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Title
Thermal State and Solidification Regime of the Martian Core:
Insights from the Fe-Ni-S Liquidus at 20 GPa

submitted in partial fulfillment of the requirements for the degree of
Master of Science in Earth and Environmental Sciences
Department of Earth and Environmental Sciences
The University of Michigan

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December 6, 2016
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Abstract

A series of multi-anvil experiments have been conducted to define the iron-rich liquidus of the iron-nickel-sulfur (Fe-Ni-S) system at 20 GPa, the estimated pressure of the Martian core-mantle boundary (CMB), across its entire temperature range. Due to the fineness of quenched liquid features at high temperatures and low S concentrations, spatial analysis techniques, in addition to electron microprobe analysis, were used to determine the compositions of some quenched liquid phases. The maximum concentration of S in the Fe(Ni) solid is only 0.6 wt.%, comparable to the Fe-S binary system, but far lower than prior results for the Fe-Ni-S system at 20 GPa. We attribute this to the tendency of FeNi alloys to form body-centered cubic (BCC) structures when at high Ni contents, in contrast with face-centered-cubic (FCC) structures when Ni contents are low. Our liquidus curve is nearly ideal, featuring a maximum temperature depression of 80 °C from 10 to 16 wt. % S, the likely range of Martian core composition. The slight negative departure from ideal behavior contrasts with the positive departure of liquidii previously applied to the Martian core without sufficient experimental constraints.

Unlike existing liquidii at 23 GPa, which predict a fully molten core for a narrow range of sulfur content between 14 and 15 wt. % S, our result is consistent with a molten state for all proposed core compositions, and establishes a new minimum CMB temperature of 1200 °C. Extrapolating our liquidus to high pressures and comparing it to calculated areotherms, we find that three core crystallization regimes are possible. For a Martian core with 10 to 12 wt. % S, crystallization takes the form of iron snow, while for cores with 13 to 16 wt. % S, solidification occurs near the center of the planet in the form of Fe$_3$S crystallization. At 13 wt. % S, Fe$_3$S would crystallize everywhere in the core, introducing a new scenario with uncertain and potentially interesting consequences for the Martian dynamo.

Keywords: Mars, core crystallization, iron snow, liquidus, Fe-Ni-S, high pressure, dynamo
Introduction

Though the thermal state and composition of the Martian core has been studied for decades (Stevenson et al., 1983; Schubert & Spohn, 1990), results from the Mars Global Surveyor in 1997 uncovered a new layer of complexity on the subject – strong remnant magnetization of ~4 Ga impact basins in the planet’s southern highlands (Acuna et al., 1999; Mitchell et al., 2001; Anderson et al., 1999). As planet-enveloping fields are generated by convection of conductive iron liquid in the core, the dearth of strongly magnetized rocks younger than 4 Ga in age is interpreted as evidence cataloging the death of an early Martian dynamo (Stevenson, 2001; Fassett & Head 2011). The initial dynamo was likely driven by thermal convection (Hauck & Phillips, 2002), due to the core being superheated relative to the mantle (Ke & Solomatov, 2009). Initial measurement of Mars’s tidal Love number, k2, and moment of inertia (MOI) suggested the Martian core is at least partially molten (Yoder et al., 2003).

As cores composed purely of Fe(Ni) would quickly crystallize (Stevenson et al. 1983), a non-solid Martian core indicates the presence of light elements capable of depressing the melting temperature. Density profiles consistent with Martian mantle and crustal mineralogy also require a significant presence of light elements in the core (Bertka & Fei, 1998, Fei & Bertka, 2005). The most common candidate is S, which has siderophilic tendencies and, as a volatile, is believed to be preferentially fractionated to Mars due to the planet’s distance from the Sun (Sohl & Spohn, 1997). Though Khan & Connoly’s (2008) thermal model allows for up 25 wt. % S in the core, rheological, geochemical, & geodesic models place constraints of 10 – 16 wt. % S on the core S content (Wanke & Dreibus, 1988; Schubert & Spohn, 1990; Lodders & Fegley, 1997; Rivoldini et al., 2011).
While significant work has been devoted to understanding the cause of the dynamo’s termination (Roberts & Arkani-Hamed, 2014; Hori & Wicht, 2013; Kuang et al. 2008) investigation of how a modern Martian dynamo might be regenerated has been limited to a single study. Based on Wanke & Dreibus’s (1988) estimation of 74 wt. % Fe, 14.2 wt. % S, and 7.6 wt. % Ni for the Martian core, Stewart et al. (2007) performed multi-anvil melting experiments on the Fe-Ni-S system to determine its melting behavior at core conditions. By constraining Fe-Ni-S’s eutectic temperature at the Martian CMB (23 GPa) and center (40 GPa), they interpolated liquidii slopes and compared them to the Martian core areotherm, which was assumed to have a gradient of 25°C /GPa (Williams & Nimmo, 2004; Fei & Bertka, 2005). The authors found that for a CMB temperature of 1423 °C, (Hauck & Phillips, 2002), S contents of less than 14 wt. %, core crystallization would have already begun. More generally, they concluded that if the S content is on the Fe-rich side of the eutectic -16 wt. % S at 23 GPa - the two would cross at shallow depths causing Fe crystallization to initially occur near the CMB. If the composition is on the S-rich side, intersection would instead occur at Mars’s center, producing solid Fe₃S.

The former core solidification scenario is colloquially referred to as the “iron snow” core crystallization regime due to its similarity to snowflakes crystallizing in the atmosphere and falling downward to accumulate on the ground. Iron crystallizes out of a sub-liquidus melt and falls inward under the force of gravity, dissolving into the liquid below before eventually precipitating at the center of the planet to form a solid inner core. While the iron snow crystallization regime has been confidently applied to small planetary bodies like Mercury (Chen et al. 2008; Dumberry & Rivoldini, 2015), Ganymede (Hauck et al. 2006), and our Moon (Jing et al. 2014), Mars's greater average core pressures render its mode of solidification ambiguous.

Work in the intervening years has helped to clarify the Martian core condition. Based on
mantle depletions of moderately siderophilic elements (Righter & Chabot, 2011; Chabot et al., 2011; Brandon et al., 2012) Rai & Van Westrenen (2013) posit the Martian core cannot exceed 10.6 wt. % S. Additional years of satellite data collection have led to improved estimates of the planet’s (MOI) and tidal k2 Love number (Konopliv et al., 2011), indicating lower CMB pressures as well as a fully molten core. If the Martian CMB temperature is within the range discussed above, Stewart et al.’s liquidii are inconsistent with a fully molten core containing 10 wt. % S. While the Martian CMB is very difficult to constrain, there is also a high amount of uncertainty in the liquidus determinations, which are reliant upon a low number of data points. Mars’s moderate size renders it amenable to being studied through high-pressure experimentation. Collectively, these new findings about the current state of the Martian core provide the impetus to re-evaluate the relationship between the Martian core areotherm and liquidii gradients.

To this end, we define the melting behavior of Fe-Ni-S at 20 GPa, the current estimate of the Martian CMB pressure (Rivoldini et al., 2011). 20 GPa is near the pressure that Fe3S stabilizes and undergoes a magnetic transition (Lin et al., 2004); as phase transitions have been linked to anomalous in the Fe-S system, our experiments will be necessary to avoid mischaracterizing the liquidus, and also to see how the Fe-Ni-S compares to its Fe-S counterpart at similar conditions. By defining the Fe-Ni-S liquidus along its entire Fe-rich domain, melting temperatures can be extrapolated to higher pressures with greater confidence. This melting data also provides a minimum estimate of the CMB temperatures. Finally, thermodynamic data will be used to calculate areotherms for the Martian core at the S end-members of 10 & 16 wt. % S. These areotherms and their relationship to the liquidii, will also determine which core crystallization regimes are possible within Mars.
Methods

Melting experiments were performed using a Walker-type multi-anvil apparatus on the University of Michigan’s campus in Ann Arbor, MI. To define the Fe-Ni-S liquidus across a range of temperatures, five unique starting materials were synthesized. The first two were produced by combining Fe (Alfa Aesar, 99.99% purity), Ni (Alfa Aesar, 99.99% purity) and S (Alfa Aesar, 99.99% purity) powders and grinding them under ethanol in an agate mortar to produce mixtures with the compositions of Fe\textsubscript{82}Ni\textsubscript{8}S\textsubscript{10} and Fe\textsubscript{91}Ni\textsubscript{8}S\textsubscript{1} (wt. %), respectively. The other three starting materials, Fe\textsubscript{85}Ni\textsubscript{10}S\textsubscript{5}, Fe\textsubscript{88}Ni\textsubscript{10}S\textsubscript{2}, and Fe\textsubscript{87}Ni\textsubscript{10}S\textsubscript{3}, were produced by a combination of Fe & Ni powders and un-ground Fe\textsubscript{64}S\textsubscript{36} grains (Alfa Aesar, 99.99% purity).

COMPRES’s 8/3 cell assembly was used for all experiments (Leinenweber, 2012). Paper-backed Grade F tungsten carbide cubes, 3mm truncated edge length, compressed an 8mm edge length bored-out MgO octahedron, which housed the cell and serve as a pressure medium. Pyrophillite gaskets were attached to the WC cubes parallel to the truncated edges so as to just touch the octahedron during final assembly. Fitted into a hole bored into the octahedra is a straight LaCrO\textsubscript{3} furnace, enclosing a cylindrical resistance-heated Re sleeve. Centered in the sleeve is a cylindrical .98mm MgO capsule into which sample powder is packed to fill its middle third. For FeS grain experiments (see Results & Discussion) we individually placed ~.2 mm diameter grains in the .6 mm diameter capsule, positioning them in the middle of the Fe-Ni powder.

For experiments featuring a thermocouple (TC), the MgO capsule is book-ended on both sides by .25mm MgO disks. The top disk is followed by a .22mm Al\textsubscript{2}O\textsubscript{3} sliver, suspended above a 1.94mm bored-out Al\textsubscript{2}O\textsubscript{3} cylinder that carries type-C thermocouple (W\textsubscript{95}Re\textsubscript{5} and W\textsubscript{84}Re\textsubscript{16}) leads towards the center of the assembly. The space between the termination of the TC leads and
the end of the plug is packed with Forsterite powder to stabilize it during compression. Above the Al₂O₃ plug, the TC wires are secured by Al₂O₃-based cement and insulated by mullite sleeves. Below the bottom MgO disk, a 2.3mm Al₂O₃ plug extends towards to the bottom of the Re heater. For non-TC experiments, the MgO capsule is followed on both ends by thicker 75mm MgO disks. Above and below these are .22mm Al₂O₃ slivers, and finally by 2.1mm Al₂O₃ plugs.

The run temperature of most experiments was estimated from a power vs. temperature calibration curve produced in our lab. This approach was adopted to maximize the chances of a successful run, as well as get a rough outline of the Fe-rich side of the liquidus, which was almost entirely unconstrained at the onset of our experiments.

**Figure 1:** Power-temperature calibration based on data from four runs. Fit is least-squares polynomial, $-0.0001x^3 - 0.0002x^2 + 8.3509x - 212.47$, $R^2 = .987$. The curve was then used to estimate the temperatures of non-TC experiments.

After the general shape of the liquidus had been determined, thermocouple runs were
conducted to provide tighter temperature constraints across the curve. With each TC run, the power-temperature calibration was updated in order to correct the temperature of the earlier runs, which relied upon an old calibration from our lab. Pressure was determined via a well-established calibration relationship between pressure experienced by the sample and the oil pressure of our multi-anvil, and was further constrained based on the stabilization of Fe(Ni)$_3$S at 18 GPa (Pike et al., 1999).

Once loaded into the press, samples were brought to the target pressure of 20 GPa at a rate of 3.33 GPa/hr. Once pressures reached 5 GPa, sintering at 600 °C was initiated in order to lower the permeability of the MgO powder and prevent interaction between the sample and the Re heater. Upon reaching the target pressure of 20 GPa, each sample was heated at a rate of 100 °C per minute. For runs using Fe-Ni-S powder, the sample was heated directly to the target temperature after sintering. For runs featuring a mixture of FeS grains and powder, the sample was first heated to super-liquidus temperatures to ensure complete melting and homogenization of the sample, prior to being brought down to the target temperature. All samples were held at target temperatures for a minimum of 1 minute being rapidly quenched to room temperature by turning off the power. Decompression took 12 hours for a rate of ~1.66 GPa/Hr.

Following each run, we removed the octahedra from the multi-anvil and created a thick section by mounting the octahedron in epoxy. The mount was then ground on a wheel, parallel to the cylindrical heater, to expose the sample. During grinding, a Zeiss Stereo Microscope was used to take periodic images of the sample to determine the number and state of its phases. This process served as a precaution against inadvertently grinding through phases. Homogeneity and light color was interpreted as Fe(Ni)-rich solid phase, while a mixture of bright dendrites and dark interstitial liquid indicates a phase that was liquid prior to quenching (Fei et al., 2000).
To determine the chemical composition of the run products, the mounted and polished samples were carbon coated and a CAMECA SX-100 was used to conduct electron microprobe microanalysis (EPMA). Pyrite served as a dual standard for Fe and S, NiS was used for Ni, and MgCO₃ was used for Mg. Mg was included to indicate whether low measurements totals were the result of the beam straying onto the surrounding MgO matrix, or some other factor. Measurements that ranged beyond 100±2 wt. % total, as well as those with more than .1 wt. % Mg were discarded. Beam conditions of 15 keV, 15 nA, and 30 second counting times with 15 s backgrounds were applied to Fe, Ni & S. For Mg, a shorter 10 s counting time was used.

Two beam sizes were employed: a “0” µm point beam and a 5µm de-focused beam. For the homogenous solid (Fig. 2, top left), the point beam and 5 µm beam gave indistinguishable results and were subsequently used interchangeably. The composition of the alloy phase was taken as the average of all measurements, with the uncertainty given as the standard error. For the quenched liquid phase (Fig. 2, right) multiple measurements with the 5µm beam, spanning
the sample surface, were taken and subsequently averaged. While this defocused beam analysis approach (DBA) was effective for most run product analysis, difficulties arose in sulfur-poor samples where the liquid phase became heterogeneous, at small scales, upon quenching. The uneven distribution of Fe(Ni)-rich dendrites and S-rich liquid introduced a large amount of variability in our 5µm measurements.

In these cases, a point beam was instead rastered across 10 x 10 µm areas of sample, covering both dendrite and interstitial liquid textures. We tested the raster method versus DBA method and found results differed by less than 1 wt. %, leading us to conclude that the two methods are directly comparable, and we used them interchangeably to create our data set. However, for some very S-poor runs, both the DBA and raster approach resulted in quenched
liquid compositions that were too depleted in S to be credible. Due to the fineness of the S-rich interstitial liquid in relation to the Fe-rich dendrites, it is likely that the beam inadvertently excited electrons in the adjacent dendrite, producing secondary fluorescence that increased Fe count totals. While lowering the beam voltage has been explored as a solution, this requires the sampling soft X-rays (Gopon et al., 2012), which have poorly constrained mass attenuation coefficients and are prone to peak shifts and C contamination due to their relatively low count rate (Merlet & Llovet, 2012). In other samples, only a very small area of quenched liquid phase was available for analysis. As a result, the number of 5 µm measurements was small, and 10 x 10 µm rasters tended to stray onto the solid or MgO matrix, and uncertainty in the data was large.

Figure 4: Quenched liquid region of run M062016. Note limited surface area, specified in scale bar at bottom, when compared to 5 µm defocused beam, and 10 µm length area needed for raster analysis. This run will hereafter be used to explain the spatial analysis process.
Following the work of others (Grande, 2000) we decided to estimate the composition of the quenched liquid phase by performing image analysis on the sample. This process was motivate by the principle that if the surface area of each phase could be accurately determined, the composition of the sample could then be estimated by multiplying each phase’s areal fraction by that phase’s individual chemical composition. Geographical Information Software (GIS) was used to perform the analysis, which we term “spatial analysis” due to the fact that we rely upon EPMA for discrete chemical information, and the image analysis for the spatial extent of phases. Though typically reserved for mapping features at the macroscopic scale, the program has been recently applied to the identification of grain boundaries in thin sections (Li et al., 2008). We began by converting back-scattered (BSE) images of the samples into a high-resolution raster. As BSE image brightness corresponds directly to the chemical composition of the object sampled, we used color as a metric dis-aggregate our sample into solid, liquid, and dendrite phases.

This process of data segmentation was accomplished by using GIS’s image classification tool to organize the raster’s cells into classes based on their color and distance to like-colored cells. While GIS offers unsupervised analysis, in which the program automatically chooses classes by prioritizing certain colors, we found that supervised analysis, in which the user manually identifies color regions, is a more accurate way to map the sample. GIS’s Training Sample Manager was used to select regions on the raster, visible as crosshatched polygons in Figs. 5 & 6, that serve as a guide to classify each cell into a group. Three of these, the gray, S-rich liquid (dark green), the bright Fe-rich dendrite (orange), and the bright solid (purple), are present within the sample, and are subsequently used to determine its chemical composition. The other two textures (the red and light green) are representative of disconnected droplets of sample and holes in the sample and are selected for the purpose of filtering them out from subsequent
analysis. Using these categorizations as a guide, cluster analysis was then performed on the sample to separate it into the classes enumerated above.

**Figure 5:** Screenshot of the classification process in GIS as applied to determining the amount of solid in run M062016. The quenched liquid phase is outlined by blue polygon in upper right. This polygon served as a mask, preventing the enclosed area from participating in image classification so that the area of the solid phase could be determined in isolation. Class 1, in purple, represents the solid, homogeneous, Fe(Ni) solid. Class 2, in red, contains droplets of sample in the MgO matrix and is meant to exclude this texture from counting as a sample. Class 3, corresponds to the MgO matrix, including sample holes, and is meant to exclude these textures from analysis. While finding the area of the solid is not critical to determining the composition of the quenched liquid phase, it was undertaken to estimate the bulk composition of all samples.

Due to the near-identical brightness of the Fe-rich solid and the Fe-rich dendrites in the quenched liquid phase, an extra step was taken in analysis of all two-phase samples to avoid combining the two textures within the same class. To this end, a polygon (shown in blue, Fig. 5) was manually drawn around the quenched liquid phase to isolate it from the solid phase. From here, analysis was constrained to the area of raster within polygon (the quenched liquid phase),
or without it (the solid phase), by means of a GIS's “mask” feature, which limits the extent to of cluster analysis. For most samples, only a single, full-sized BSE image was needed to perform this analysis, however the smallness of the quenched liquid in Fig. 4 results in the resolution being insufficient to provide an accurate estimation of the liquid and dendrite areas. Therefore, this region was analyzed at higher magnification, visible in Fig. 6, in the same manner as described in Fig. 5, save that cluster analysis is restricted to the area within the mask rather than without.

The areal fraction of liquid and dendrite is determined by dividing their individual areas
by their combined total. As can be seen in Fig. 6, some of these droplets are included in the dendrite, solid, or liquid classes, providing proof that the image classification process is not perfect. Uncertainties in associated with the classification process were estimated by evaluating how well the resulting classified image matched the original. The accuracy of classifying a particular phase is the sum of the number of training cells correctly classified as that phase, divided by the total number of training cells that should have been classified as the phase based on our initial assessment (see Suppl. Figs. 1 & 2). All fractional accuracy values were above .9, indicating the classification process was effective at reproducing the original image.

When possible, a point beam was used to determine the composition of the S-rich liquid and dendrite. However, for S-poor experiments the area of the liquid was often too small to get an accurate measurement, while for S-rich experiments the same was true of the dendrite. In these cases, we assigned the dendrite a composition of 89.9 ± .1 wt. % Fe, 8.69 ± .02 Ni, and 0.58 ± .02 wt. % S, the measurement of the highest S concentration in the solid of any run in our dataset. The liquid was likewise assigned a value of 75.36 ± .09 wt. % Fe, 9.57 ± .16 wt. % Ni, and 15.84 ± .05 wt. % S, Zhang & Fei’s (2008) sub-solidus result at ~ 10 wt. % Ni. While it is not our data point, this value is reasonable given the system’s proximity to the stabilization of Fe$_2$S & Fe(Ni)$_2$S (Fei et al., 2000; Pike et al., 1999). Uncertainties for the quenched liquid phase are the combined errors of the liquid and dendrite values, multiplied by the inverse of the classification accuracy of the given run.
The spatial analysis (SA) technique yields estimates of the quenched liquid phase composition are comparable to EPMA results, deviating an average of 1.3 wt. %. As expected, the SA method resulted in substantially higher estimates for low S runs. While we do not view this method as a substitute for EPMA in all cases, there are certainly applications in this line of research. By allowing us to quickly estimate the composition of our run products, we were able to carry out new experiments without the need to use the electron microprobe, which was frequently unavailable due to constant demand for its use. As we had little idea of the shape of the liquidus at the onset of the project, the ability to keep conducting experiments without pausing to wait for EPMA results was vital in defining the curve in a reasonable amount of time.

SA estimations were also closer to EPMA results than EDS measurements taken with the JEOL SEM, an observation is supported by the literature (Ritchie et al., 2013; Nagoshi et al., 2014). Image classification took a manner of minutes, while the actual processing time for cluster analysis with GIS was only a manner of seconds. This compares quite favorably to EPMA
analysis of the samples, which required an average of two hours per sample, or mapping on the electron microprobe that takes 10’s of hours to complete (Carpenter et al., 2013).

**Figure 8:** Comparison of EPMA and spatial analysis estimations of the sulfur content of the quench phase. Black line represents exact reproduction of EPMA results: for data above line, spatial analysis value is greater than EPMA result, while for data below the line it has produced a lower value. Systematically higher S estimates for S-poor experiments are notable. The larger number of data as compared to Table 1 and Fig. 10 is because runs with bad starting composition are included to compare the results from the EPMA and SA methods.

We also applied spatial analysis to estimate the bulk composition of the sample. This effort was motivated by a need to see if run product compositions matched our targets for each experiments, as well as a desire to assess the effectiveness of the FeS grain loading method in controlling S content. To this end, the area of the solid phase was also determined, using an
identical procedure and setup as described in Fig. 5. Following this, the fraction of the liquid, dendrite, and solid was determined by dividing their individual areas by their combined totals.

The difference between target compositions and observed compositions are too large to be explained by random errors resulting from aliquot creation (see Suppl. Table). We believe this inconsistency is primarily caused by difficulties in filling the capsules with ~1 mg of uniform material. We loaded sample powder by depositing a small amount on creased weighing paper and coaxing it into the capsule with a needle. A loading rod was then use to pack grains down until the capsule is filled.

The metallic needle, however, proved to be slightly magnetic, which we believe biased the purely powdered samples to higher S-contents by preferentially removing Fe. An initial solution to the problem of the magnetic needle was to vibrate the edges of the weighing paper, without physically touching the powder with a needle. While this eliminated the removal of Fe grains via magnetism, we believe this method also biased the sample against S. We suspect that sliding the grains with the needle preferentially transported the heavier Fe & Ni grains further down the paper’s slope. This biased the sample against lighter S by leaving it behind, an effect observed of grain sorting processes at larger scales (Kannan, 2016).

A second solution was the substitution of a braided W\textsubscript{95}Re\textsubscript{5} thermocouple wire for the needle. We observed that the non-magnetic wire was effective at transporting all compositions of grains with equal ease. One point of concern, however, was significant Re contamination in two of the runs (M090216 & M070216, not represented in Table 1). Contamination could not be explained by interaction of TC wires in the assembly and the sample, so we suspect the Re loading wire may have eventually broken after repeated use and thus contaminated the sample.
Despite these concerns, the Re wires were replaced and used for all other runs without issue, though we advise the use of thicker wires for sample loading.

Unlike the powders, the FeS grains were individually placed in the capsule with tweezers, and thus the magnetic effect of the loading needle was avoided. Additionally, the FeS grains, being large and spherical in comparison to the powders, did not cling to the loading rod. While the Fe-Ni powder was still subject to bias due to the higher relative magnetism of the Fe grains, this partiality had no bearing on the S content and thus had less effect on the overall experimental results, due to Ni’s low contribution to the melting temperature of the alloy (Stewart et al., 2007). Comparison of the powder and FeS grain S-control methods via volumetric spatial analysis of run products, however, did not indicate a clear advantage in meeting target compositions, with both methods struggling to consistently meet targets (see Suppl. Table). There was an overall tendency to produce S concentrations that were poorer than intended, which is more favorable than the alternative at high temperature runs.
## Results & Discussion

Table 1: Summary of Experimental Results.

<table>
<thead>
<tr>
<th>RunID</th>
<th>$T$ (°C)</th>
<th>Duration</th>
<th>Phase</th>
<th>Fe (wt.%)</th>
<th>Ni (wt.%)</th>
<th>S (wt.%)</th>
<th>Total (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M052516</td>
<td>769</td>
<td>24 hr</td>
<td>Solid</td>
<td>87.4(4)</td>
<td>12.2(3)</td>
<td>0.14(3)</td>
<td>99.7(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Solid</td>
<td>94.6(8)</td>
<td>4.1(7)</td>
<td>0.10(4)</td>
<td>98.8(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe(Ni)$_2$S</td>
<td>77.0(1)</td>
<td>6.08(1)</td>
<td>15.8(1)</td>
<td>98.8(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe(Ni)$_2$S</td>
<td>73.1(1)</td>
<td>3.5(2)</td>
<td>22.3(1)</td>
<td>98.8(1)</td>
</tr>
<tr>
<td>M063016$_{TC}$</td>
<td>1000</td>
<td>60 m</td>
<td>Solid</td>
<td>68.5(7)</td>
<td>3.5(1)</td>
<td>26.7(3)</td>
<td>99.7(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Solid</td>
<td>76.2(9)</td>
<td>9.5(1)</td>
<td>14.7(8)</td>
<td>100.4(2)</td>
</tr>
<tr>
<td>M053016</td>
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<td>77.4(2)</td>
<td>7.69(3)</td>
<td>22.3(1)</td>
<td>99.9(1)</td>
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<td>Solid</td>
<td>90.7(4)</td>
<td>7.5(1)</td>
<td>0.5(3)</td>
<td>98.7(1)</td>
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<tr>
<td>M020116</td>
<td>1130</td>
<td>4 m</td>
<td>Liquid</td>
<td>74.9(5)</td>
<td>8.8(1)</td>
<td>14.7(8)</td>
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<tr>
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<td>0.58(2)</td>
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<td>M090116</td>
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<td>Liquid</td>
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<td>8.9(4)</td>
<td>13.4(3)</td>
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<tr>
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<td>Liquid</td>
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<td>Liquid</td>
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<td>8.7(1)</td>
<td>8.5(7)</td>
<td>99.6(2)</td>
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<td>Liquid</td>
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<td>9.3(2)</td>
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<td>0.309(3)</td>
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<tr>
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<td>60 m</td>
<td>Liquid</td>
<td>76.3(2)</td>
<td>7.0(1)</td>
<td>15.0(1)</td>
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<td>Solid</td>
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<td>9.15(1)</td>
<td>0.311(1)</td>
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<td>60 m</td>
<td>Liquid</td>
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<td>10.5(1)*</td>
<td>6.8(5)*</td>
<td>98.2(6)*</td>
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<td>10.8(1)</td>
<td>0.4(1)</td>
<td>99.1(2)</td>
</tr>
<tr>
<td>M022516</td>
<td>1405</td>
<td>1 m</td>
<td>Liquid</td>
<td>82.3(7)</td>
<td>8.9(1)</td>
<td>8.6(6)</td>
<td>99.8(2)</td>
</tr>
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<td>Liquid</td>
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<td>10.33(4)</td>
<td>5.4(3)</td>
<td>99.5(2)</td>
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<tr>
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<td>Solid</td>
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<td>0.189(4)</td>
<td>99.1(1)</td>
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<tr>
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<td>81.1(14)</td>
<td>7.9(1)</td>
<td>9.9(14)</td>
<td>98.9(2)</td>
</tr>
<tr>
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<td>Liquid</td>
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<td>10.6(1)*</td>
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<tr>
<td>M061616$_{TC}$</td>
<td>1700</td>
<td>60 m</td>
<td>Liquid</td>
<td>82.7(9)</td>
<td>10.5(1)</td>
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<td>Liquid</td>
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<td>3.3(2)*</td>
<td>101.8(4)*</td>
</tr>
<tr>
<td>M062916</td>
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<td>60 m</td>
<td>Liquid</td>
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<td>14.2(1)</td>
<td>0.3(1)</td>
<td>99.9(3)</td>
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<tr>
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<td>14.6(1)</td>
<td>0.09(1)</td>
<td>99.9(1)</td>
</tr>
</tbody>
</table>

Note: _TC_ denotes a thermocouple run. * Indicates compositions determined by spatial analysis rather than EPMA. Parenthetical value is uncertainty in last digit(s). For EPMA results, this value is the standard error of the sample of measurements. For spatial analysis results, this value is the combined uncertainty of EPMA standard errors, multiplied by the inverse of the accuracy of the classification of those phases.

The maximum concentration of sulfur in the Fe(Ni) solid is 0.58 (± .02) wt. % in our experiments, much lower than Zhang & Fei’s (2008) maximum concentration of 2.72 (± .07) wt. %. While our value is not located at the eutectic, the trend of our solid data indicates this S
deficiency extends across temperatures. This result is in close agreement with Li et al.’s (2001) value of .54 (± .05 wt. %) for Ni-free data at 21 GPa. Additionally, Zhang & Fei’s use of 28 - 50 wt. % Ni in their runs, suggests the addition of Ni has a large effect on the concentration of S in the solid. This effect appears to strongly persist at higher pressures as well, as Stewart et al.’s (2007) 23 GPa data for the Fe-Ni-S system features a greater concentration of S in solid Fe(Ni) than Li et al.’s (2001) data for the Fe-S system at 25 GPa.

We posit the primary cause of these discrepancies to be the effect that Ni has on the solid structure of the alloy. In synthesizing a Fe(Ni)S solid for study at higher pressures, Sakai et al. (2012) produced a body-centered cubic (BCC) alloy at 21 GPa. In comparison, at these conditions pure iron exists solidly as a face-centered cubic (FCC) structure. Huang et al. (1988) found that Fe-Ni alloys with 35.1 wt. % Ni are present in the FCC structure at 25 GPa, while alloys with 10.26 & 24.4 wt. % were also observed with BCC & HCP structures. Despite its relatively large ionic radius, S is thought to occupy interstitial sites within the Fe lattice according to the lattice strain model, modified to study metal-metal partitioning (Stewart et al., 2009). BCC & FCC phases feature differing numbers and types of interstitial sites so a structural transition should affect the number of S atoms able to enter the solid.

FCC structures contain eight tetrahedral interstitial sites and thirteen octahedral interstitial sites, while a BCC structure contains 18 octahedral interstitial sites and 4 tetrahedral sites. Octahedral holes are larger their tetrahedral counterparts, so the BCC structure undergoes less strain to accommodate S atoms than the FCC counterparts. This fact, coupled with BCC’s greater number of octahedral sites, suggests that the concentration of S should be higher in this structure than for FCC. As increased Ni improves the stability of the BCC structure versus the FCC, the discrepancy in the concentration of S between our results and the literature suggests
that our data, like Li et al.’s (2001) features solids of FCC structure, while Zhang & Fei (2008) and Stewart et al.’s (2007) results are likely for run products with a BCC solid structure.

In most of our experimental products FeO was present as a dark gray texture in the S-rich interstitial region of the quenched liquid phase (Fig. 3), or as blobs in a manner similar to those Martin et al. (2014) describe in their study of Fe-FeS-Fe₃C at high pressures. All starting materials were stored in a dehumidifying cabinet prior to use to keep them free from H₂O, and Raman analysis of their contents did not reveal chemical contamination. Furthermore, all assemblies were kept in a vacuum oven set above 100 °C for at least 1 hour prior to being sintered in the multi-anvil. Pike et al. (1999) found FeO in all sub-solidus experiments, despite the substitution of a BN capsule for some runs, and suggest inherent oxygen fugacity at pressure (18-25 GPa) is to blame. EPMA & EDS revealed that O did not exceed 1 wt. % in any experiment. At this concentration, O is not expected to significantly depress the melting temperature of Fe-S liquidus (Terasaki et al., 2011). Unlike O, H is posited to be the cause of significant melting temperature depression in the Fe-S system (Buono & Walker, 2015). Hydrogen was not detected with Raman or EDS, and our electron microprobe was not equipped to detect its presence. However, we are confident our use of furnaces to dry powders used in the experiments, as well as ovens and sintering to drive off H₂O was sufficient to keep samples free from the effects of H.

Phases were identified by their chemical compositions, typically derived from EPMA, or EDS in the case of sub-1 μm features. Analysis of the quenched liquid phase determined it to be a combination of Fe-rich dendrite ranging from .32 to .52 wt. % S, and S-rich interstitial liquid ranging from 15.4 to 16.4 wt. % S. EDS analysis of the interstitial liquid microstructures revealed them to be a mixture of solid (bright, spherical texture, Fig. 3) and Fe(Ni)₃S (darker
texture, Fig. 3). In addition to these runs, our sub-solidus experiment contained five distinct phases, Fe(Ni)₃S, Fe(Ni)₃S₂, Fe(Ni)₂S, and two varieties of Fe(Ni) solid, a bright phase with Ni content of 12.15 wt. % and a duller phase with 4.1 wt. % Ni. While the number of phases exceeds the amount allowed by the phase rule at all non-eutectic points, we believe that the sluggishness of solid-state kinetics prevented the formation of a single, homogenous solid phase.

The occurrence of Fe(Ni)₂S in our 20 GPa runs contrasts with the first appearance of Fe₂S at 21-22 GPa (Fei et al., 2000; Koch-Müller et al., 2002). Additionally, the presence of Fe(Ni)₂S’s at 769 °C in run M052516 is significantly lower than Fei et al.’s (2000) minimum temperature of 1050 °C for Fe₂S at 21 GPa, indicating Ni significantly lowers its minimum temperature of stability. Both observations are corroborated by Urakawa et al.’s (2011)
conclusion that the addition of Ni broadens the phase stability of Fe-S compounds. Thermodynamic study of the Fe-Ni-S at 1 bar indicates that increasing Ni content decreases the stability of the Fe(Ni) solid versus the liquid phase, causing a slight depression in melting temperatures (Walder & Pelton, 2004; Raghavan, 2004) that is also observed at higher pressures.

All experimental data, including those of solid phases at the eutectic and pure Fe end-members are plotted in Fig. 10. Anzellini et al.’s (2013) melting experiments to estimate the pure Fe melting temperature, while the eutectic was given by Zhang & Fei's (2008) data. Both were normalized to 9 wt. % Ni by a correction of 7°C/wt. % Ni (the average of Zhang & Fei (2008), Stewart et al.’s (2007) and Pike et al.’s melting temperature depressions, resulting in 2047 °C and 940 °C, respectively). Fitting the data to a 3rd-ordered polynomial results in liquidus that features nearly ideal behavior.

As the Fe-S system exhibits pressure-induced changes in liquidus behavior, we sought a thermodynamic explanation for our melting curve’s expression. Inspired by Buono & Walker’s (2011) treatment of the Fe-S system from 1-14 GPa, we employed the asymmetric Margules formulation of the Gibbs free energy to examine our system at 20 GPa. The Margules formulation assumes a regular solution, and uses interaction parameters to describe deviations in the mixing behavior of components. Prior to modeling, all sulfur measurements and their accompanying errors were converted from wt. % S to molar fraction FeS. While our experiments contain Ni, we ignore its presence, and instead employ focus on only the Fe and Fe₃S components.

The asymmetric Margules solution model contains a term for the excess free energy of mixing, represented by interaction parameters $W_{GFe}$ and $W_{FeS}$, the compositional end-members of the system. The total free energy of the liquid phase is a sum of that of the liquid Fe and liquid
FeS components, which in turn have contributions from the ideal entropy of mixing, and the non-zero enthalpy of mixing, term 3 below, quantifying the departure from ideal behavior.

1) \( G_{\text{Liq}} = G_{\text{FeLiq}} \cdot (1 - x) + G_{\text{FeS}} \cdot x + x \cdot (1 - x) \cdot [W_{\text{GFe}} \cdot x + W_{\text{GFeS}} \cdot (1 - x)] + R \cdot T \cdot x \cdot \ln(x) + R \cdot T \cdot (1 - x) \cdot \ln(1 - x) \)

Where \( R, G_{\text{Liq}}, G_{\text{FeLiq}}, G_{\text{FeS}} \), \( W_{\text{GFe}} \), & \( W_{\text{GFeS}} \) are the gas constant \( (0.00831 \text{ kJ mol}^{-1} \text{K}^{-1}) \), Gibbs free energy of the liquid, the Gibbs free energy of liquid iron, the Gibbs free energy of liquid FeS, pure iron’s Gibbs interaction parameter, and FeS’s Gibbs interaction parameter, respectively. \( T \) is the temperature, in K, produced by our polynomial fit of the data, while \( x \) is our experimental data’s sulfur content, in mole fraction FeS. Recalling the definition of the Gibbs free energy, the interaction parameters are themselves broken into sub-components:

2) \( W_{\text{GFe}} = W_{\text{HFe}} + T \cdot W_{\text{SFe}} + W_{\text{VFe}} \cdot P \)

\( W_{\text{GFeS}} = W_{\text{HFeS}} + T \cdot W_{\text{SFeS}} + W_{\text{VFeS}} \cdot P \)

Where \( W_{\text{HFe}}, W_{\text{SFe}}, W_{\text{VFe}}, W_{\text{HFeS}}, W_{\text{SFeS}}, W_{\text{VFeS}}, \) and \( P \) are the enthalpy interaction parameters of iron, the entropy interaction parameter of iron, the volumetric interaction parameter of iron, the enthalpy interaction parameters of FeS, the entropy interaction parameter of FeS, the volumetric interaction parameter of FeS, and the pressure (20 GPa). As our data is isobaric, the volumetric and pressure terms, \( W_{\text{VFe}}, W_{\text{VFeS}}, \) and \( P \) are hereafter ignored. Taking the partial derivative of equation 2 with respect to composition results in:

3) \( \frac{\partial G_{\text{Liq}}}{\partial x} = \left( (W_{\text{HFeS}} + T \cdot W_{\text{SFeS}} - (G_{\text{FeLiq}} - G_{\text{FeS}_{\text{Liq}}})) \right)
+ 2 \cdot (W_{\text{HFe}} + T \cdot W_{\text{SFe}} - W_{\text{HFeS}} + T \cdot W_{\text{SFeS}}) \cdot x
+ 3 \cdot (W_{\text{HFeS}} + T \cdot W_{\text{SFeS}} - W_{\text{HFe}} + T \cdot W_{\text{SFe}}) \cdot x
+ R \cdot T \cdot x \cdot (1 - x) \)
Equation 3 can be simplified by assuming the liquid is at equilibrium with solid Fe, an acceptable generalization due to sulfur’s low concentration in Fe at pressures that bracket 20 GPa (Li et al., 2001; Andrault et al., 2009). The reference temperature for solid Fe is given as 1273 K. On a Gibbs free energy-composition plot, this condition is satisfied when the curves of solid Fe and the liquid cross, and a tangent line to this point arrives at the Gibbs free energy of the pure Fe and Fe$_3$S end-members.

$$\frac{\partial G_{\text{Liq}}}{\partial x} \text{ at equilibrium} = \frac{G_{\text{Liq}} - G_{\text{FeSol}}}{x}$$

Where $G_{\text{Liq}}$ at equilibrium is the Gibbs free energy of the composite liquid, and $G_{\text{FeSol}}$ is the Gibbs free energy of solid iron at a fixed pressure and temperature. Using the relationship discussed above, and made discrete in Eq. 4, $G_{\text{Fe3S}}$ can be substituted out of Eq. 4 in favor of $G_{\text{Fe}}$. Thus, Eq. 3 contains only solid and liquid Fe terms, and can be re-arranged in order to regress a 3$^{rd}$-ordered polynomial.

$$5) \ (G_{\text{FeSol}} - G_{\text{FeLiq}}) = 2(WH_{\text{Fe}} - T \cdot WS_{\text{Fe3S}}) \cdot x^3 + 2(WH_{\text{Fe3S}} - WH_{\text{Fe}}) \cdot x^2 + RT \cdot \ln(1 - x)$$

To define the Gibbs free energy of solid and liquid Fe at our experimental conditions, thermodynamic data from Chase (1995) was integrated to the temperatures of interest via the Shomate equation (Shomate, 1954). To solve for $WH_{\text{Fe}}$, $WH_{\text{FeS}}$, $WS_{\text{Fe}}$, & $WS_{\text{FeS}}$, the equation was solved with an iterative, linear least squares method. T was set equal to the temperatures given by our polynomial fit (Fig.13, solid black line), while the Margules parameters were allowed to vary to minimize the difference between the phase boundary conditions observed in our experiments, and $x$, and those predicted by the model (Eq. 5). Additionally, an ideal curve was calculated to compare to our experimentally determined liquidus. Two equations of state (EOS)
were used, the Mie Gruneisen and the Birch Murnaghan high temperature equation of state. Both EOS’s successfully reproduced our results, with all values for solid and liquid iron derived from Komabayashi & Fei (2010), whose reference conditions of 300 K and atmospheric pressure. Table 2 summarizes this data, as well as values used the areotherm calculations discussed below.

Figure 10: Plot of all experimental data, along with fitted liquidus, Margules, and ideal curves. Zhang & Fei’s (2008) eutectic result is used to anchor the fit, while Anzellini’s melting temperature of pure Fe is presented as a reference. Both the melting temperature of pure Fe and the eutectic data point are normalized to 9 wt. % Ni, with a correction of 7 °C/wt. % Ni (average of depressions observed by Pike et al. (1999), ~8°C/wt. %, Stewart et al. (2007), 3.75°C/wt. %, and Zhang & Fei (2008), 9°C/wt. %). The markers obscure compositional errors smaller than .1 wt.% and temperature errors for the solid of two-phase runs are omitted for the sake of clarity. Ideal and Margules curves were calculated for the Fe-S binary system, neglecting the presence of Ni.

The liquidus’s curvature at 20 GPa closely resembles that of the Fe-S system at 10 GPa (Chen et al., 2008) as well as Andrault et al.’s (2009) limited results for the Si-doped Fe-S sytem at 20.6 GPa. Deviation from an ideal liquidus is small, but not trivial. For the likely S contents of
the Martian core, temperature depression ranges from a negligible amount at 10 wt. % S to 80 °C at 15 wt. % S. The fact that the Fe-Ni-S system is nearly ideal at 20 GPa appears surprising given the proximity to the stabilization of Fe₃S at 20 GPa, however there is reason to believe that the addition of Ni has significantly lowered its pressure of initial stability. Pike et al. (1999), who used a starting composition of 6.5 wt. % Ni in contrast to our average of 9 wt. %, observe Fe(Ni)₃S at 18 GPa. Data on the Ni-S system supports this finding, in that Ni₃S₂ is observed at atmospheric pressure, as opposed to 14 GPa for Fe₃S₂ (Fei et al., 1997) while Ni₃S has been observed at pressures as low as 5.1 GPa (Urakawa et al., 2011). Thus, condition may be enough removed from the stabilization of Fe(Ni)₃S, that its effects on the liquidus are not felt.

Table 2: Fitted Margules Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( W_{1}\text{Fe} ) (KJ/mol)</th>
<th>( W_{1}\text{FeS} ) (KJ/mol)</th>
<th>( W_{3}\text{Fe} ) (KJ/mol*K)</th>
<th>( W_{3}\text{FeS} ) (KJ/mol*K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>0.82905</td>
<td>0.06198</td>
<td>0</td>
<td>3.20584</td>
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</table>

The slightly positive values of \( W_{1}\text{Fe} \) and \( W_{1}\text{FeS} \) indicate a small amount of repulsion between the Fe and S in the formation of both end-members. However, Fe’s greater values indicate the two phase region will be destabilized closer to this end member, and therefore broader away from it (Dehoff, 2006, Chapter 10). The entropy values are temperature dependent, and Fe₃S’s positive value means its Gibbs free energy is reduced with increasing temperature, thus Fe₃S becomes increasingly favorable as temperatures decrease. These tendencies cause the liquidus to broaden more rapidly than the solidus, rendering it flat from 10 – 16 wt. % S.

Given the tendency of Ni to stabilize compounds towards lower pressures, and the fact that no new compounds have been discovered in the Fe-S system at pressures above 21 GPa, it is likely that melting behavior in the Fe-Ni-S system remains nearly ideal throughout the domain of Martian core pressures. Thus combining our rigorously defined melting curve with data at higher
pressures should yield interpolations that approximate the evolution of the Martian core’s liquidus. The Fe-Ni-S eutectic is constrained at 20 and 23 GPa by Zhang & Fei’s (2008) measurements, and at 40 GPa by Stewart et al.’s bracketed solid and two phase data. Under the assumption of a linear relationship between Ni content and temperature depression, Ni-free data from the Fe-S system, as well as Ni rich data were normalized to our average value of 9 wt. % Ni by a correction of 7 °C (see Fig. 10).
The negative slope between Stewart et al.’s 23 & 40 GPa liquidii determinations is obvious when they are overlaid (Fig 11a.). However, this observation hinges on a single data point taken of the Fe-Ni-S system at 23 GPa, with the 40 GPa melting curve entirely unconstrained by their experiments. In the absence of experimental support, the assumed concave-down liquidii are suspect, given their basis on old assumptions of Fe-S liquidus behavior at lower pressures (Fei & Bertka, 1997) that have subsequently proven to be incorrect (Chen et al., 2008). Given these uncertainties in liquidus shape, we suggest that the negative slope has little experimental basis and may instead an artifact. However, as Stewart et al.’s results are the only non-eutectic data for the Fe-Ni-S system at these pressures, we intend to briefly explore the consequences.

Figure 11b: Solid black line is the fit to our 20 GPa data (Fig. 10). Black dashed line is anchored by FeS melting temperatures determined by Boehler (1992) and is a power-law fit to Zhang & Fei’s (2008) results, black diamonds and black circle. Liquidii at 20 & 40 GPa, red & blue dashed lines, are translational offsets to 20 GPa data. Gray points and arrowed line traces evolution of the eutectic with pressure from 23 to 31 to 36 GPa (Chudinovskh & Boehler, 2007). Red and blue diamonds are not used to fit lines in this figure, but are included as visual frames of reference to Fig. 11b. 23 GPa eutectic determined by Zhang & Fei (2008) and 40 GPa eutectic bracketed by Stewart et al.’s results for Fe-S and Fe64Ni36-S.
Based on our results at 20 GPa, we postulate a concave up liquidus persists to greater pressures. Study of the Fe-S system at greater pressures indicates no new solid structures form after Fe\textsubscript{3}S stabilizes at roughly 21-22 GPa (Morard et al., 2007; Fei et al., 2000; Koch-Müller et al., 2002). While our pressures are below this phase boundary, the addition of Ni extends the stability fields of Fe-S compounds to lower pressures (Urakawa et al., 2011), resulting in a revised boundary of 18 GPa (Pike et al., 1999). As Fe(Ni)\textsubscript{3}S is observed in our data set (Run M052516, Table 1), the absence of phase transitions leaves us comfortable extending our experimentally – determined liquidus shape to higher pressures. A prominent feature is the shift in eutectic position of roughly 200 °C and 4 wt. % S from CMB pressures to those at the center of the planet (Chudinovskh & Boehler, 2007). As a result, the liquidus is considerably steeper on the S-rich side of the eutectic, meaning that intersection with the areotherm likely occurs at high pressures (Stewart et al., 2007).

An additional facet to is that a given core composition may cross from one side of the eutectic to the other with pressure. The result is that cores with S contents above 12 wt. % shift from the Fe-rich side of the liquidus near the CMB to the S-rich side at the planet’s center. This affects the core liquidii by producing a pressure-induced jump in temperature at these compositions. With the liquidii at 20 GPa from this study, and those at 23, & 40 GPa given in the literature, we calculated core areotherms representative of our end-members of 10 wt. % and 16 wt. % S, hereafter referred to as A10 and A16, respectively. For the sake of brevity, in the following discussion we use only the values employed for the A16, unless explicitly stated. These numbers, as well as those used in the calculation of the 16 wt. % areotherm, are found in Table 2. Assuming the core is well-mixed and defined by constant entropy, we treat the areotherm as an adiabatic gradient such that:
6) \[
\frac{dT}{dP} = \frac{\alpha T \cdot Vm}{\rho \cdot Cp}
\]

Where \( \alpha \) is the thermal expansion, \( T \) is the temperature, \( \rho \) is the pressure-dependent density, \( Vm \) is the molar volume, and \( Cp \) is the constant-pressure heat capacity. A \( Cp \) value of 50.615 J/molK was obtained by a weighted average of the pure iron value, 46.024 J/molK and the FeS value of 62.551 J/molK (Chase, 1998) for 1723 °C, the estimated temperature of the CMB (Williams & Nimmo, 2004). The 3rd order Birch Murnaghan EOS was employed to determine \( \rho \) at pressure:

7) \[
P = \frac{3}{2} K_T \left[ \left( \frac{\rho}{\rho_{OT}} \right)^{7/3} - \left( \frac{\rho}{\rho_{OT}} \right)^{5/3} \right] \left\{ 1 + \frac{3}{4} \left( K'_{TO} - 4 \right) \left[ \left( \frac{\rho}{\rho_{OT}} \right)^{2/3} - 1 \right] \right\}
\]

Where \( P, K_T, \rho_{OT}, \) and \( K'_{TO} \), are the pressure of interest, bulk modulus, zero pressure density, and pressure derivative of the bulk modulus. A \( K' \) value of 4.8 is given by Balog et al. (2003).

The bulk modulus increases slightly with temperature, formulated as:

8) \[
K_T = K_{TO} + \left( \frac{\partial K_T}{\partial T} \right)_P \cdot (T - T_0)
\]

\( K_{TO} \), the zero temperature bulk modulus at the pressure of interest, is calculated by combining \( K'_{TO} \) with the ambient density of 45 GPa (Sanloup et al., 2002). Hixson et al.’s (1990) value was used for \( (\partial K_T/\partial T)_P \), the temperature dependence of the bulk modulus. \( T_0 \) is the reference temperature, corresponding to 1377 °C, the temperature of Sanloup et al.’s (2002) experiments. The temperature-dependent zero pressure density is given as:

9) \[
\rho_{OT} = \rho_O \exp \left[ \int_{T_0}^{T} \alpha_O dT \right]
\]

Where \( \rho_O \) is 5,200 kg/m\(^3\) (Sanloup et al., 2003) and \( \alpha_O \) is the zero pressure thermal expansion coefficient. Following the advice of Williams (2009) a thermal expansion value of 13.2 \( \times \) 10\(^{-5} \)/K (Assael et al., 2006) was used for liquid iron, which was combined with 1.7 x
10^{-4}/K from Kaiura, & Toguri (1979) to interpolate a value of (1.51 \times 10^{-4}/K). Using different weights, an identical procedure was followed to interpolate a value of 1.57 \times 10^{-4}/K for the 16 wt. % S areotherm. With the density at our desired pressure and temperature determined, the pressure-dependent thermal expansion can be found. Assuming the product of the thermal expansion and bulk modulus is a constant (Birch, 1968) the thermal expansion at high pressures is constrained by the following relationship posited by Duffy & Ahrens (1993):

\[ \alpha = \frac{K \alpha_o}{K} \cdot \left( \frac{\rho}{\rho_o} \right)^5 \cdot \alpha_o \]

Where \( \rho_o \) and \( \alpha_o \) are the density and thermal expansion of the alloy at ambient pressure, and \( K \) and \( \alpha \) are the bulk modulus and thermal expansion at the pressure of interest, all of which were previously determined. Finally, we calculated the molar volume by dividing the densities by the molar mass of the alloys. For A10, this mass was .0535 kg/mol, and for A16 it was .0520 kg/mol. Plugging in the results from Eqs. 7-10 to Eq. 6, the core areotherms were calculated.

<table>
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<th>(dln(ao)/dV)_T</th>
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Their similar gradient demonstrates the Martian areotherm is insensitive to small to moderate changes in S. Significantly, both are lower than the adiabat applied to the Martian core by Fei & Bertka (2005) an effect that is magnified at depth. For a CMB temperature of 1723 °C, A10 decreases in slope from 17.5°C/GPa at the CMB to 9.9 °C/GPa at the center, while A16 decreases from, 18.4°C/GPa at the CMB to only 10.2 °C/GPa at Mars’s center. For a CMB temperature of 1423 °C, A10 decreases in slope from 14.5 °C/GPa at the CMB to 8 °C/GPa at the center, while A16 decreases from, 15°C/GPa at the CMB to only 8.4°C/GPa at Mars’s center. Shallowing the areotherm has the effect of causing initial with the liquidus at higher pressures.

![Figure 12a](image)

**Figure 12a:** Comparison of Fig. 11a liquidus and areotherm gradients at starting temperatures of 1423 °C and 1723 °C. Solid lines represent liquidus compositions whose color corresponds to S contents provided by the color bar, right. For both areotherms, intersection with a core containing 10-14 wt. % S initially occurs near the CMB due to the kink at 23 GPa. For cores with 15-16 wt. % S, the two cross at depth, leading to the formation of Fe₃S at the planet’s center.

All of Stewart et al.’s liquidus are consistent with a CMB temperature of 1723 °C, although the pronounced kink at 23 GPa results in a lower bound of ~1700 °C corresponding to a 10 wt. % S core. An abrupt change in liquidus slope is also observed by Chen et al. (2008) at
14 GPa, yet there is no evidence for a phase transition at 23 GPa that might explain this behavior. For a CMB temperature of 1423 °C, only cores with 14 or 15 wt. % S are located at or above the areotherm, meaning the rest would have begun solidifying. If we consider Stewart et al.’s (2007) initial assessment of the 40 GPa melting curve to be accurate, most liquidii would cross the areotherm near the CMB, resulting in iron snow, while the 15 & 16 wt. % liquidii initially cross the areotherm at the planet’s center, producing bottom-up crystallization of Fe₃S.

Figure 12b: Comparison of Fig. 11b liquidii and areotherm gradients at starting temperatures of 1423 °C and 1723 °C. For both areotherms, intersection with a core containing 10-12 wt. % S occurs near the CMB, resulting in the crystallization of iron snow. For cores with 13-16 wt. % S, the two cross at depth, leading to the formation of Fe₃S at the planet’s center.

Our liquidus constructions are completely consistent with a molten core for the estimated CMB temperature range of 1423 to 1723 °C. As such, they define new lower temperature limits the core can exist at prior to the onset of solidification. These range from 1610 °C, corresponding to a core with 16 wt. % and a CMB temperature of 1423 °C to 1205°C for a core with 10 wt. % S. Comparison of core areotherms and our liquidii (Fig. 12b) show that a core with 10-12 wt. %
S will initially crystallize near the kink at 23 GPa in the form of iron snow. When the iron snow sinks and dissolves, it enriches the surrounding melt in Fe, creating a higher density layer above the undisturbed, lighter core below (Breuer et al., 2015). As this density inversion is unstable, large-scale compositional overturn eventually occurs, and the heat dissipated by sinking iron is thought to be sufficient to drive a dynamo (Zhan & Schubert, 2012). Interestingly, the kink also opens up the possibility of a dynamo above the snowing layer, as latent heat released by the solidification of Fe, as well as liberated S would rise, stimulating convection in the core up until the CMB at 20 GPa. In the case of 10 wt. % S, top-down formation of Fe snow would be quickly accompanied by bottom-up crystallization of Fe in a manner similar to Earth. Crystallization of Fe cause heat and S-rich fluid to rise through the core providing a more stable source of energy for the dynamo that avoids the risk of compositional stratification (Laneuville et al., 2014).

Cores with 13-16 wt. % S experience initial solidification at depth, leading to the formation of Fe$_3$S at the planet’s center. Since Fe$_3$S is more dense than the remaining core liquid (Stewart et al., 2007), it is expected to remain at the center of Mars upon crystallization, providing a steady source of heat as the compositional domain at sub-areotherm temperatures extends to lesser depths as the core grows outward. Interestingly, our 13 wt. % liquidus is nearly parallel to the calculated areotherms, so given cooling the two would intersect at multiple depths, leading to solidification throughout the Martian core, including of Fe$_3$S snow at depths greater than ~ 36 GPa. Doubly snowing cores with conflicting dipole orientations and are thought to explain the surprisingly weak field observed around Mercury (Vilim et al., 2010). If snow is occurring at multiple depths in Mars, evidence of the resulting weak field might be shielded by the mantle, which is much thicker than Mercury’s, opening up the possibility that core solidification has already begun.
Conclusion

Stewart et al.’s liquidus temperatures are too high to be compatible with estimates of the Martian areotherm, given a non-solidifying core. The especially high temperatures at 23 GPa produce an abnormally high temperature gradient when interpolated to our data at 20 GPa. If trends in the evolution of solid and liquid FeS with pressure are accurate (Morard et al. 2007; Li et al., 2001) the change in concavity between the two pressures is difficult to explain. Additionally, the melting curve results are inconsistent with most estimations of the CMB temperature, as well as our determination of the Martian core areotherm. These observations, combined with the dubious construction of the liquidii, suggest that Stewart et al.’s 23 GPa are not reliable predictors of the state of the Martian core. While we are confident in our liquidus determination, and are optimistic its shape persists to greater depths, additional, non-eutectic melting data is needed at to get a comprehensive understanding of the Martian core’s state.

Applying surface-based determinations of 300 °C/Ga for the cooling rate of the Martian core (Ruiz, 2014; Lessel & Putirka, 2015) to the results of Fig 12. For a CMB temperature of 1773 °C the most optimistic estimate for compositions currently below the areotherm is that Mars will require 193 million years to initiate crystallization, with pessimistic estimates stretch to over 1 billion years, perhaps even longer if reverse-fault analysis is accurate (Nahm et al., 2011). However, the thermal state of the planet remains very poorly constrained. If, instead, the Martian CMB is at 1423 °C and its core is S-rich, Mars would be significantly closer to the onset of solidification, and may even house a hidden dynamo if solidification is occurring at multiple depths. New data, particularly seismic as well as high-pressure melting data, is required to better define the Martian core across its pressure, temperature, and compositional conditions.
By experimentally defining the Fe-Ni-S melting curve at Martian core conditions, and calculating liquidus and adiabatic gradients across its pressure domain, we have improved the knowledge of its current and future status. Our work highlights the importance of using accurate thermodynamic values and starting materials in gaining the most detailed and nuanced understanding of natural systems. Spatial analysis proved to be a powerful tool in estimating the compositions of fine textures to a high degree of accuracy, while S content control remains a challenge at high temperatures and pressures. We hope this work raises questions about our understanding of other planetary bodies, and encourages others to put hypothesis to the test through experimentation.

Most evidence indicates the Martian core is in a "Goldilocks" state: long since too cool for thermal convection, but too warm for solidification-driven chemical convection to begin. If core crystallization does occur, it is more likely to do so from the bottom up, giving Martian more in common with larger bodies like Earth and the gas giants than the smaller planets and moons. While Mars may not begin forming an inner core in the near future, there are undoubtedly planets in our galaxy that share many of its characteristics. Knowledge of the Martian core is critical to predict the habitability of similar planets, with older and therefore cooler worlds more likely to have regenerated dynamos capable of producing the magnetic fields that shelter life.
References


## Supplementary Tables & Figures

### Supplemental Table 1: Target S Composition Vs. Estimate

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Supplemental Figure 1: Point-based classification assessment of run M061816. Red dots are shape files generated across surface of the run. Green polygon is liquid training sample, pink polygon is droplet training sample, orange polygon is MgO training sample, and purple polygon represents both the solid and dendrite. Points are assigned a class identity based on the color of the raster beneath them, and are then converted to raster data.
Supplemental Fig. 2: Result of image classification. Green color is dendrite, blue is liquid, red is solid, orange is droplet, and MgO is white. The rasterized point’s color has been made black to enhance clarity against classification colors. Once classification is performed, each point’s identity assigned in the first step (Suppl. Fig. 1) is compared to what class it belongs to in the above image. The image’s accuracy is the number of points that should have been assigned to a class divided by the amount that were actually assigned to that class (Shi, 2009).