Experimental constraints on mantle sulfide melting up to 8 GPa (Revision 2)

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ABSTRACT

We present high pressure experiments up to 8 GPa that constrain the solidus and liquidus of a composition, Fe_{0.69}Ni_{0.23}Cu_{0.01}S_{1.00}, typical of upper mantle sulfide. Solidus and liquids brackets of this monosulfide are parameterized according to a relation similar to the Simon-Glatzel equation, yielding, respectively, \( T(°C) = 1015.1\left[ \frac{P(GPa)}{1.88+1} \right]^{0.206} \) and \( T(°C) = 1067.3\left[ \frac{P(GPa)}{1.19+1} \right]^{0.149} \) (1 \( \leq P \leq 8 \)). The solidus fit is accurate within ± 15 °C over the pressure intervals 1-3.5 GPa and within ± 30 °C over the pressure intervals 3.5-8.0 GPa. The solidus of the material examined is cooler than the geotherm for convecting mantle, but hotter than typical continental geotherms, suggesting that sulfide is molten or partially molten through much of the convecting upper mantle, but potentially solid in the continental mantle. However, the material examined is one of the more refractory among the spectrum of natural mantle sulfide compositions. This, together with the solidus-lowering effects of O and C not constrained by the present experiments, indicates that the experimentally-derived melting curves are upper bounds on sulfide melting in the Earth’s upper mantle and that the regions where sulfide is molten are likely extensive in both the convecting upper mantle and, potentially, the deeper parts of the oceanic and continental lithosphere, including common source regions of many diamonds.

Keywords: Sulfide, mantle, solidus, melting, experimental constraint, calibration
Molten sulfides are important geochemical and geophysical agents in Earth’s interior. Sulfide mineral and melt are the chief carriers of siderophile and chalcophile elements in the upper mantle (Pearson et al. 2003) and mobilization of sulfide melts may produce fractionated chalcophile and platinum group element (PGE) patterns (Alard et al. 2000, 2002; Ballhaus et al. 2006; Bockrath et al. 2004; Delpech et al. 2012; Hart and Gaetani 2006; Li and Audétat 2012; Powell and O’Reilly 2007). Furthermore, sulfides are key hosts of Os, Pb, and potentially He and therefore play an important role in evolution of important isotopic systems (Hart and Gaetani 2006; Huang et al. 2014; Pearson et al. 2002; Roy-Barman et al. 1998). Consequently, they are widely-used targets for Re-Os and Pb-Pb geochronologic studies (Pearson et al. 1998, 2003) but interpretation of resulting ages depends on sulfide parageneses. Sulfide melts are also potentially responsible for mantle geophysical anomalies, as their physical properties differ greatly from those of silicates. These include higher density, surface tension, electrical conductivity and lower melting points (Bockrath et al. 2004; Helffrich et al. 2011; Mungall and Su 2005). For example, it has been speculated that sulfide melts are responsible for seismic anomalies at ~100 km in continental cratons (Helffrich et al. 2011).

A key feature of natural sulfide is that it may be molten in large parts of the mantle (e.g., Bockrath et al. 2004; Hart and Gaetani 2006) and so constraining its geochemical and geophysical role requires defining the conditions of sulfide melt stability. Although detailed one atmosphere studies have explored the Fe-Ni-S phase diagrams at 900 °C-1350 °C (e.g., Hseih et al. 1987; Waldner and Pelton 2004 and references therein), the majority of high pressures studies on sulfide melting to date have been performed on simple stoichiometric or eutectic compositions (Boehler 1992, 1996; Ryzhenko and Kennedy 1979; Sharp 1969; Usselman 1975).
Many of these have focused on the influence of sulfide on core formation, and so have examined relations in metal-rich compositions, including studies to very high pressures (Boehler 1992; Fei et al. 1997; Morard et al. 2011; Stewart et al. 2007). But fewer studies have considered melting relations of compositions appropriate for the modern upper mantle, and these have been limited to relatively low (≤ 3.5 GPa) pressures (Ballhaus et al. 2006; Bockrath et al. 2004).

Comparison of experimental studies of stoichiometric sulfides to those conducted in metal-rich sulfide-metal eutectics shows that melting temperatures are strongly variable depending on metal/sulfide ratios (Fig. 1). Further, substitution of Ni and Cu for Fe also influences melting temperatures (Hseih et al. 1987; Urakawa et al. 1987). Consequently, understanding melting of upper mantle sulfides requires perspective on the range of compositions likely to be present. Compositions of natural mantle sulfides are quite variable, in part owing to their tendency to exsolve on cooling (Pearson and Wittig 2014; Richardson et al. 2001). The most reliable records derive from reintegrated compositions from inclusions in olivine or diamond, studies of which (Aulbach et al. 2009; Westerlund et al. 2006) indicate that most upper mantle sulfides have compositions close to monosulfide stoichiometry with metal/sulfide (M/S) ratios typically between 0.9-1.2 (Fig. 2).

Previous experimental constraints on the high pressure melting of monosulfide similar to natural mantle composition derive chiefly from the studies of Bockrath et al. (2004) and Ballhaus et al. (2006). Bockrath et al. (2004) documented the melting interval of a bulk composition \( \square \) with an M/S ratio of 0.93, which is at the low end of the range present in natural mantle compositions (Fig. 2a; Table 1). Ballhaus et al. (2006) reported further compositional details about the phases produced by melting at \( \square \) and extended this work to include two more metal-rich compositions, \( \square \) with M/S of 1.06 and \( \square \) with M/S of 1.11. All three compositions had Ni contents (15.5 wt.%)
appropriate for mantle sulfides as calculated Fe-Ni exchange equilibrium with mantle olivine, and small amounts of Cu. The solidus of the low M/S is near 1075°C at 0.1 MPa and 1275 °C near 3 GPa, placing it below the convecting mantle adiabat (Katsura et al. 2010), above typical continental geotherms (Pollack and Chapman 1977), and similar to temperatures for intermediate-age oceanic lithosphere (Turcotte and Schubert 2002). More metal rich compositions and have markedly lower solidi: that of is 75-100 °C lower than for . The solidus of appears to be as low as 800 °C and with very little pressure dependence, perhaps because its composition falls outside of the field for mss (Fig. 2b). It likely has more than one phase below the solidus and so its melting behavior is similar to that at the Fe-FeS or (Fe,Ni)S-(Fe,Ni)O eutectics (Fig. 1).

Together, these data indicate that mantle sulfide is partially molten in the hotter parts of the upper mantle, but significant questions remain. The experiments on natural monosulfide (mss) compositions extend only to 3.5 GPa and so do not pertain to the deeper parts of continental lithosphere or the oceanic low velocity zone. Also, constraints on the liquidus are absent for and and produce curious results for , indicating a concave upward trend that is contrary to expected melting behavior (e.g., Hart and Gaetani 2006). Here we present partial melting experiments on a bulk composition similar to up to 8 GPa. Our purpose is to verify the solidus and liquidus determined by Bockrath et al. (2004), and to determine the phase relations of this relatively refractory composition to higher pressure. An additional motivation is to refine pressure and temperature calibrations in the piston cylinder and multi-anvil devices, to enhance the reliability of the sulfide melting results.
EXPERIMENTAL METHODS

Starting materials and preparation of sample capsules

Experimental starting materials were prepared by mixing Alfa-Aesar reagents including Fe (99.9% powder), FeS₂ (99.9% powder), Ni (99.8% powder) and Cu (99.9% powder). The mixture was homogenized by grinding under ethanol in an agate mortar for 1 hour. After mixing, samples were dried at 110 °C in a vacuum oven for 5 minutes. Subsequently, starting mixes were stored in a sealed glass container in a sealed glass desiccator to avoid oxidation. Subsequent electron microprobe analysis of post-experiment samples indicate <0.6 wt.% oxygen, suggesting minimal oxidation of the starting material.

Starting mixtures were loaded into silica glass capsules, which consisted of a tube closed with a cap on both ends. For piston cylinder experiments, tubes were 2 mm long with inner and outer diameters of 2 and 3 mm and the caps were each 1 mm long. For multi-anvil experiments, the tubes were 1 mm long, with inner and outer diameters of 1 and 2 mm, and caps were 1 mm long.

High-pressure experiments

Experiments were performed using an end-loaded piston cylinder (PC) device and a 1000-ton Walker-style multi-anvil (MA) apparatus using procedures described in detail by Xirouchakis et al. (2001) and Dasgupta et al. (2004). The PC experiments were conducted in 1.27 cm diameter pressure vessels from 0.8-3.3 GPa using a hot piston in technique, with hydraulic pressure maintained constant during the run period and with temperature controlled by a type B (Pt₀₇Rh₃₀/Pt₀₅Rh₆) thermocouple located 1 mm above the top of the capsule. Assemblies consisted of BaCO₃ cells with MgO spacers and a graphite heater. MgO assemblies were dried at 1000 °C for
8-15 hours and stored in a drying oven at 110 °C. The MA experiments were conducted at 2.7-
8.0 GPa using 18/12 OEL/TEL assemblies, including cast MgO-Al₂O₃-SiO₂-Cr₂O₃ octahedra and
integrated gasket fins. Straight-walled graphite furnaces and type C (W₇₄Re₂₆/W₉₅Re₅)
thermocouples were used for all MA experiments and are located ~1 mm from the sulfide
charges. Samples were compressed to target pressures, dwelling for 5 hours to allow assembly
stabilization and then heated to the target temperature. Both PC and MA experiments were
quenched by power termination. Individual experimental run conditions are detailed in Table 3.

Pressure and temperature calibration experiments

To ensure that experimental temperatures and pressures were accurate for the conditions of the
sulfide melting experiments, we conducted several new calibrations to refine previous
documentation of PC and MA performance in the UMN experimental petrology laboratory by
Xirouchakis et al. (2001), Dasgupta et al. (2004), Withers et al. (2011) and Tenner et al. (2012).
Pressure calibrations were conducted against the quartz-coesite transition (Bohlen and Boettcher
1982; Bose and Ganguly 1995). Temperature calibration was conducted against the melting
temperature of Au (Mirwald and Kennedy 1979).

For quartz-coesite experiments in the PC device, a homogeneous mixture of the two phases
(50:50) was sealed in Pt capsules. The quartz was taken from a crushed natural gem-quality
crystal. The coesite was presynthesized from Corning silica glass in a graphite capsule at 900 °C
and 4 GPa, based on previous syntheses conducted by Luo et al. 2002, and verified by XRD.
Each experiment lasted 2 to 12 hours at the target temperature and pressure and then the Pt
capsule was cut and the portion of the post-run product that had been closest to the thermocouple
was collected for XRD analysis. Because reaction was not always complete, the intensities of the
XRD peaks of experimental samples were compared to those of the starting mixture. In the MA apparatus, the silica glass capsule sample lids from sulfide melting experiments were examined post-experiment. The top lid of the silica capsule was recovered and analyzed by Raman Spectroscopy and ground to a powder for XRD.

For the Au melting experiments, a 2-mm diameter and 2-mm length hole was drilled into the MgO spacers in the same geometry as the capsule would residue during a normal experiment, and the hole was filled with NaCl powder into which an Au wire was placed. The sample was heated to 30 °C below the target temperature and held for 2 hours to ensure pressure stabilization. After that, temperature increased by 10 °C/min to the target temperature. The experiment was held at the target temperature and pressure for 6 minutes and was then quenched to room temperature. The post-run sample was placed in a beaker filled with water, thereby dissolving the NaCl. Au spheroids indicated melting whereas relict wires remained in subsolidus melting experiments (Fig. 3).

Analytical methods

Following sulfide melting experiments, the assembly was gradually decompressed to minimize sample fracturing and the recovered capsules were mounted in epoxy and ground to expose the medial section of the charges. Owing to the low hardness of sulfide, the sample was impregnated with epoxy prior to grinding. Polishing was conducted with diamond polishing pads, starting from 9.0-micrometer grit down to 0.5-micrometer. Run products and standards were carbon coated and analyzed using a JEOL JXA8900R electron microprobe by WDS analyses with an accelerating voltage of 15 kV and a probe current of 20 nA. Counting times were 20 s on peak centroid and 10 s on each background for all elements. Oxygen was measured using a multilayer
crystal (LDE2 with 2d = 9.7 nm). Primary standards used for major elements analysis were pyrite (FeS2) for Fe and S, Ni metal for (Ni), chalcocite (Cu2S) for Cu and S, and magnetite (Fe3O4) for O. Troilite was used as a secondary standard for Fe and S. Pyrite was used as a blank for oxygen. We employed a focused beam on crystalline sulfides and a defocused beam (1-20 micron diameter) on quenched melts.

RESULTS AND DISCUSSION

Pressure and temperature calibration

Comparison of the quartz-coesite reaction at 1100 °C bracketed by the PC with the reaction determined by Bohlen and Boettcher (1982) and Bose and Ganguly (1995) suggests a pressure correction of -0.4 GPa (Table 2). For the MA, the coesite-quartz bracket 1230-1250 °C in this study falls between the previously-determined force-pressure curves determined at low temperature (1000-1200 °C, Dasgupta et al. 2004), and high temperature (1440-1700 °C, unpublished data) (Fig. 4a) and suggests a similar force-pressure relationship to that from enstatite-pyrope experiments in the same assembly at 1300-1400 °C (Tenner et al. 2012). Because the high temperature and low temperature F-P curves converge at high pressure, the intermediate temperature quartz-coesite and enstatite-pyrope brackets can be used to construct a force-pressure calibration curve valid from 3 to 8 GPa (Fig. 4a).

Comparison of gold melting experiments to the Au fusion curve of Mirwald et al. (1975) and Mirwald and Kennedy (1979) indicate that sample temperatures are 10-15 and 15-20 °C hotter than thermocouple readings for the PC and MA assemblies, respectively. The former is in good agreement with the 12 °C offset determined in the PC from multiple thermocouple measurements (Xirouchakis et al. 2001) and the latter is similar to that estimated by previous studies in the MA
Dasgupta et al. 2004; Withers and Hirschmann, 2007; Tenner et al. 2012). All sulfide melting

temperatures and pressures reported in Table 1 have been adjusted for the pressure and
temperature calibrations reported here.

The pressure calibration determined for the BaCO$_3$ assemblies in the PC at 1100 °C suggest a
friction correction of -12%, which is nearly twice to that determined at comparable pressures in
the same assembly in the UMN laboratory at 1250 °C based on the anorthite breakdown reaction
(Xirouchakis et al. 2001). The difference is presumably owing to greater friction at lower
temperature. Previous studies for BaCO$_3$ assemblies at comparable pressures have found similar
friction corrections (15% Fram and Longhi 1992; 9% McDade et al. 2002). In contrast to results
in the UMN laboratory, McDade et al. (2002) found friction in the BaCO$_3$ pressure assembly to
be independent of temperature from 1000-1600 °C. It remains unclear whether differences in
calibration are owing to subtle differences in assemblies or piston cylinder performance, but
comparison between different calibrations suggest that interlaboratory pressure accuracies for PC
experiments are, in best cases, ±0.1 GPa.

**Phase relations, solidus, and liquidus determinations**

Phase relations were determined chiefly from textural and compositional observations based on
optical backscattered electron (BSE) images (Fig. 5) and electron microprobe analyses (Table 3)
Combining both textures and compositions, phase relations are determined on melt and mss. On
the one hand, textures of mss and melt are different based on the observation of optical images
and backscattered electron (BSE) images. Mss in the post-run charge is homogenous granular
grains in texture; melt was quenched into crystals with a wormlike intergrowth texture. On the
other hand, Cu, Ni, Fe and S are fractionated between melt and mss if both phases coexist and
equilibrate at high temperature before quenching, with Cu and Ni being incompatible in the Fe-
Ni-Cu-S monosulfide system (discussion in the next section below). In addition, mss phases are
homogenous by composition at micron scale while quenched melts are highly heterogeneous by
composition at micron scale. This is the reason for the employment of a focused beam on
crystalline sulfides and a defocused beam (1-20 micron diameter) on quenched melts. From the
perspective of polishing, due to the hardness contrast between quartz and sulfide, post-run
products were polished with prevalent cracks on the surface. During polishing, subsolidus
aggregates tend to disintegrate whereas superliquidus and partially melted experiments do not
tend to disintegrate.

Exposed charges were unavoidably pervasively cracked during polishing, owing to the hardness
contrast between sulfide charges and surrounding silica minerals. In some cases, this prevented
high quality polishes across the entire charge, but sufficient material was always exposed to
allow textural and compositional analysis. Selected BSE images are shown in Fig. 5 and electron
microprobe analyses are reported in Table 3. The subsolidus samples consist of a homogeneous
single monosulfide (mss) phase with granular texture and grain diameters typically 100-300
microns (Fig. 5a) with a composition that in all cases is within analytical uncertainty of the
starting material (Fig. 5a). Experiments that underwent partial melting produced two phases (Fig.
5b): a homogenous Fe-rich mss phase granular mss crystals typically > 100 microns and a Ni-Cu
rich heterogeneous phase material that, following quench, consists of smaller (50 micron) grains
interspersed with darker (on BSE) with wormlike intergrowths between grains textures. Crystals
and quenched melt are well-segregated by gravity. Electron microprobe analyses indicate
compositions that are more heterogeneous than subsolidus mss, but the bulk compositions are
comparable to that of the starting composition (Fig. 5b). Experiments inferred to have been
superliquidus quench to textures consisting of two sulfide phases in a wormlike intergrowth, similar to those produce by partially molten samples with the same composition as the starting material within starting powder mixing uncertainty and analytical uncertainty (Fig. 5c). Additional textural evidence that aided the interpretation of solidus location was the behavior during polishing: subsolidus aggregates tended to disintegrate, whereas superliquidus and partially melted experiments were more cohesive.

Crystalline mss produced in subsolidus experiments are compositionally homogeneous within analytical uncertainty and are not distinguishable from the bulk composition (Table 3). When melt and crystals coexist at high temperature, granular sulfides are compositionally homogeneous and enriched in Fe and S and poor in Ni and Cu relative to the bulk composition. In comparison, the quenched melt phase is heterogeneous on a micron scale, necessitating analysis with an unfocussed electron beam. The quenched melt phase is depleted in Fe and S and enriched in Ni and Cu relative to the crystalline solids or the bulk composition. In one case (Experiment M794, 6.9 GPa, 1400 °C), quenched melt was observed but coexisting granular crystals were not evident. However, sub-liquidus conditions were inferred because the melt composition was enriched in Cu and Ni relative to the bulk composition. Melts interpreted to be quenched from superliquidus conditions based on textural features are also heterogeneous, but have compositions within analytical uncertainty of the starting composition.

Experimental determinations of the mss solidus and liquidus up to 8 GPa can be fit with an empirical relation that minimizes the disagreement between observations and the computed curve according to a penalty function as described by Hirschmann (2000), for which an objective variable, $Y$, given by $Y=\Sigma(T_i)^2$, is minimized, where $T_i$ is given by
\[ T_i = (T_i - T_{\text{model}})^2; \quad \text{if the assemblage observed at } T_i \text{ disagrees with } T_{\text{model}} \]

= 0; \quad \text{if the assemblage observed at } T_i \text{ agrees with } T_{\text{model}}

and \( T_{\text{model}} \) is the temperature calculated from the solidus or liquidus curve. We examined several types of functions to fit to the solidus and liquidus brackets, including polynomial and logarithmic forms, and though the differences among these fits are small, ultimately chose to employ an equation similar to that proposed by Simon and Glatzel (1929),

\[ T = T_{\text{ref}} \left( \frac{P}{a} + 1 \right)^c \]

where \( T \) is temperature (°C) and \( P \) is pressure (GPa). For the solidus up to 8 GPa, we find \( T_{\text{ref}} = 1015.1°C, a=1.88, \) and \( c=0.206 \) (0 ≤ \( P \) ≤ 8) \( (Y=768) \), and, for the liquidus, \( T_{\text{ref}} = 1067.3°C, a=1.19, \) and \( c=0.149 \) (Fig. 6).

In this study, the solidus fit \( T(°C)=1015.1[P(GPa)/1.88+1]^{0.206} \), is thought to be accurate within ± 15 °C over the pressure interval from 1 to 3.5 GPa and within ± 30 °C from 3.5 to 8.0 GPa, owing to different temperature uncertainties in PC and MA devices and different \( P-T \) densities of experimental brackets (typically 25 °C for PC and 50 °C for MA experiments). The fit from 0.1 MPa to 0.8 GPa might be less accurate because brackets constraining solidus at 0.1 MPa were taken from previous studies and the present study included no experiments between 0.1 MPa-0.8 GPa. Therefore, this solidus is constrained chiefly to mantle depths of 30 km to 250 km.

At high pressures, the solidus and liquidus curves tend to converge, producing a narrowed melting interval. This may be an artifact of imperfections in the regressed curves, with the Simons equation predicting solidus temperatures that are near the high limit of the experimental brackets, and the liquidus curve poorly constrained owing to few high pressure observations.
The melting interval for mss can be compared to that determined by Bockrath et al. 2004 for an apparently identical composition in similar capsules up to 3.5 GPa (Fig. 7). Solidus temperatures are consistent, but the liquidus found by Bockrath et al. 2004 extends to much higher temperature – e.g., at 3 GPa Bockrath et al. (2004) observed mss coexisting with melt up to 1400 °C, but the new results place the liquidus near 1275 °C. As noted by Hart and Gaetani (2006), the high melting temperatures indicated by Bockrath et al.’s experiments suggest a concave upward liquidus slope and, at pressures near 3 GPa, liquidus temperatures hotter than the melting of pure Fe$_{1-x}$S (Ryzhenko and Kennedy 1973) (Fig. 1), both of which are unlikely. These inconsistencies are absent from the new liquidus curve.

The melting interval for mss determined in this study is intermediate between the high temperature fusion curves of pure troilite, FeS, or pyrrhotite, Fe$_{1-x}$S, and eutectic melting in the system FeS-Fe (Fig. 1). The pyrrhotite studied by Ryzhenko and Kennedy (1973) had similar metal/sulfide stoichiometry to the mss studied here (Table 1), meaning that the lower melting temperature of the mss is owing chiefly to the effects of Fe-Ni solid solution. This is consistent with many previous studies that have found that Ni reduces the melting temperature of monosulfide (Hsieh et al. 1987; Urakawa 1987).

**Partial melting and fractionation of elements between melt/mss**

For experiments that produce coexisting melt and monosulfide crystals, melt fractions calculated independently from Fe and Ni mass balance (Table 2) agree well with one another (Fig. 8). Melt fractions calculated from Ni are considered most accurate because of the strong mineral/melt partitioning and high concentrations (compared to Cu) produce phase compositions that are most strongly separated compared to analytical uncertainties. Therefore, Ni concentration in melts is
chosen to represent melt evolution. In all samples, the melts have slightly higher metal/sulfur ratio than their coexisting residue mss (Table 3). Ni and Cu preferentially partition into melts and Fe is concentrated in residue mss (Fig. 9). The detection limit for oxygen established by analyzing pyrite is ~0.05 wt.%, with the analytical uncertainty of ±0.1 wt.%. Oxygen is detected in small amounts in both mss and melt. Oxygen concentrations in the post-run products vary from 0.2-0.6 wt.%, with slightly greater concentrations in quenched melts compared to crystals (Table 3). The concentrations detected in our study are comparable to those (~0.37 wt.%) found previously in pyrrhotite annealed at 700 °C (Graham et al. 1987; Graham and McKenzie 1987).

Partial melt compositions have higher M/S ratios than residual mss solids (Table 3), consistent with relations established previously for melting of mss (Kullerud 1963; Bockrath et al. 2004; Ballhaus et al. 2006) and in simple systems (Ryzhenko and Kennedy 1973). MSS compositions change comparatively little, being restricted chiefly to M/S ratios between 0.90-0.93 owing chiefly to the constraints of M/S stoichiometry in mss solid solutions (Ballhaus et al. 2006), whereas melt compositions are more variable (M/S=0.94-1.02). Partial melts are also enriched in Ni and especially Cu compared to coexisting mss, whilst Fe concentrations are similar in the two phases. This is as expected owing to the respective radii of the cations (Cu>Ni>Fe). Mineral/melt partition coefficients for Cu and Ni become more extreme at low melt fractions, likely owing to the increased Ni/(Fe+Ni) of the melts (Fig. 9). Based on the enrichment or depletion of Cu and Ni, sulfides from mantle xenoliths or diamond inclusions has been interpreted as either trapped melts or residual mss crystals (Bulanova et al. 1996; Guo et al. 1999; Lorand and Alard 2001). Such interpretations are broadly consistent with the experimental compositions observed here.

The variations in metal/silicate and Cu-Ni-Fe fractionations with melt fraction and temperature are linked to the constraints on mss stoichiometry and the influence of Ni on partitioning
behavior. These relationships vary only weakly with pressure, as has been previously
documented for M/S partitioning (Ballhaus et al. 2006) and Ni partitioning (Jones and Walker
1991). The lack of pressure influence on partitioning suggests that the melting interval between
solidus and liquidus curves should not become significantly wider or narrower with pressure, and
reinforces the assertion above that the liquidus, which is under-constrained at pressures above
3.5 GPa, likely is slightly hotter at high pressure than indicated by the parameterization.

Sulfide composition in the mantle

The sulfide solidus is affected by composition, which in the mantle, is controlled by reactions
between sulfides and coexisting silicate minerals (Eggler and Lorand, 1993; Gaetani and Grove,
1997). Solidus temperatures are lower when sulfide has higher M/S ratios (e.g. Ballhaus et al.
2006), and when additional components (such as C or O) are soluble (Ballhaus et al. 2006; Chi et
al. 2014; Dasgupta et al 2009; Gunn and Luth 2006; Urakawa et al 1987). The sulfide M/S (0.93)
investigated in this study is on the low end of natural mss (0.9-1.1) (Fig. 2), with low content of
oxygen and nominally carbon-free.

In the shallow oxidized mantle, oxygen dissolved in sulfide might be high (Gataeni and Grove
1999) and drive the sulfide solidus downward (Gunn and Luth 2006; Urakawa et al 1987). As the
mantle becomes more reduced with increasing depth (Frost and McCammon 2008), the oxygen
content should diminish, but this can be countered by increases in the M/S ratio owing to an
increase in metal activity, as the reactions

$$\text{Fe}_2\text{SiO}_4 \text{ (ol)} = \text{FeSiO}_3 \text{ (opx)} + \frac{1}{2} \text{O}_2 + \text{Fe (sulfide)}$$

$$\text{Ni}_2\text{SiO}_4 \text{ (ol)} = \text{NiSiO}_3 \text{ (opx)} + \frac{1}{2} \text{O}_2 + \text{Ni (sulfide)}$$
shift to the right. Equivalently, Eggler and Lorand (1993) suggest that oxygen fugacity ($f_{O_2}$) and sulfur fugacity ($f_{S_2}$) are positively correlated for peridotite-sulfide systems. Reactions similar to:

$$\text{Fe}_2\text{SiO}_4 \text{ (ol)} + \frac{1}{2} \text{S}_2 = \text{FeSiO}_3 \text{ (opx)} + \text{FeS} \text{ (sulfide)} + \frac{1}{2} \text{O}_2$$

also produce increases in M/S ratio of the sulfide as oxygen fugacity decreases. Furthermore, as mantle enters the graphite/diamond stability field (>4 GPa) (Frost and McCammon, 2008), dissolved carbon will likely further depress sulfide solidus temperatures.

All of these considerations together suggest that the sulfide solidus constrained in this study is near an upper bound. At low pressures and more oxidized conditions, the solidus would be lowered by greater dissolved oxygen, and at higher pressures and more reduced conditions, it would be diminished by higher M/S ratio and dissolved C.

**Sulfide melts in the mantle**

The solidus and liquidus of monosulfide constructed from this study is below the calculated mantle adiabat (Katsura et al. 2010) up to the limit of the experimental data at 8 GPa (Fig. 10), meaning that sulfide is molten in the convecting mantle at least to depths of 250 km. We note that the composition investigated has comparatively low M/S ratio, and that sulfides with higher ratios melt at lower temperature (e.g. Ballhaus et al. 2006), so that melting is expected for most or all mantle sulfide compositions. The steeper temperature/pressure slope of the melting curves compared to the adiabat may indicate that sulfide becomes crystalline deeper in the mantle.

Increased M/S should in turn decrease the sulfide crystallization temperature (e.g. Ballhaus et al. 2006). If conditions at depth become sufficiently reducing such that a metal alloy phase is stabilized (Frost et al. 2004; Rohrbach et al. 2007, 2011), then sulfide melting is controlled by
the (Fe,Ni)S-(Fe,Ni) eutectic, which remains below the adiabat at least until pressures reached deep in the lower mantle (>60 GPa; Campbell et al. 2007; Morard et al. 2011; Stewart et al. 2007). Thus, sulfide melt may in fact be stable throughout the convecting upper mantle and perhaps into the transition zone.

The sulfide melting curves intersects geotherms for typical oceanic lithosphere shallower than the intersection with the adiabat, meaning sulfide could be partially molten in the thermal boundary layer and deeper portions of the oceanic lithosphere (Fig. 10). In the continental lithosphere, sulfides are less likely molten in the colder settings such as the root of cratons. Of course, sulfides with higher M/S ratios and dissolved carbon could become molten at lower temperatures.

**Sulfide inclusions in diamond**

Sulfide inclusions are abundant in diamond, and are typically Ni-rich (22 wt.%-36 wt.%) in peridotitic parageneses (age >3 Ga) and Ni-poor (0-12 wt.%) in eclogitic diamonds (age <3 Ga), which corresponds to high bulk Ni contents (~3000 ppm) in peridotite or and low bulk Ni (~300 ppm) concentrations typically found in eclogite (Bulanova et al. 1996; Pearson et al. 2003; Shirey and Richardson 2011; Stachel and Harris 2008). The overabundance of sulfide in diamond suggests that sulfide acts either as a reducing reagent or as a co-precipitating product during diamond formation, more than likely as a liquid phase (Bulanova 1995; Stachel and Harris 2008; Westerlund et al. 2006). Although the solidus of monosulfide investigated here is hotter than typical diamond P-T, molten sulfide could be trapped in diamond if it originates from compositions with comparatively high M/S ratios, or if additional components (such as C or O) lower the solidus (Ballhaus et al. 2006; Gunn and Luth 2006). In addition, for sulfides that were
trapped as inclusions in large melt extraction process from peridotite, sulfides might be molten
due to this high temperature process in the earlier geological history. This is indicated by the
mantle sulfides Re-Os modal age peaks of 1.2, 1.9, and 2.7 billion years which match similar
periods of high tectonic activity recorded in zircon populations (Pearson et al. 2007). If sulfides
are trapped as liquids, then they are syngenetic with their hosts and geochronologic
interpretations of their Re-Os or Pb-Pb isotope systematics can be related to the timing of the
formation of the enclosing minerals.

Mobility of sulfide melts

Having established that sulfide is molten or partially molten in significant portions of the mantle,
a natural question is whether such melts are mobile. Sulfide melt mobility is affected by oxygen
fugacity and pressure in the mantle (Gaetani and Grove, 1999; Shannon and Agee 1998; Shi et al.
2013). At conditions similar to the fayalite-magnetite-quartz oxygen buffer, molten sulfide may
potentially dissolve up to 9 wt.% oxygen (Gaetani and Grove, 1999) and sulfide melt can
potentially form an interconnected network along silicate grain edges, as the olivine–melt
dihedral angle is 52° (Gaetani and Grove, 1999). As conditions become more reduced and
dissolved oxygen diminishes, the dihedral angle increases (e.g., 90° at near the iron-wüstite
buffer, Gaetani and Grove 1999) and interconnectivity is less likely. At lower mantle conditions,
where the principle silicate is perovskite rather than olivine, high dihedral angles for Fe-Ni-S
melts prevail (Shannon and Agee 1998; Shi et al. 2013), inhibiting connectivity. Therefore, in the
shallow mantle (e.g. 30-60 km), sulfide melts, if stable, potentially form an interconnected
network in olivine-rich rocks. In the deep lithosphere (e.g. >120 km), percolation may be limited
as conditions become more reduced (Frost and McCammon, 2008). Additionally, sulfide melt
transport may be coupled to movement of associated silicate or carbonate melts (Delpech et al.
In some cases, natural peridotite textures indicate sulfide wetting silicate grain boundaries (Lorand et al. 2013). Furthermore, geochemical variations observed in xenoliths may not be easily explicable without sulfide mass transport (Lorand 1989; Lorand et al. 2013).

Sulfide melt mobility may be a key factor determining their geophysical and geochemical influence. For example, despite molten sulfide’s extreme physical properties relative to silicate rock, it may not impart significant geophysical anomalies simply by melting in situ, as the melt fraction for rocks with typical mantle S concentrations (200 ppm, McDonough and Sun 1995) would be merely 0.05-0.10 vol.%. If sulfide melts can migrate and concentrate in isolated areas, they may feasibly produce noticeable effects on shear wave velocities (e.g., Helffrich et al. 2011) and other properties. Likewise, sulfide melts are most likely to be responsible for geochemical variations in chalcophile or PGE elements (e.g., Alard et al. 2002; Powell and O’Reilly 2007) if they are mobile.

**IMPLICATIONS**

We emphasize that we have investigated only a single composition of sulfide Fe$_{0.69}$Ni$_{0.23}$Cu$_{0.01}$S$_{1.00}$ (M/S=0.93), which is calculated as in equilibrium with mantle olivine at FMQ, with trace amounts of oxygen (and likely carbon). As the upper mantle becomes more reduced with depth (Frost and McCammon, 2008), the M/S ratio of sulfide should increase, leading to further depression of the sulfide solidus (Ballhaus et al. 2006; Rohrbach et al. 2007). Also, in the oxidized shallow mantle (e.g. < 3 GPa), sulfides melts should have higher content of oxygen and in the graphite/diamond stability field (e.g. > 4 GPa), dissolved carbon should
increase, and both of these should affect melting temperatures. Therefore, the solidus constrained in this work is likely an upper bound on sulfide melting in the Earth’s upper mantle.

ACKNOWLEDGEMENTS

We are grateful for the constructive reviews from James Brenan and Glenn Gaetani. We appreciate the aid and advice of UMN colleagues: Anthony Withers in the experimental petrology laboratory, Anette von der Handt in the electron microprobe laboratory, and Chris Crosby in the geobiology laboratory. We acknowledge the support of grants NSF EAR1119295 and EAR1426772.

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FIGURE CAPTIONS

FIGURE 1. Melting relations from selected previous sulfide melting experiments up to 15 GPa. Compositions and data sources are given in Table 1.

FIGURE 2. (a) Sulfide compositions projected into the metal-sulfur-oxygen atomic ternary. Metal is the sum of Fe, Ni and Cu. Natural sulfide compositions are taken from bulk composition estimates of sulfides trapped in diamonds and olivine as inclusions (Aulbach et al. 2009; Bulanova et al. 1996; Westerlund et al. 2006;); (b) Sulfide compositions projected into the Fe-S-Ni ternary. Minor amounts of Cu and O have been projected to the Ni and S apices, respectively. The yellow and pink areas correspond to the fields of stability of mss and mss+melt at 0.1 MPa, 1000 °C (Hsieh et al. 1987). Numbered circles refer to sulfide compositions that have been investigated experimentally, as listed in Table 1. Natural sulfide compositions are plotted as grey circles from the same references as (a).

FIGURE 3. Optical images of Au recovered from pressure and temperature calibration experiments. Gold spheroids are produced from experiments that exceeded the melting temperature of Au, whereas relict wires are observed from experiments that remained below the Au fusion curve.
FIGURE 4. Revised pressure and temperature calibrations of multi-anvil device at UMN using the 18/12 TEL/OEL assembly. (a) Pressure-force relations of the best fit functions are $P = -1.15 \times 10^{-5} F^2 + 2.44 \times 10^{-2} F + 4.56 \times 10^{-3}$ for 1000-1200 °C (Dasgupta et al. 2004), $P = -1.29 \times 10^{-5} F^2 + 2.61 \times 10^{-2} F - 5.17 \times 10^{-3}$ for 1200-1400 °C (this study), and $P = -1.65 \times 10^{-5} F^2 + 3.03 \times 10^{-2} F - 1.76 \times 10^{-3}$ for 1400-1700 °C (unpublished data), where $P$ is pressure (GPa) and $F$ is force (tons). The blue square corresponds to 170 tons and 3.49-3.53 GPa (Tenner et al. 2009) and the purple circles represent coesite and red diamonds represent quartz; (b) Temperature calibration results on PC and MA. Thermocouple temperatures and corrected sample pressures are plotted together with gold melting curve calibrated with previous calibration work by Mirwald and Kennedy (1979). Lower temperatures read by thermocouples compared to the fusion curve reflect the offset in temperature between the thermocouple location and the sample hotspot.

FIGURE 5. Backscattered electron images of typical textures from quenched experiments exemplifying (a) super-liquidus conditions (B536: 1.8 GPa, 1300 °C), (b) partially molten (A1075: 1.8 GPa, 1200 °C), and (c) subsolidus (B534: 1.8 Ga, 1100 °C).

FIGURE 6. Experimentally determined melting relations of Fe$_{0.69}$Ni$_{0.23}$Cu$_{0.02}$S$_{1.00}$. Blue diamonds are sub-solidus mss, with filled diamonds from piston cylinder (PC) experiments and empty diamonds from those conducted in the multi-anvil (MA), respectively. Red and orange circles are melt-mss pairs by PC and MA, respectively. Green and black triangles are superliquidus runs by PC and MA, respectively. Solid curve is the parameterization of the solidus, given by $T(°C)=1015.1[P(GPa)/1.88+1]^{0.206}$ and the dashed curve is liquidus, given by $T(°C)=1067.3[P(GPa)/1.19+1]^{0.149}$. Melting relations at 0.1 MPa are taken from Bockrath et al. (2004).
FIGURE 7. Comparison of mss melting relations calibrated from experiments in this study (Fig. 6) with experiments done by Bockrath et al. (2004). Diamonds are sub-solidus mss; circles are melt-mss pairs; triangles are superliquidus runs. The square bracket with a red filling and green triangle is the “problem bracket”, which is labeled as “melt + solid” by Bockrath et al. (2004), but is listed as “solid only” in their supplementary material. Our results suggest that the experiment should have been completely melted at the stated run conditions. The solidus and liquidus derived from the parameterization of the present study (Fig. 6) are shown as solid and dashed curves, respectively.

FIGURE 8. Comparison of melt fractions calculated by Fe and Ni mass balance. Calculations are in close agreement, but those from Ni are believed to be more accurate because concentrations of Ni are more distinct in mss and partial melts, giving more leverage to calculated mass balances.

FIGURE 9. Variations in mss/melt partition coefficient of Cu, Ni and Fe as a function of Ni content of the melt. Partitioning of Cu and Ni between crystalline and solid sulfide is more extreme for Ni-rich smaller-degree partial melts, and less so for higher-degree Fe-rich melts.

FIGURE 10. Comparison of mss solidus (solid black curve) and liquidus (dashed black curve) with mantle geotherms and domains of potential silicate melting. The mantle adiabat is given in the solid red line, with the shaded area representing the temperature uncertainty (Katsura et al. 2010). A geotherm applicable to oceanic lithosphere of plate ages ranging from 20 Ma and 80 Ma is calculated from a cooling half-space model (Turcotte and Schubert 2002) and representative continental geotherms are shown in the shaded dark areas, bounded by calculations for heat flows of 40 mW/m² and 50 mW/m² (Pollack and Chapman 1977). Regions
of diamond formation as inferred from inclusion thermobarometry are from Stachel and Harris
peridotite is shown as the green solid curve (Hirschmann 2000); hydrous peridotite (0.1 wt.%
bulk water) is the blue solid curve (Katz et al. 2003).
Figure 1

[Diagram showing a phase diagram with various temperatures and pressures, indicating phase transitions and eutectic points.]
Figure 2

(a) Fe+Ni+Cu vs S

- Natural sulfides
- MSS(0.93)
- MSS(1.06)
- MSS(1.11)
- Pyrrhotite(0.92)
- Troilite(1.00)
- Fe-FeS Eutectic
- FeO-FeS

(b) S+O vs Fe+Ni+Cu

- Natural sulfides
- mss
- mss+melt

Legend:

1. MSS(0.93)
2. MSS(1.06)
3. MSS(1.11)
4. Pyrrhotite(0.92)
5. Troilite(1.00)
6. Fe-FeS Eutectic
7. FeO-FeS

Natural sulfides
mss
mss+melt
Figure 4

(a) Graph showing the relationship between pressure (GPa) and force (tons). The lines represent different temperature ranges: 1000-1200 °C (solid blue), 1200-1400 °C (dashed blue), and 1440-1700 °C (red).

(b) Graph showing the thermocouple reading (°C) against pressure (GPa). The gold melting line (Mirwald and Kennedy, 1979) is depicted. Points labeled PC and MA with different markers indicating PC gold ball, PC gold wire, MA gold ball, and MA gold wire.
Figure 5

(a) Melt

(b) Melt MSS

(c) MSS

B536

A1075

B534
Figure 3

Gold Wire

Gold Ball

0.5 mm
Figure 6
Figure 7

From Bockrath et al., 2004

- Melt only
- Melt + MSS
- MSS only

Temperature (°C) vs. Pressure (GPa)
Figure 8
Figure 9

The diagram shows the relationship between the Mss/Melt Partitioning Coefficient and Ni concentration in melts (wt.%) for different elements.

- Fe (black squares)
- Ni (blue diamonds)
- Cu (red circles)
Figure 10
Table 1. Summary of high pressures studies on sulfide melting up to 15 GPa

<table>
<thead>
<tr>
<th>#</th>
<th>Description*</th>
<th>Chemical Formula (atomic)</th>
<th>Chemical Composition (wt.%)</th>
<th>Capsule</th>
<th>Apparatus†</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>FeₙNiₘCuₜOₘSₙ</td>
<td>Fe</td>
<td>Ni</td>
<td>Cu</td>
<td>O</td>
</tr>
<tr>
<td>1a</td>
<td>MSS (0.93) solidus</td>
<td>Fe₆.₆₅Ni₂₅Cuₐ.0₁S₁₀₀</td>
<td>45.3</td>
<td>15.8</td>
<td>1.0</td>
<td>--</td>
</tr>
<tr>
<td>1b</td>
<td>MSS (0.93) liquidus</td>
<td>Fe₆.₆₅Ni₂₅Cuₐ.0₁S₁₀₀</td>
<td>45.3</td>
<td>15.8</td>
<td>1.0</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>MSS (1.06) solidus</td>
<td>Fe₆.₇₅Ni₂₅Cuₐ.0₃S₁₀₀</td>
<td>47.9</td>
<td>15.6</td>
<td>1.9</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>MSS (1.11) solidus</td>
<td>Fe₇.₆₅Ni₂₅Cuₐ.0₃S₁₀₀</td>
<td>48.9</td>
<td>15.5</td>
<td>1.9</td>
<td>--</td>
</tr>
<tr>
<td>4a</td>
<td>Pyrrhotite (0.92)</td>
<td>Fe₉.₉₂S₁₀₀</td>
<td>62.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>4b</td>
<td>Pyrrhotite (0.92)</td>
<td>Fe₉.₉₂S₁₀₀</td>
<td>62.0</td>
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<td>--</td>
<td>--</td>
</tr>
<tr>
<td>5</td>
<td>Trolite</td>
<td>Fe₁.₁₀S₁₀₀</td>
<td>63.5</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>6a</td>
<td>Fe-FeS Eutectic†</td>
<td>Fe₇.₃₄S₁₀₀</td>
<td>69.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>6b</td>
<td>Fe-FeS Eutectic†</td>
<td>Fe₇.₃₄S₁₀₀</td>
<td>69.0</td>
<td>--</td>
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<td>--</td>
</tr>
<tr>
<td>6c</td>
<td>Fe-FeS Eutectic†</td>
<td>Fe₇.₃₄S₁₀₀</td>
<td>69.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>7a</td>
<td>FeS-FeO</td>
<td>Fe₈.₇₃O₁.₈₈S₁₀₀</td>
<td>85.7</td>
<td>--</td>
<td>5.0</td>
<td>9.3</td>
</tr>
<tr>
<td>7b</td>
<td>(Fe,Ni)S-FeO</td>
<td>Fe₄.₄₅Ni₅₆O₃₅S₁₀₀</td>
<td>78.2</td>
<td>9.1</td>
<td>--</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Notes: # refers to the curves labeled in Fig. 2. * Number in parentheses represents metal/sulfur atomic ratio. † The eutectic composition at 1 atmosphere. ‡ PC: piston cylinder; MA: multianvil; DAC: diamond anvil cell; BA: belt apparatus.
TABLE 2. Pressure and temperature calibration experiments using the quartz-coesite transition and gold fusion

**Quartz - coesite transition experiments**

<table>
<thead>
<tr>
<th>PC Run #</th>
<th>Uncorrected Pressure (GPa)</th>
<th>T (°C)</th>
<th>t (hrs)</th>
<th>Run product</th>
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<tbody>
<tr>
<td>A1199</td>
<td>3.50</td>
<td>1100</td>
<td>6</td>
<td>coesite</td>
</tr>
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<td>A1204</td>
<td>3.70</td>
<td>1100</td>
<td>6</td>
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<tr>
<td>A1209</td>
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<td>1100</td>
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<td>A1210</td>
<td>3.10</td>
<td>1100</td>
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<td>quartz</td>
</tr>
<tr>
<td>A1218</td>
<td>3.45</td>
<td>1100</td>
<td>6</td>
<td>quartz</td>
</tr>
<tr>
<td>A1219</td>
<td>3.40</td>
<td>1100</td>
<td>6</td>
<td>quartz</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>MA Run #</th>
<th>Force (metric tons)</th>
<th>T (°C)</th>
<th>t (hrs)</th>
<th>Run product</th>
</tr>
</thead>
<tbody>
<tr>
<td>M767</td>
<td>165</td>
<td>1250</td>
<td>2</td>
<td>coesite</td>
</tr>
<tr>
<td>M770</td>
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<td>coesite</td>
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<tr>
<td>M771</td>
<td>155</td>
<td>1230</td>
<td>2</td>
<td>coesite</td>
</tr>
<tr>
<td>M749</td>
<td>145</td>
<td>1250</td>
<td>3</td>
<td>quartz</td>
</tr>
<tr>
<td>M743</td>
<td>131</td>
<td>1250</td>
<td>3</td>
<td>quartz</td>
</tr>
<tr>
<td>M762</td>
<td>155</td>
<td>1250</td>
<td>2</td>
<td>quartz</td>
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</table>

**Gold melting experiments**

<table>
<thead>
<tr>
<th>PC Run #</th>
<th>Corrected Pressure (GPa)</th>
<th>Tc reading (°C)</th>
<th>t (hrs)</th>
<th>Run product</th>
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<tr>
<td>A1141</td>
<td>0.80</td>
<td>1086</td>
<td>0.1</td>
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<tr>
<td>A1137</td>
<td>1.80</td>
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<td>A1144</td>
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<td>A1135</td>
<td>1.80</td>
<td>1155</td>
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<td>A1142</td>
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<td>1150</td>
<td>0.1</td>
<td>gold ball</td>
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<tr>
<td>A1139</td>
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<td>A1147</td>
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<thead>
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<th>MA Run #</th>
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<th>Tc reading (°C)</th>
<th>t (hrs)</th>
<th>Run product</th>
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<tbody>
<tr>
<td>M762</td>
<td>3.23</td>
<td>1230</td>
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<td>gold ball</td>
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<td>M767</td>
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<tr>
<td>M771</td>
<td>3.23</td>
<td>1210</td>
<td>0.1</td>
<td>gold wire</td>
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TABLE 3. Experimental results and sulfide compositions by electron microprobe analysis.

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<thead>
<tr>
<th>P (GPa)</th>
<th>T (°C)</th>
<th>t (hrs)</th>
<th>n</th>
<th>Chemical Composition (wt.%)</th>
<th>Cu</th>
<th>O</th>
<th>S</th>
<th>Fe</th>
<th>Ni</th>
<th>Total</th>
<th>M/S</th>
<th>F_Fe</th>
<th>F_Ni</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Subsolidus runs: solid only</td>
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<td></td>
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<tr>
<td>A1078</td>
<td>0.8</td>
<td>1050</td>
<td>15</td>
<td>22 mss</td>
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<td>0.4</td>
<td>37.3</td>
<td>45.8</td>
<td>15.7</td>
<td>100.1</td>
<td>0.93</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>1100</td>
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<td>24 mss</td>
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<td>37.1</td>
<td>45.6</td>
<td>16.1</td>
<td>100.4</td>
<td>0.93</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>0.4</td>
<td>37.4</td>
<td>45.5</td>
<td>16.1</td>
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<td>18 mss</td>
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<td>36.6</td>
<td>45.7</td>
<td>16.1</td>
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<td>0.95</td>
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<td>-</td>
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<td>1150</td>
<td>14</td>
<td>19 mss</td>
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<td>0.3</td>
<td>36.6</td>
<td>46.1</td>
<td>16.3</td>
<td>100.2</td>
<td>0.96</td>
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<td>B554</td>
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<td>1200</td>
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<td>18 mss</td>
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<td>0.3</td>
<td>37.2</td>
<td>45.0</td>
<td>16.2</td>
<td>99.8</td>
<td>0.94</td>
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<td>-</td>
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<td>B641</td>
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<td>12</td>
<td>12 mss</td>
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<td>0.4</td>
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<td>45.5</td>
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<td>-</td>
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<td>0.4</td>
<td>36.7</td>
<td>45.5</td>
<td>16.2</td>
<td>99.7</td>
<td>0.94</td>
<td>-</td>
<td>-</td>
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<td>M749</td>
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<td>4</td>
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<td>0.3</td>
<td>37.1</td>
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<td>99.7</td>
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Notes: a. Number of electron probe spot analyses averaged to obtain the reported elemental concentrations. b. Atomic metal/sulfur ratio, oxygen is regarded as replacing sulfur in mss or melts. c. Melt fractions (F) are calculated by mass balance of Fe and Ni according to \( F = \frac{C_{bulk} - C_{mss}}{C_{melt} - C_{mss}} \), where \( C_{bulk} \) is the starting composition (\( C_{bulk} = 45.5 \) wt.% Fe or 16.2 wt.% Ni); \( C_{melt} \) is the concentration of Ni or Fe in the melt, and \( C_{mss} \) is the respective concentration in the crystalline phase.