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Widespread evidence for high-temperature formation of pentlandite in chondrites

Devin L. Schrader [a,*], Jemma Davidson [b], Timothy J. McCoy [a]

[a] Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, 10th & Constitution Avenue NW, Washington, DC 20560-0119, USA

[b] Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Road NW, Washington, DC 20015-1305, 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.

Keywords: Pentlandite; Pyrrhotite; Exsolution; High-temperature; Annealing; Aqueous alteration; Meteorite; Chondrite

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,

* Corresponding author at: Center for Meteorite Studies, School of Earth and Space Exploration, Arizona State University, P.O. Box 871404, Tempe, AZ 85287, USA.

E-mail address: schraderd@asu.edu (D.L. Schrader).

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1995; Bullock et al., 2005; Rubin, 2006; Righter 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 [$(Fe,Ni,Co,Cr)_{9-x}S_8$], pyrite [FeS_2], and chalcopyrite [$CuFeS_2$].

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 h) 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,b; 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