inversion and enhances the long-period signal of regional climate change [H. N. Pollack, P. Y. Shen, S. Huang, *Pure Appl. Geophys.* **147**, 537 (1996)].

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22. The HCN data set contains raw SAT (SAT_{raw}) data as well as data adjusted for time-of-observation biases (SAT_{tob}) and data adjusted for both the time-of-observation biases and nonclimatic biases (SAT_{ncb}). The time-of-observation bias, owing to different observation schedules, is adjusted on the basis of an empirical model [T. R. Karl, C. N. Williams Jr., P. J. Young, W. M. Wendland, *J. Climate* **25**, 145 (1986)]. Nonclimatic biases resulting from instrument changes and station relocations are adjusted on the basis of correlations between a candidate station and its 20 closest neighbors [T. R. Karl and C. N. Williams Jr., *J. Climate* **26**, 1744 (1987)]. In southeastern Utah, the average misfit between transient temperatures and synthetic transients for the preferred ties is 30, 25, and 9 mK for SAT_{raw}, SAT_{tob}, and SAT_{ncb}, respectively. These misfits illustrate the progression one would expect; each succeeding correction brings the SAT data and transient temperatures into better agreement. In western Utah, however, average rms misfits between the transient temperatures and the synthetic transients are 16, 6, and 21 mK for the SAT_{raw}, SAT_{tob}, and SAT_{ncb}, respectively. This implies that whereas the time-of-observation bias adjustment improves the correlation between the SAT time series and the transient borehole temperatures, the nonclimatic bias adjustment does not. Because meteorological stations in western Utah fall in an area of extremely sparse coverage, the nonclimatic bias correction is not as well constrained as in areas where station density is greater. In this study, we use SAT_{ncb} and SAT_{tob} for southeastern and western Utah, respectively.

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High-Pressure Iron-Sulfur Compound, Fe_3S_2, and Melting Relations in the Fe-FeS System

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An iron-sulfur compound (Fe_3S_2) was synthesized at pressures greater than 14 gigapascals in the system Fe-FeS. The formation of Fe_3S_2 changed the melting relations from a simple binary eutectic system to a binary system with an intermediate compound that melted incongruently. The eutectic temperature in the system at 14 gigapascals was about 400°C lower than that extrapolated from Usselman's data, implying that previous thermal models of Fe-rich planetary cores could overestimate core temperature. If it is found in a meteorite, the Fe_3S_2 phase could also be used to infer the minimum size of a parent body.

Cosmochemical and geophysical arguments (*1*) suggest that sulfur (S) may be the lighter alloying element in the Fe-rich cores of planets such as the Earth and Mars. Because the Earth consists of a liquid outer core and a solid inner core, the melting relations in the system Fe-FeS at high pressure (*P*) are used to estimate the core temperature (*T*). For Mars, we do not know if the core is solid or liquid. The melting relations could place a constraint on the state of the core for a given composition and core *T*. The eutectic melting *T* is used to evaluate the efficiency of Fe-rich core segregation in early core formation processes. Many models of core *T* and core formation processes were based on extrapolation of melting data in the system Fe-FeS obtained at relatively low *P* (<10 GPa) (*2–4*). The extrapolations were based on an assumption that no intermediate compound formed in the system, and therefore the melting behavior could be predicted based on simple thermodynamic relations. We report a Fe-S compound formed at $P > 14$ GPa, which changes the melting relations in the Fe-FeS system.

Iron and FeS form a binary system at ambient *P* with a eutectic melting point at 988°C and 31% S (all percentages are given by weight) (*5*). The eutectic composition becomes more Fe-rich with increasing *P*, whereas the eutectic *T* remains nearly constant to at least 6 GPa (*2–4*). At $P > 6$ GPa, Usselman (*2*) reported that the eutectic *T* rose with a slope of ~34 K/GPa to at least 10 GPa. We conducted melting experiments in the Fe-FeS system in a multianvil apparatus (*6*) to a *P* higher than that of (*2*). The experimentally determined eutectic *T* and composition in this study are in good agreement with previous studies (*2–4*) to 5 GPa. Eutectic melting was determined on the basis of quenched textures, similar to those described in (*2–4*), and composition maps. At $P < 14$ GPa, the quenched textures and compositions are due to eutectic melting in the Fe-FeS binary system in which two solids, Fe and FeS, coexist below the eutectic *T* (Fig. 1A), whereas one solid FeS (or Fe, depending on the composition of the starting material) and a liquid phase coexist between the eutectic and liquidus *T*'s (Fig. 1B). The composition of the liquid at the eutectic *T* represents the eutectic composition of the system. The S content of the eutectic linearly decreases with increasing *P*, from 31% S at 1 bar to 20.7 ± 0.4% S at 7 GPa, consistent with (*3*, *4*). Pressure has very little effect on the eutectic composition between 7 and 14 GPa. The eutectic *T* linearly decreased with increasing *P*, from 988°C at 1 bar to 860°C at 14 GPa, contrary to the results of Usselman (*2*), who reported a cusp in the eutectic curve at 5.2 GPa. Our eutectic *T* at 10 GPa was about 200°C less than that of Usselman at the same *P*.

At $P > 14$ GPa, we found a Fe-S compound, Fe_3S_2 (27.9 ± 0.3% S) (*7*). An intergrowth of metallic Fe and Fe_3S_2 was quenched from runs with *P* between 14 and 18 GPa and *T* of less than the eutectic *T* (Fig. 1C), when starting materials with 16.1 and 22.3% S were used. At $T = 875$°C and $P = 14$ GPa, Fe_3S_2 coexisted with a eutectic liquid composition (18.2 ± 0.3% S) (Fig. 1D). When comparing the results from the two unmelted runs at 10 and 14 GPa (Fig. 1, A and C), it is evident that

Table 1. Crystallographic parameters for the phases found in the quenched sample of Fe_3S_2. The numbers in parentheses are the errors in the last digits.

Quantity (unit)	Troilite	α-Fe	Monoclinic	Triclinic
a (Å)	5.9656(7)	2.8676(5)	5.0481(9)	2.372(1)
b (Å)	5.9656(7)	2.8676(5)	4.436(1)	3.427(1)
c (Å)	11.757(6)	2.8676(5)	4.387(1)	5.999(4)
α	90	90	90	82.09(2)
β	90	90	99.75(1)	79.50(6)
γ	120	90	90	73.99(4)
V (Å^3)	362.4(2)	23.58(1)	96.84(2)	45.90(2)

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the simple Fe-FeS binary eutectic melting system changed to a binary system with an intermediate compound, Fe_3S_2, at $P > 14$ GPa. Our interpretation of melting relations at $P > 14$ GPa is that there is a peritectic point with an intermediate Fe_3S_2 compound that melts incongruently (Fig. 2).

Once we identified the Fe_3S_2 compound in the melting experiments, we synthesized the Fe_3S_2 phase at 15 GPa and 880°C, using its stoichiometric composition with a slight excess of metallic Fe as the starting material (27.0% S). The synthetic sample showed uniform Fe_3S_2 composition ($27.9 \pm 0.3\%$ S) and less than 2% metallic Fe, according to the electron microprobe analyses. The x-ray powder diffraction pattern (Fig. 3) (*8*) was collected at high resolution, and the diffraction lines were broad, which in this case arises from the small particle size. This property is intrinsic to the sample, rather than induced by grinding. In addition, the pattern demonstrated a large number of lines, especially in the region between 21° and 23°, which cannot be indexed on a structure of an analogous phase, Ni_3S_2 (*9*). The line at 2.0277 Å (22.705°) arises from the presence of α-Fe, which is expected on the basis of the excess of Fe in the starting composition. Most of the rest of the strong peaks are representative of troilite in the 2H hexagonal cell. As the remaining peaks could not be indexed by a single phase, a special version of the program TREOR90 (*8*) was prepared. Using a random number generator and the desired fraction of incident *d* spacings to include in the calculation, we made an attempt to index the partial pattern. If no satisfactory solution was found, the program looped back through the incident data, selecting a different subset each time. The first iteration found a triclinic unit cell with a figure of merit of >200. This small cell volume, $V = 45.9$ Å^3 (Table 1), explained a large number of the lines remaining after the troilite and Fe metal lines were removed. All but one of the rest of the spacings could be explained by an additional monoclinic phase. Because this process is ad hoc, it is not possible to be certain of the identification of the lattices corresponding to the extra phases. What is important, however, is that the pattern cannot be fitted by a single sulfide.

The widths of the peaks suggest that the average particle size of this material is <400 Å, which is consistent with a model in which Fe_3S_2, at high *P* and *T*, decomposed to FeS plus Fe-rich sulfides during the quench. Not only the extra phases, but the relative amounts of FeS and Fe argue against the breakdown of Fe_3S_2 to 2FeS + Fe. Because iron sulfides such as FeS typically undergo several phase transitions at high *P* and *T*, it is not surprising that the Fe_3S_2 phase is not quenchable. The structure of the Fe_3S_2 phase in its stability field can only be solved by in situ x-ray diffraction measurements under conditions of simultaneous high *P* and *T*.

The presence of an intermediate compound, Fe_3S_2, in what was presumed to be a simple binary system, requires a reevaluation of planetary core models that are based on the Fe-FeS system. The eutectic *T* of the

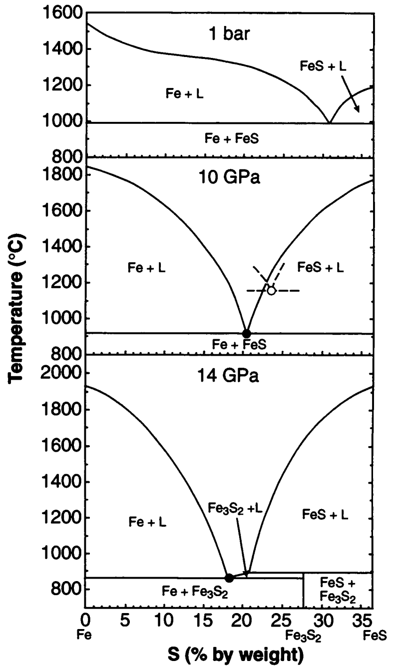

Fig. 2. Melting relations in the Fe-FeS system at pressures of (**A**) 1 bar, (**B**) 10 GPa, and (**C**) 14 GPa. An intermediate compound with composition Fe_3S_2 forms at pressures >14 GPa. The eutectic points at 10 and 14 GPa were determined in this study (solid circles). The eutectic point determined by Usselman (*2*) at 10 GPa is also shown (empty circle) for comparison. L, liquid.

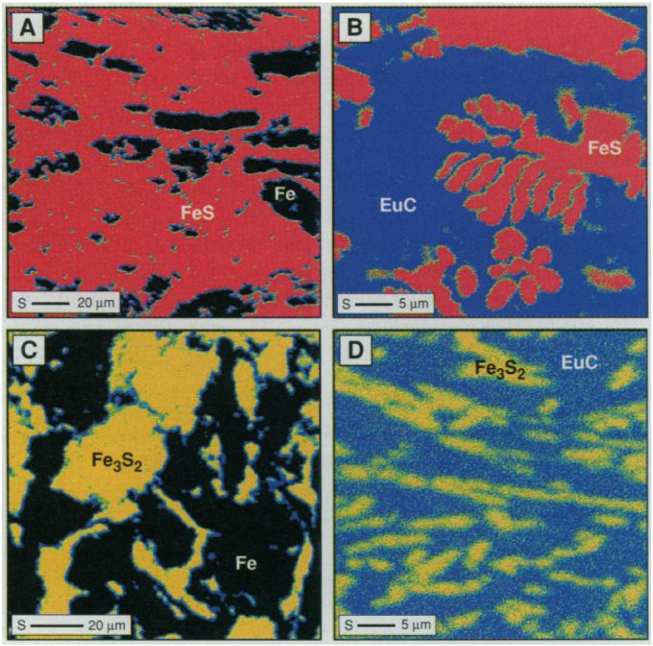

Fig. 1. Sulfur x-ray maps of the recovered samples. (**A**) The sample was quenched from 10 GPa and 900°C (below the eutectic *T*). The irregularity of the Fe grains (black) embedded in a FeS matrix indicates that this sample is unmelted. (**B**) The sample was quenched from 10 GPa and 965°C. Dendrites of FeS (red) were formed during the quench from a temperature above the eutectic temperature. The blue matrix (EuC) represents eutectic composition. (**C**) The sample was quenched from 14 GPa and 850°C. The intergrowth feature of Fe (black) and Fe_3S_2 (yellow) grains indicates that this sample is reacted, but unmelted. (**D**) The sample was quenched from 14 GPa and 875°C. Melting quench texture from a temperature greater than the eutectic temperature. The blue matrix (EuC) is of eutectic composition. The yellow strips are Fe_3S_2.

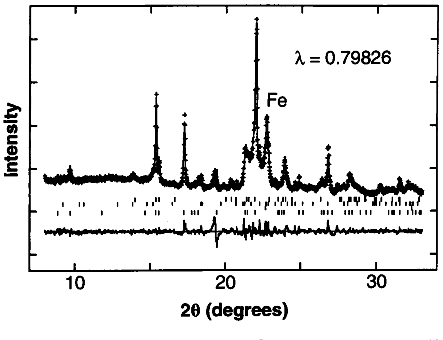

Fig. 3. Fitted peaks for Fe_3S_2 x-ray powder diffraction pattern. Crosses represent the observed data points, the solid line represents the "calculated" pattern, and the bottom trace is the difference between the observed and calculated patterns. The vertical ticks under the observed pattern represent the location of reflections for each of the phases included. The bottom row is for the troilite form of FeS, and the second row for α-Fe. The upper two rows represent the triclinic and monoclinic phases believed to be unknown sulfides. See the text for a description of the procedure used to obtain parameters for these lattices. Intensity is measured in arbitrary units. λ, wavelength.

system helps determine the *T* or physical state of the planetary cores. The eutectic *T* determined in this study is 860°C at 18 GPa, which is about 500°C less than that extrapolated from (*2*). The extrapolation to higher *P* based on (*2*) could result in the overestimation of core *T*. In fact, such extrapolation should not be exercised in the Fe-FeS system because of the formation of the intermediate compound and changes in physical properties of end-member FeS (*10*) at high *P* and *T*. Theoretical calculations also showed that other Fe-S compounds such as Fe_3S could form at higher *P* (*11*), and melting relations in the Fe-FeS system at the core *P* of the Earth (135 to 360 GPa) may be different from what we observed at relatively low *P*. In addition, the presence of Ni in the system could further complicate the phase relations.

Iron sulfides are found in many classes of meteorites. If Fe_3S_2 were indeed found in a meteorite, it would indicate the minimum size of the parent body and the maximum *T* of the core. The Fe_3S_2 compound could only be found in meteorites that come from parent bodies with a center $P > 14$ GPa and *T* less than the eutectic temperature (which is ~900°C, depending on the pressure).

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7. Quantitative chemical analyses were obtained with a JEOL JXA-8900 electron microprobe, using pyrite FeS_2 as a standard. The composition of the samples synthesized at 14 GPa is very close to stoichiometric Fe_3S_2 (27.7% S). The compound may be of nonstoichiometric nature, because the samples synthesized at 18 GPa have a lower sulfur content (27.1 ± 0.2% S) than does Fe_3S_2 stoichiometric composition.
8. Powder x-ray diffraction data were collected at beam line X7A of the National Synchrotron Light Source of Brookhaven National Laboratory, using the high-resolution mode with a Si(111) channel-cut monochromator and a Ge(110) analyzer crystal at 0.79826(2) Å. See D. E. Cox, B. H. Toby, M. M. Eddy [*Aust. J. Phys.* **41**, 117 (1988)] for details of the instrument. The wavelength and diffractometer zero were calibrated with Si powder. Program GSAS [A. C. Larson and R. B. Von Dreele, *Report LA-UR 86-748* (Los Alamos National Laboratory, Los Alamos, NM, 1986)] was used for all profile fitting. A modified version of TREOR90 [P.-E. Werner, L. Eriksson, M. J. Westdahl, *J. Appl. Crystallogr.* **18**, 367 (1985)] was used to determine the unit-cell parameters for the unknown phases. For the method of intensity extraction, see A. Le Bail, H. Duray, J. L. Fourquet [*Mater. Res. Bull.* **23**, 447 (1988)]. The intensity values do not imply any knowledge of the crystal structures of these phases.
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Melting of $(Mg,Fe)_2SiO_4$ at the Core-Mantle Boundary of the Earth

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The lower mantle of the Earth is believed to be largely composed of (Mg,Fe)O (magnesiowüstite) and $(Mg,Fe)SiO_3$ (perovskite). Radiative temperatures of single-crystal olivine $[(Mg_{0.9},Fe_{0.1})_2SiO_4]$ decreased abruptly from 7040 ± 315 to 4300 ± 270 kelvin upon shock compression above 80 gigapascals. The data indicate that an upper bound to the solidus of the magnesiowüstite and perovskite assemblage at 4300 ± 270 kelvin is 130 ± 3 gigapascals. These conditions correspond to those for partial melting at the base of the mantle, as has been suggested occurs within the ultralow-velocity zone beneath the central Pacific.

The major minerals of Earth's lower mantle are thought to be $(Mg_{0.94},Fe_{0.06})SiO_3$ perovskite and $(Mg_{0.84},Fe_{0.16})O$ magnesiowüstite (*1*). Thus, the melting behavior of this assemblage is important for determining the temperature of the mantle and the origin of the seismically imaged structures at the core-mantle boundary (CMB). Recent studies of the solidi of this mantle assemblage are disparate: The melting temperature of pure $MgSiO_3$ perovskite (Pv) at the CMB has been estimated at 7000 to 8500 K (*2*) and 4500 ± 350 K (*3*). Measurements of the melting of MgO [periclase (Per)] at pressures up to 31.5 GPa (4000 ± 200 K) (*4*) imply, when extrapolated to 133 GPa, that it melts at 5100 ± 750 K. Phase equilibrium experiments (*5*) demonstrate that at lower mantle pressures, the stable high-pressure phase (hpp) assemblage for Mg_2SiO_4 [forsterite (Fo)] is MgO (Per) + $MgSiO_3$ (Pv); thus, Fo can be used as a representative starting material in shock experiments. Syono and co-workers' (*6*) shock-recovery experiments on Fo indicate that MgO (Per) + $MgSiO_3$ (glass that is inferred to have been Pv at high pressure and temperature) is actually recovered from samples that were at high pressure for the short (10^{-7} s) time scale of a shock-wave experiment (*6*). In previous shock experiments using olivine crystals, Brown *et al.* (*7*) inferred the onset of melting of the assemblage Per + Pv above ~140 GPa on the basis of a sharp decrease in longitudinal elastic wave velocity. Brown *et al.* (*7*) also suggested that the previous shock temperatures measured in Fo in the range of 160 to 180 GPa (*8*) are representative of the liquid regime of the Fo Hugoniot. Because Fo shocked below 160 GPa has a low Planck emissivity, temperatures in the pressure range where the Hugoniot curve crosses the solidus (~90 to 133 GPa) were not measurable. Here, we determine the onset of melting at lower pressures using higher emissivity olivine samples and a more sensitive detector system (*9*). We used samples of San Carlos and Burma peridot $[(Mg_{0.9},Fe_{0.1})_2SiO_4$ (*10*)] for shock-temperature experiments because they are green rather than transparent. Their ambient-condition emissivities are ~0.7 and ~1.0 at 560 and 900 nm. Moreover, their solidi are within 110°C of the melting point of Fo at 1 bar (*5*). Using 5 mm by 5 mm by 2 mm samples, we conducted measurements from 94 to 192 GPa (Table 1) (*11*). As the shock wave propagated through the sample (*12*), the com-

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