magnetite was observed in the matrix of Semarkona. The compositions of pyrrhotite and pentlandite within chondrules and matrix in Semarkona are generally consistent with equilibration temperatures between 600 and 230°C, but pentlandite is too Ni-poor to indicate equilibration between 100 and 135°C (Fig. 5d and EA-3). The compositions of the sulfides are most consistent with equilibrating at ~230°C, however we cannot rule out equilibration at temperatures up to 600°C because data lies along tie lines on phase diagrams up to 600°C (EA-3). In the LL4-6 chondrites, pyrrhotite and pentlandite are richer in Ni and S than in Semarkona, indicating equilibration at higher temperatures. The compositions of pentlandite in the LL4-6 chondrites measured here are too S rich to have equilibrated at or below 230°C, and are most consistent with equilibrating between 600 and 500°C (Fig. 5d and EA-3). These temperatures are higher than the peak metamorphic temperature inferred for Semarkona (<220°C; Busemann et al., 2007), but agree with pentlandite formation during cooling after thermal metamorphism for the LL4–6 chondrites (~600–900°C; McCoy et al., 1991; Slater-Reynolds and McSween, 2005; this study; Fig. 4 and Table 1). This contradicts the suggestion that pentlandite within Semarkona is solely an aqueous product (Rubin, 2006). This suggests two possible formation mechanisms: (1) pentlandite within Semarkona is primary (i.e., formed during cooling after high temperature events, such as during chondrule cooling [e.g., as in the CR chondrites; Schrader et al., 2010b; 2015a]), or less likely (2) Semarkona experienced brief high-temperature (600–230°C) sulfide equilibration that did not affect other diffusion-driven geothermometers (e.g., graphite ordering; olivine-chromite equilibration). Due to sulfide equilibration temperatures and the presence of pentlandite lamellae within pyrrhotite in Semarkona, we suggest that pentlandite observed within Semarkona is primary; however we cannot rule out some low-temperature annealing. Since the presence of phyllosilicates, smectite, and magnetite in the matrix of Semarkona shows that it has experienced low-temperature aqueous alteration (Hutchison et al., 1987; Alexander et al., 1989), we also cannot rule out that some sulfides formed via aqueous alteration in Semarkona (e.g., Rubin, 2006).

High-temperature formation of pentlandite in equilibrated LL chondrites is consistent with the presence of molybdenite in Soko-Banja (LL4; Fig. 2b), which is present in high-

temperature terrestrial hydrothermal veins (e.g., Anthony et al., 1990) and primary molybdenite (i.e., not formed via aqueous alteration) has also been reported in CV calcium-aluminum rich inclusions (El Goresy et al., 1978). While we do not find that pyrrhotite-pentlandite intergrowths in the LL4–6 chondrites have an aqueous origin, phosphate minerals in equilibrated LL chondrites indicate the presence of fluids during metamorphism (Jones et al., 2014). Therefore, we suggest that sulfides in Semarkona are primary and formed during chondrule cooling prior to accretion while those in LL4–6 chondrites formed at high-temperature after thermal metamorphism. Due to the duration of heating experienced by the LL chondrites (10–100 Myr; McCoy et al., 1991), low-temperature annealing may also have played a role in sulfide equilibration.

4.2.4. *R chondrites*

Pentlandite is common in the R chondrites and is present as blocky grains, lamellae, and oriented blebs within Ni-poor pyrrhotite (Fig. 1d,e; McCanta et al., 2008). The compositions of pyrrhotite and pentlandite in the R chondrites are too S rich to have equilibrated between 100 and 230°C (EA-3). The S content of pyrrhotite and pentlandite in the R chondrites are consistent with equilibration temperatures between 600 and 500°C (Fig. 5e and EA-3). Metamorphic temperatures for R chondrites were previously only constrained for the R6 chondrites LAP 04840 (~670°C; McCanta et al., 2008) and MIL 11207 (~700–900°C; Rubin, 2014). However, two-pyroxene closure temperatures indicate that the R5 chondrite LAP 03639 was heated to $853 \pm 62^\circ\text{C}$ (Table 1). Fe-Ni-S veining observed in MIL 11207 indicates sulfide melt migration, suggesting a minimum metamorphic temperature of ~950°C (Fe,Ni-FeS eutectic; Kullerud, 1963b; McCoy et al., 2006). Therefore, sulfide closure temperatures are lower than the metamorphic temperatures for the R chondrites (Fig. 4 and Table 1), consistent with sulfide formation during retrograde metamorphism. The consistent presence of chromite with sulfides (Figs. 1d,e and EA-3) indicates the sulfides formed under oxidizing conditions. The presence of chalcopyrite in LAP 031275 and LAP 03639 (e.g., Fig. 2c) is consistent with high-temperature formation, as it is also observed in terrestrial magmatic sulfide ores in association with pentlandite and pyrrhotite; exsolution of these phases occurred during cooling <650°C (e.g., Keays et al., 1981; Dare et al., 2010).

Chalcopyrite in R chondrites is suggested to form via aqueous alteration or exsolution upon cooling from high temperature (Miller et al., 2014). While LAP 04840 (McCanta et al., 2008) and MIL 11207 (Gross et al., 2013; Rubin, 2014) are aqueously altered, no chalcopyrite was observed in either sample in this study. In the R3–5 chondrites studied here, chalcopyrite is surrounded by pentlandite and pyrrhotite (Fig. 2c) with closure temperatures between 600 and 500°C (e.g., Fig. 5e and EA-3), suggesting a high-temperature origin for this chalcopyrite. The presence of magnetite in MET 01149 (EA-1) may indicate low-temperature aqueous alteration of sulfides, co-genetic crystallization, or decomposition of pentlandite into magnetite during metamorphism under highly oxidizing conditions; similar to the CK chondrites (Geiger and Bischoff, 1995; Section 4.2.2).

4.2.5. Brachinite

Sulfides are uncommon, and pentlandite is rare, in the brachinite EET 99402 and is present as lamellae and blebs within Ni-poor pyrrhotite (Fig. 1f). The compositions of sulfides in this brachinite are too S rich to have equilibrated below 400°C, and are most consistent with equilibration temperatures of 600 to 400°C (e.g., Fig. 5f and EA-3). This is consistent with sulfide formation during cooling after partial melting for brachinites at temperatures in excess of 980°C (Gardner-Vandy et al., 2013; Fig. 4 and Table 1). Brachinites show similarities to laboratory heated R chondrites, suggesting the brachinite precursor material was similar to the R chondrites (Gardner-Vandy et al., 2013). This sample provides a potential thermal metamorphic extreme to compare to the less heated R chondrites, and the rarity of sulfides compared to R chondrites suggest brachinites lost sulfides. Whole rock O-isotope compositions suggest distinct parent bodies for both the R chondrites and the brachinites; the brachinite parent body experienced a higher degree of thermal metamorphism (e.g., Gardner-Vandy et al., 2013). However, similar sulfide equilibration temperatures suggest they are representative of closure temperatures during retrograde metamorphism.

4.3. Duration of thermal metamorphism

The composition and morphology of pyrrhotite-pentlandite intergrowths are also indicative of formation timescales. Pyrrhotite-pentlandite textures similar to those observed in meteoritic samples studied here have been produced via annealing experiments of Fe-Ni-S charges between ~500 and 200°C by exsolution of pentlandite and pyrrhotite from mss (e.g., Craig, 1973; Misra and Fleet, 1973; Etschmann et al., 2004). However, experimental pyrrhotite is Ni-rich while pyrrhotite in meteorites is typically Ni-poor. Some Ni-rich pyrrhotite analyses in this study likely result from overlap of micron-scale intergrowths of Ni-poor pyrrhotite and pentlandite blebs. Although pentlandite-pyrrhotite exsolution experiments were conducted on laboratory timescales of 24 hrs, extrapolation to geological timescales suggest that exsolution in nature may be on the order of 3,000 to 30,000 years (for sulfides rich in S; Etschmann et al., 2004). Some meteorite parent bodies were heated in excess of this exsolution timescale; for example, the CK chondrites were metamorphosed between 70,000 years (Chaumard and Devouard, 2016) and 11 Ma (Davidson et al., 2014b), while the equilibrated LL chondrites were heated on the order of 10–100 Ma (McCoy et al., 1991). In contrast, pentlandite completely exsolved from pyrrhotite in CR chondrite sulfides, which cooled from immiscible Fe-Ni-S melts (Schrader et al., 2015a) on the order of hours to days during chondrule cooling (e.g., Hewins et al., 2005; Schrader and Lauretta, 2010). Therefore, complete partitioning of Ni into pentlandite from pyrrhotite at temperatures <500°C appears possible only over long timescales on the order of thousands of years, or by cooling from above Fe-Ni-S liquidus temperatures (>950°C) on the order of hours to days. Sulfide formation at low-temperature is also possible on the order of hours via hydrothermal methods (Kissin and Scott, 1982), which is likely relevant for some sulfides in the CM chondrites.

4.4. Implications for Sample Return

Understanding the formation pathways of individual minerals within extraterrestrial materials is essential for constraining the formation and evolution of their parent bodies. The presence of Ni-rich sulfides, primarily pentlandite, was used to suggest that comet Wild 2 may have experienced limited aqueous alteration (Zolensky et al., 2008);

consistent with the identification of rare carbonates and apparent lack of phyllosilicates in Wild 2 samples (e.g., Zolensky et al., 2008). Pyrrhotite grains in Stardust samples from Wild 2 were found to be structurally and compositionally consistent with equilibration temperatures of 100 to 135°C, indicating low-temperature aqueous alteration (Berger et al., 2011). A re-examination of the data reported by Berger et al. (2011), in light of our measurements of chondritic sulfides here, suggests an alternative interpretation. The Ni-poor and Ni-rich sulfide compositions from Wild 2 reported by Berger et al. (2011) contain >50 at.% S, which is consistent with equilibration at temperatures >230°C (up to 600°C) and not between 100 and 135°C (e.g., Fig. 5 for phase diagrams). A sulfide equilibration temperature between 230 and 600°C indicates that low-temperature annealing or cooling from high temperature are also viable formation mechanisms. This interpretation is supported by recent work on the compositions and textures of Wild 2 sulfides, which indicate they formed at high temperatures and crystallized from Fe-Ni-S melts (Joswiak and Brownlee, 2016). This conclusion is also consistent with the observation of other high temperature phases, such as in chondrule-like objects, identified in comet Wild 2 (e.g., Ogliore et al., 2012; Nakashima et al., 2015).

Therefore, the presence of pentlandite in extraterrestrial samples (meteorites, IDPs, and returned samples from comets and asteroids) does not indicate a particular formation mechanism. If possible, the morphology and composition of pentlandite and coexisting sulfide minerals should be considered and compared to the thermal history of the host sample. If petrographic context is lost, as may be the case for returned samples, the morphology and composition of pentlandite alone can provide valuable information on pre- and post-accretionary processes (i.e., time, temperature, fO_2 , and aqueous history). This framework should be utilized if pentlandite is observed in returned samples from the C- and B-type asteroids, asteroid 162173 Ryugu and 101955 Bennu, to be collected by Hayabusa2 and OSIRIS-REx, respectively (Hasegawa et al., 2008; Emery et al., 2014; Tachibana et al., 2014; Lauretta et al., 2015).

5. CONCLUSIONS

The combined morphologic, compositional, and petrographic setting characteristics of pyrrhotite-pentlandite intergrowths can be utilized to constrain their formation mechanism(s).

1. CM and CK chondrite sulfides are complex as they equilibrated over a wide range of temperatures; between 600 and 100°C, and 500 and 230°C, respectively. CM chondrite sulfides mostly formed during low-temperature during aqueous alteration and/or annealing, although some may have formed at high-temperature during chondrule cooling. CK chondrite sulfides formed during cooling after thermal metamorphism and by ‘low-temperature’ annealing; ~230°C for the CK4, and ~500°C for CK5-6 chondrites.
2. Sulfides in the LL chondrites, R chondrites, and brachinite equilibrated between 600 and 230°C, 600 and 500°C, 600 and 400°C, respectively. Sulfides in Semarkona (LL3.00) are consistent with formation during chondrule cooling, although we cannot rule out some low temperature annealing. Sulfides from the R and equilibrated LL chondrites (types 4–6) and the brachinite formed during cooling after thermal metamorphism.
3. The duration of thermal metamorphism for the CK chondrites (>11 Ma; Davidson et al., 2014b) and the equilibrated LL chondrites (10^7 – 10^8 years; McCoy et al., 1991) were sufficient for complete separation of pentlandite and pyrrhotite.
4. The presence of pentlandite alone does not indicate a particular formation mechanism but can constrain a minimum fO_2 of ~IW–2.2, although the formation of pentlandite is also dependent on the availability of S. The morphology and composition of pentlandite-pyrrhotite/pyrite are required to determine the formation mechanism: low-temperature annealing; aqueous alteration; and pre- and post-accretionary high-temperature formation. Most pyrrhotite and pentlandite in chondrites formed via high temperature processes, either upon cooling after chondrule melting prior to accretion or thermal metamorphism on the parent body.
5. The evaluation of a single mineral system, Fe-sulfides, within meteorites that retain petrographic context is vital to interpret the formation and alteration

processes recorded by small extraterrestrial samples, such as those returned by the Stardust (comet 81P/Wild 2) and Hayabusa (asteroid 25143 Itokawa) missions and will be returned by OSIRIS-REx (asteroid 101955 Bennu) and Hayabusa2 (asteroid 162173 Ryugu).

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FIGURE CAPTIONS

Figure 1. BSE images of sulfides showing the range of pentlandite textures observed. (a) Blocky pentlandite (pn) along the edge of the sulfide assemblage, along with pn blebs within pyrrhotite (po) in the CM2 Mighei (b) Islands of pyrite (py) within pentlandite in the CK4 ALH 85002. Magnetite (mag) is present within the sulfide grain. (c) Pentlandite blebs and ‘flame’ texture within po in the LL3.00 Semarkona. (d) Blocky pn and pn lamellae within po in the R3 MET 01149. Pentlandite lamellae with variable orientation across the sulfide grain indicate it is polycrystalline. Opaque assemblage also contains chromite (chr). (e) Well-formed pn lamellae along with poorly oriented pn blebs within po in the R6 MIL 11207. (f) Pentlandite along the edge of a sulfide grain dominated by po in the brachinite EET 99402. Where met = Fe,Ni metal.

Figure 2. BSE images of uncommon sulfides observed. (a) Cobalt-rich pentlandite (Co-pn) in the CK4 Karoonda. (b) Molybdenite (mo; MoS_2) in association with pentlandite (pn) and pyrrhotite (po) in the LL4 Soko-Banja. (c) Chalcopyrite (ccp) surrounded by po and pn in the R5 LAP 03639.

Figure 3. (a) Ni vs. Co (wt.%) composition of sulfides, and (b) for sulfides with less than 3 wt.% Co for clarity. (c) Ni vs. Co (wt.%) for sulfides from the brachinite, and CK and R chondrites. (d) Ni vs. Co (wt.%) for sulfides from the CM and LL chondrites. With the exception of the CK chondrites, pyrrhotite is typically Co-poor while pentlandite is Co-rich. A marked increase in Co abundance occurs at ~16 wt.% Ni.

Figure 4. Minimum metamorphic temperatures (with uncertainties) for samples of this study compared to the 610°C ‘barrier’ for dissolution or exsolution of pentlandite in mss. Pentlandite in samples that were not heated above 610°C is either primary or low-temperature secondary. Pentlandite in samples heated above 610°C is high-temperature secondary. Temperatures for LEW 87009, Siena, Saint-Séverin, LAP 03639, and MIL 11207 were determined in this study. Temperatures are weighted means (with 2SE uncertainties) determined with two-pyroxene geothermometry; except MIL 11207, which is inferred from petrographic indicators such as FeNiS-veins. Temperature references for remaining samples are included in Table 1; samples with estimated minimum metamorphic temperature ranges are represented with multiple data points.

Figure 5. Fe-Ni-S ternary phase diagrams with sulfide data from all samples studied here. Sulfides from each group are consistent with phase diagrams over a range of temperatures, e.g., some sulfides in the CM chondrites are consistent with equilibration temperatures of (a) 100–135°C, while others of (b) 600°C. Representative isothermal phase diagrams are given for the (c) CK chondrites (230°C), (d) LL chondrites (600°C), (e) R chondrites (400°C) and (f) the brachinite (400°C). Where po = pyrrhotite, pn = pentlandite, mss = monosulfide solid solution, hz = heazlewoodite (Ni_3S_2), vs = vaesite (NiS_2), vio = violarite (Ni_3S_4). Phase diagrams adapted from Raghavan (2004a); original data from Naldrett (1989) (100–135°C), Misra and Fleet (1973) (230°C), Craig et al. (1968) (400°C) and Kosyakov et al. (2003) (600°C). See EA-3 for all phase diagrams.

Table 1

Table 1. List of samples and parent body thermal history

Meteorite	Type	Fall/Find	Weathering	Minimum Metamorphic Temperature (This Study) weighted mean $\pm 2\sigma$	Method (This Study)	Metamorphic Temperature (Literature)	Method (Literature)	Reference
CM chondrite								
Mighei USNM 3483-3	CM2	Fall	W0			<220°C	graphite-ordering	a
C chondrite (CM-like breccia)								
Sutter's Mill ¹	C	Fall	W0			~150–500°C	various	b
CK chondrites								
ALH 85002,87	CK4	Find	A			647–867°C	Fe-Mg ol diffusion	c
Karoonda USNM2428-3	CK4	Fall	W0			647–867°C	Fe-Mg ol diffusion	c
LAR 06868	CK5	Find	A/B			647–867°C	Fe-Mg ol diffusion	c
LEW 87009	CK6	Find	Ae	740 $\pm$ 38°C	two-pyx	800–1000°C	two-pyx	d
LL chondrites								
Semarkona USNM1805-17	LL3.00	Fall	W0			<220°C	graphite-ordering	a
Soko-Banja USNM3078-1	LL4	Fall	W0			>600°C	Fe-Mg ol diffusion	e
Siena USNM3070-3	LL5	Fall	W0	867 $\pm$ 28°C	two-pyx	677–727°C	ol-chr	f
Saint-Séverin USNM2608-3	LL6	Fall	W0	899 $\pm$ 70°C	two-pyx	897 $\pm$ 104°C	two-pyx	g
R chondrites								
MET 01149,27	R3	Find	A					
LAP 031275,2	R4 ²	Find	B/C					
LAP 03639,2	R5 ²	Find	A/B	853 $\pm$ 62°C	two-pyx			
MIL 11207,2	R6	Find	Ce	$\geq$ 950°C	Fe-Ni-S veins ³	700–900°C	dehydration	h
LAP 04840,4	R6	Find	A/B			670 $\pm$ 60°C	amph-plag	i
Brachinite								
EET 99402,6	Brachinite	Find	B			980 $\pm$ 16°C	ol-chr	j

(1) Sutter's Mill thin section from stone SM8 (19.05 grams), 'post-rain' stone recovered April 27th, 2012.

(2) Since LAP 03639 is more equilibrated than LAP 031275, we revise their classifications with LAP 03639 now considered an R5, and LAP 031275 an R4.

(3) temperature of Fe,Ni-FeS eutectic ~950°C (Kullerud, 1963b; McCoy et al., 2006).

Where two-pyx = two-pyroxene equilibration temperature; O-isotopes = temperature determined by O-isotope equilibration;

Fe-Mg ol diffusion = Fe-Mg diffusion in olivine; ol-chr = olivine-chromite equilibration temperature; amph-plag = amphibole-plagioclase thermometry

(a) Busemann et al. (2007); (b) Jenniskens et al. (2012); (c) Chaumard and Devouard (2016); (d) Geiger and Bischoff (1991); (e) McCoy et al. (1991);

(f) Kessel et al. (2007); (g) Slater-Reynolds and McSween (2005); (h) Rubin (2014); (i) McCanta et al. (2008); (j) Gardner-Vandy et al. (2013).

Table 2

Table 2. Representative sulfide compositional analyses (wt.%)

Sample	Mighei	Mighei	ALH 85002	ALH 85002	Karoonda	Semarkona	Semarkona	MET 01149	MET 01149	MET 01149	MIL 11207	MIL 11207	EET 99402	EET 99402
Type	CM2	CM2	CK4	CK4	CK4	LL3.00	LL3.00	R3	R3	R3	R6	R6	Brach	Brach
Area	Mx4	Ch3	Ch1	Ch1	Ch3	Ch1	Ch1	M5	M5	Ch3				
Grain	OA8	OA10	OA3	OA3	OA10	OA8	OA8			A5	OA5	OA5	OA1	OA1
Mineral	po	pn	py	pn	Co-pn	po	pn	po	pn	ccp	po	pn	po	pn
Fe	60.9	34.7	43.1	27.2	13.1	62.1	47.6	61.6	35.4	30.2	60.5	32.1	62.7	39.9
Ni	0.64	32.1	0.84	38.0	31.0	0.34	17.8	0.17	30.3	0.25	0.89	32.7	bdl	19.6
P	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
S	38.0	32.4	53.3	33.9	42.7	37.4	34.1	38.1	33.2	35.3	39.2	34.3	36.7	34.0
Cr	bdl	bdl	bdl	bdl	bdl	0.04	0.05	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Co	bdl	0.62	2.23	0.76	13.1	bdl	0.30	bdl	1.07	bdl	bdl	0.86	bdl	6.16
Si	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Al	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cu	0.09	bdl	bdl	bdl	bdl	0.09	0.16	bdl	0.11	32.8	bdl	bdl	bdl	bdl
Total	99.6	100.0	99.5	99.9	99.8	99.9	100.0	99.9	100.1	98.6	100.5	100.0	99.4	99.7

Where po = pyrrhotite; pn = pentlandite; py = pyrite; Co-pn = Co-rich pentlandite; ccp = chalcopyrite.

With the exception of uncommon sulfides (Co-pn and ccp), data here are typically pairs of coexisting low- and high-Ni sulfides (po-pn and py-pn) within individual sulfide grains. Standards and detection limits (in wt.%) are troilite for Fe (0.05) and S (0.01), schreibersite for P (0.02), chromium metal for Cr (0.03), cobalt metal for Co (0.05), silicon metal for Si (0.03), aluminium for Al (0.02), and copper metal for Cu (0.08).

Table 3

Table 3. Representative two-pyroxene mineral pairs (wt.%)

Sample	LEW 87009		Siena		Saint-Séverin		LAP 03639	
Type	CK6		LL5		LL6		R5	
Area	Mx4		Mx3		Mx3		Clast	
Mineral	LCP	HCP	LCP	HCP	LCP	HCP	LCP	HCP
SiO ₂	54.3	52.8	54.9	54.3	54.4	53.5	54.1	53.5
TiO ₂	bdl	0.09	0.12	0.41	0.14	0.43	bdl	0.23
Al ₂ O ₃	0.27	2.38	0.18	0.44	0.21	0.52	0.43	0.83
Cr ₂ O ₃	bdl	0.24	0.07	0.74	0.14	0.84	0.48	0.49
FeO	17.6	7.38	15.5	5.55	15.8	5.86	14.9	5.87
MnO	0.25	0.09	0.50	0.24	0.49	0.22	0.22	0.14
MgO	27.1	14.4	27.7	16.5	28.2	16.7	28.5	16.2
CaO	0.36	22.7	0.48	21.7	0.84	21.4	0.65	22.6
NiO	0.33	0.13	0.08	bdl	bdl	bdl	bdl	bdl
Na ₂ O	bdl	0.84	bdl	0.59	bdl	0.59	bdl	0.56
P ₂ O ₅	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.09
Total	100.2	101.1	99.6	100.5	100.2	100.0	99.2	100.5
Closure Temperature (±2σ)	741±50°C		798±68°C		897±102°C		846±80°C	

Representative analyses and individual mineral pair closure temperatures only.

Weighted means of closure temperatures are given in Fig. 4.

Ch = chondrule; Mx = matrix; LCP = low-calcium pyroxene; HCP = high-calcium pyroxene.

Standards and detection limits (in wt.%) are diopside for Mg (0.01) and Si (0.02), VG-A99 USNM 113498 for Na (0.03), Kakanui hornblende for Al (0.01), Ti (0.05), and K (0.02), Rockport fayalite for Fe (0.04), fluorapatite for Ca (0.02)

Table 4

Table 4. Major and minor element compositional averages and ranges of sulfides (wt.%).

	Fe	S	Ni	Co	Cr	P	Cu	Total	# Analyses
CM chondrites									
Pyrrhotite	61.0±2.0 (55.1–63.7)	35.6±0.9 (35.6–39.1)	1.37±2.27 (0.26–9.67)	bdl	bdl	bdl	0.01±0.03 (bdl–0.10)	100.0±1.1	16
Pentlandite	34.9±3.4 (32.0–43.0)	32.3±1.0 (30.6–34.6)	31.5±3.6 (22.2–35.0)	0.71±0.21 (0.26–1.06)	0.01±0.02 (bdl–0.06)	0.00±0.01 (bdl–0.04)	0.01±0.03 (bdl–0.11)	99.5±0.8	34
CK chondrites									
Pyrrhotite/Pyrite	45.6±3.4 (38.0–57.3)	50.1±6.1 (37.7–54.8)	3.03±4.53 (0.08–15.7)	1.02±0.61 (bdl–2.23)	0.01±0.02 (bdl–0.08)	0.01±0.02 (bdl–0.08)	0.01±0.04 (bdl–0.14)	99.9±1.0	53
Pentlandite	28.0±3.2 (21.0–41.4)	34.0±2.0 (30.9–43.0)	36.9±4.9 (17.3–41.8)	0.70±0.46 (bdl–4.10)	0.02±0.04 (bdl–0.24)	0.00±0.01 (bdl–0.05)	0.03±0.05 (bdl–0.27)	99.6±0.9	135
Co-rich pentlandite	13.1±0.4 (12.6–13.6)	42.1±0.6 (40.9–42.7)	30.7±0.41 (30.2–31.4)	13.2±0.5 (12.4–13.8)	bdl	bdl	bdl	99.1±0.5	7
Chalcopyrite	29.9±0.3 (29.5–30.1)	35.3±0.3 (35.0–35.6)	0.17±0.04 (0.12–0.19)	bdl	0.04±0.06 (bdl–0.11)	0.01±0.02 (bdl–0.03)	32.8±0.4 (32.4–33.2)	98.2±0.2	3
LL3.00 chondrite (Semarkona)									
Pyrrhotite	62.1±1.8 (51.3–63.8)	37.0±0.5 (34.1–38.1)	0.47±2.23 (bdl–15.3)	0.00±0.03 (bdl–0.23)	0.04±0.04 (bdl–0.21)	0.00±0.01 (bdl–0.05)	0.00±0.02 (bdl–0.10)	99.6±0.7	47
Pentlandite	47.8±0.8 (46.7–50.1)	33.9±0.5 (32.7–34.7)	17.6±0.6 (16.0–18.5)	0.28±0.12 (bdl–0.46)	0.03±0.05 (bdl–0.19)	bdl	0.11±0.08 (bdl–0.29)	99.8±0.9	18
LL 4-6 chondrites									
Pyrrhotite	62.5±1.0 (57.4–64.3)	37.0±0.6 (34.5–38.1)	0.08±0.50 (bdl–5.57)	bdl	0.02±0.07 (bdl–0.49)	0.00±0.00 (bdl–0.03)	0.00±0.03 (bdl–0.36)	99.7±1.0	139
Pentlandite	44.2±2.0 (39.7–49.3)	33.8±0.5 (31.9–34.9)	20.1±1.7 (16.2–23.7)	0.60±0.58 (bdl–2.41)	0.01±0.07 (bdl–0.41)	0.00±0.01 (bdl–0.03)	0.14±0.22 (bdl–1.19)	98.8±0.6	47
R chondrites									
Pyrrhotite	59.0±3.3 (48.2–64.2)	38.5±0.8 (34.7–40.5)	2.2±3.1 (bdl–15.3)	0.01±0.07 (bdl–0.90)	0.02±0.05 (bdl–0.28)	0.01±0.03 (bdl–0.31)	0.02±0.08 (bdl–0.65)	99.8±0.8	217
Pentlandite	33.5±2.7 (27.1–54.8)	33.8±0.9 (22.7–35.7)	31.9±2.5 (19.1–38.6)	0.92±0.16 (0.40–1.55)	0.02±0.05 (bdl–0.30)	0.01±0.06 (bdl–0.73)	0.07±0.35 (bdl–4.26)	100.2±0.7	201
Chalcopyrite	30.1±0.2 (30.0–30.2)	35.2±0.3 (35.0–35.3)	0.21±0.06 (0.16–0.25)	bdl	bdl	bdl	32.7±0.2 (32.5–32.8)	98.1±0.7	2
Brachinite									
Pyrrhotite	61.3±2.4 (50.3–62.7)	36.8±0.7 (33.9–37.3)	0.51±2.41 (bdl–11.6)	0.13±0.62 (bdl–2.96)	0.05±0.09 (bdl–0.32)	bdl	bdl	98.8±0.4	23
Pentlandite	39.9±0.5 (39.4–40.5)	34.2±0.3 (33.9–34.6)	19.3±0.3 (18.9–19.6)	5.92±0.32 (5.53–6.19)	bdl	bdl	bdl	99.4±0.2	4

Average ± one standard deviation, (minimum–maximum).

Standards and detection limits (in wt.%) are troilite for Fe (0.05) and S (0.01), schreibersite for P (0.02), chromium metal for Cr (0.03), cobalt metal for Co (0.05), silicon metal for Si (0.03), aluminium for Al (0.02), and copper metal for Cu (0.08).

bdl = below detection limit.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5