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# Thermodynamics of Fe-S at ultra-high pressure

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ABSTRACT

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*Keywords:* Earth's core Fe–S binary Eutectic Temperature of the core Earth's core is believed to consist of a solid inner core and an outer liquid core. Since the inner core is mostly solid iron, most geophysical work has focused on melting of pure iron at core conditions. The inner core density is well matched with seismological data if some S is added to iron. The available phase equilibrium experimental data in the binary Fe–S system to pressures as high as ~200 GPa is used to create a thermodynamic database extending to core pressures that can be used to calculate the inner core density if S were the only other constituent. Such a calculation gives the maximum temperature of the solid inner core as 4428 ( $\pm$  500) K (363.85 GPa, density=13.09 g/cm<sup>3</sup>) with a sulfur content of ~15 wt%. To be consistent with the seismically determined density, the outer liquid core requires mixing of yet another light element or elements; both oxygen and carbon are suitable.

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## 1. Introduction

If pure iron density matched the PREM model (Preliminary Earth Reference Model, [12]) density, iron physical data could be used to estimate the melting temperature of the core. Iron or iron with some nickel is too dense to match the seismologically estimated density of the core. Sulfur is one of the several elements (Si, O, C) that could lower the density. If we choose S as that component, then the melting temperature of the core will correspond to the melting of a composition in the Fe–S binary system. The solution of the problem, then, lies in the domain of thermodynamics.

Kamada et al. [21] performed melting experiments on the Fe– Fe<sub>3</sub>S system to a pressure of 175 GPa and did an excellent review of the binary system experiments ([8,9,15,17,21,27,30,44]. Komada et al. [21] estimated the effect of pressure on the eutectic temperature and used the Kraut–Kennedy [25] melting model to extrapolate the melt data to core pressures. There is abundant experimental data to perform a Calphad type study [35] to create an assessed thermodynamic database for the binary system so that a model based extrapolation may not be needed. The experimental data on iron, sulfur and iron–sulfur phases at high pressures are used to create a thermodynamic database to calculate phase equilibrium to core pressures. The Fe–S binary is eutectic [43] at 1 bar. Above the eutectic temperature, a melt exists alone or with a

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http://dx.doi.org/10.1016/j.calphad.2015.09.009 0364-5916/© 2015 Elsevier Ltd. All rights reserved. solid phase and therefore determines the maximum temperature of the solid core in the Fe–S system.

When the physical data on properties of iron at core pressures is compared with seismological observations, it becomes necessary to reduce the density of the core material by adding some lighter element [27,34]. This was also required by the liquid like behavior of the outer core material. The light elements that are present in significant concentration in the solar nebula are S, O, Si and C. Ohtani et al. [31] studied the oxygen solubility in the core. Recent condensation calculations [37] show that as much as 25% of the solids forming in the nebula below 900 K may be iron sulfides. Morard et al. [30] and Li and Fei [28] studied the behavior of a number of elements under core conditions. Carbon has also been considered as a possible light element [10,13]. Usselman [42] studied the Fe–S eutectic at moderate pressures. This paper presents the thermodynamics of Fe, S and the binary Fe-S systems basing the work on the recently published experimental and theoretical data [43,30,28,42,14-18,41,21,8]. The assessment of the thermodynamic data is done with the CALPHAD method [2], which involved the use of an existing thermochemical database [43] at ambient pressures and its improvement by fitting to experimental phase equilibrium data at higher pressures. This description consists of the newly assessed thermodynamic data on iron [37] which is used with, sulfur, FeS and the Fe–S binary system to over pressures up to170 GPa. The assessed high pressure thermodynamic data on S, sulfur compounds and the effect of pressure on the mixing parameters in the binary Fe-S system is given in the Supplementary Section.



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#### 2. Thermodynamic data on iron and the equation of state

Saxena and Eriksson [38] recently used the experimental and theoretical data on iron and created an assessed thermodynamic database. An important property of this database and the work to follow on the binary system is that we use a new equation of state [5] that is consistent with the quasi-harmonic model and the Mie– Grüneisen EOS at high pressures [22]. It permits the use of existing ambient-pressure thermochemical databases while avoiding some unphysical predictions that occur with other EOS [36]. It can be used to calculate thermodynamic properties such as heat capacity and entropy to very high temperature and pressure.

#### 3. Thermodynamics of sulfur

In a recent study, Liu et al. [26] described the phase diagram of S. This is a very complex phase with many phase transitions and it is difficult to find extreme pressure data. Liu et al. [26] used S melting curve to about 12 GPa basing the diagram on the work of Paukov et al. [32]. For this broad analysis of the iron–sulfur binary system, the orthorhombic S is used as the stable phase melting into a homogeneous sulfur liquid. For thermochemical data on S (orthorhombic phase and melt), the data is from [40]. The pressure-volume-data on the melt and solid permit the melting to be extrapolated to high pressure. Melt data at 1 bar is from [43] and the high pressure data is assessed here producing a melting curve (Fig.1 Suppl.). Table 1 (Suppl.) shows the thermodynamic data.

The thermophysical data as derived may not violate any theoretical constraints such as heat capacity or volume becoming negative at high pressure. The calculated  $C_p$ , S and molar volume data on S phases (orthorhombic and melt) as a function of temperature at pressures up to 100 GPa is very systematic, not violating the theoretical constraints. The trends clearly show (as confirmed by calculations) that one can extrapolate the data to core pressures (for example the S melt has a  $C_p$  of 28.19 and molar volume of 5.35 cm<sup>3</sup> at 365 GPa) but there is no data of any kind to confirm this (Table 1).

#### 4. Thermodynamics of the binary Fe-S system

Several iron–sulfur phases exist at 1 atm for which the thermochemical data are well documented [43]. Kress [24] modeled the Fe–S binary using a one constant Margules parameter. Buono and Walker [7] extended the formulation to include the asymmetric formulation. Waldner and Pelton used modified quasichemical solution model [33] for the mixing of Fe and S with formation of pyrrhotite, pyrite and other iron deficit phases at 1 bar. For the pyrrhotite, the compound energy formation model is used. Here the focus is on the new high pressure phases [15,16,16– 18]. At high pressure of 10 to 21 GPa, Fei et al. [16,15,17,18] found new phases Fe<sub>3</sub>S and Fe<sub>3</sub>S<sub>2</sub> with variable S content and possibly a metastable phase Fe<sub>2</sub>S. With the assessed data on the elements S and Fe, we can extend the Fe–S database of [43] to high pressures. One of the tasks is to assess the effect of pressure on the

Table 1

Inner Core parameters.

Density (PREM)	Pressure (GPa)	Eutectic T,K	wt% S at eutectic	Estimated T, K	wt% S matching the density
12.763	328.85	4200	9.91	4191	15.57
13.09	363.85	4441	9.65	4428	15.65



**Fig. 1.** Eutectic temperature in the binary system is plotted as a function of pressure. Solid symbols are solidus and open are liquidus or partial melts. Data from: triangles [21], squares [8], circles [30], crosses [42]. Open circles with no error bars are from [15–18]. Solid line is thermodynamically calculated path of the eutectic temperature (this study). The thin solid line is from Kamada et al. [21] with extrapolated melting with the Kraut–Kennedy model. The other two lines, one dashed and one medium solid, are for Fe–FeO [8] and FeFe<sub>3</sub>C [29,13] eutectics respectively. If we assume the same errors in the temperature as in the determination of eutectics, we estimate the error at 4441 K to be  $\pm$  500.

quasichemical model mixing parameters. The experimental data on eutectic points determined to pressures of 175 GPa is used [14,17,21,8,9,30] (Fig.1) with the optimization procedure as described in [23,22]. From the assessed database, one may calculate the binary Fe–S phase equilibrium

diagrams at any pressure and temperature. Fig. 2 shows the calculated diagram at 21 GPa which is quite similar to the experimental phase diagram [16] at that pressure.

The liquid phases are modeled with the modified quasichemical excess energy formulation with pressure terms determined in this work. For solids only pyrrhotite is treated as a solid solution (compound energy model). The excess volume term is determined in this work.

Fig. 1 shows a plot of experimentally determined eutectic temperatures varying as a function of pressure. The solid line is the thermodynamically calculated path of the eutectic temperature. The thermodynamically calculated extrapolation to a pressure of 363.85 GPa is shown with an eutectic temperature of 4441 K. The pressure value is according to the PREM model. This is then the temperature above which the inner core will totally (for a eutectic



**Fig. 2.** Binary Fe–S system at 21 GPa. The diagram is similar to the experimental diagram [16] as it shows the presence of the two new phases  $Fe_3S$  and  $Fe_3S_2$  with a matching peritectic point of 1356 K.



**Fig. 3.** Fe–S binary at 328 GPa (top of inner core). The composition of the cores is constrained by the densities and only a certain amount of S or any other light element can be part of the cores. Such temperatures and densities can only occur at certain compositions. Increasing the S content, beyond that shown, is not an option because for example at a temperature of 4100 K, we will enter a two phase (S-rich melt and Fe<sub>3</sub>S) and not a single melt. The solid black points show examples of calculated temperatures and compositions.

composition of 9.65 wt% S) or partially melt and it must be the absolute upper temperature at the center of a solid inner core. Error estimates using the points above eutectic (e.g. connecting the open triangles in Fig. 1) would raise the temperature by about 500 K not affecting the final conclusion of this study because the melt temperature will be raised similarly.

The calculated phase diagram such as Fig. 2 for the Fe–S binary shows the stability fields of  $Fe_3S$  and  $Fe_3S_2$  along with the eutectic and peritectic points. Above the eutectic temperature melt or melt plus solid may exist depending on the composition.

## 5. Discussion

If the seismological model [12] is followed, one may determine the temperature and the added S content to iron that matches the seismological density. This is possible because we have a pressuredensity-temperature database on all phases in the Fe-S system. Our constraint is that the solid phases may not exist above the eutectic temperature without a coexisting melt. Therefore the inner core temperature at 363.85 GPa has to be lower than the eutectic temperature of 4441 K. If PREM density is followed, we may calculate the chemical composition at the center by matching the density with the S content at a certain temperature immediately below 4441 K. The density values are calculated for the PREM density. The density of 13.088 g/cm<sup>3</sup> (PREM density at 363.85 GPa is 13.093 g/cm<sup>3</sup>) is reached at a composition of 15.9% wt% S. At a pressure of 328.85 GPa (the inner-outer core boundary with PREM density of 12.73 g/cm<sup>3</sup>), the density of 12.763 g/cm<sup>3</sup> is reached with a S content of 15.57 wt% at 4191 K. On the top of the inner core (bottom of outer core) the PREM density falls to 12.166 g/cm<sup>3</sup> (328.85 GPa). The difference of 0.6 g in density may change if we use the more recent density model such as the AK135 [20] with a range of values extending up to a difference of 1 g. While the temperature in the inner core can be assumed to be just below the eutectic temperature, we cannot do so for the outer core because of the lack of the ternary (Fe–S–C or O) thermodynamic data. The binary phase diagram (Fig. 3) illustrates the method of calculation.

The inner core is supposedly all solid. Therefore the inner core temperature must lie below the eutectic everywhere. If we use the seismic density models (PREM or AK-135) and the maximum

solidus as at the eutectic, we obtain the following data

At the top of the inner core (P=328 GPa, D=12.763 g/cm3) the temperature is estimated as 4191 K. At this depth the outer core density is 12.166 g/cm<sup>3</sup>. If the temperature does not vary across the boundary the drop of 6 g/cm3 is to be attributed to compositional difference between the inner and outer core. Since we have maximized the S content in the inner core, the dilution must involve the mixing of another light element. While there are several possible light elements, oxygen and as shown in Fig. 1, carbon may easily fit the need.

Based on melting of pure iron at high pressures, the temperature at the inner core outer core boundary has been commonly inferred to lie between  $4000 \pm 200$  K [3] and  $6230 \pm -500$  K [1]. Brown and McQueen [4] estimated the temperature to be  $5500 \pm 500$  K at 2.4 Mbar from their shock wave experiments. A comparison of the densities from the PREM model with the density of pure iron at high pressure indicates that we require iron to be diluted with a light element. In this case we have used S as the dilutent bringing the melting temperature down from 6200 K, as established by Anzellini et al. to 4200 K (the Fe–S eutectic). This conclusion is based on thermodynamic data (Fig. 3) and is independent of how much S we need to put in the inner core to match the PREM density.

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#### Appendix A. Supplementary material

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#### References

- S. Anzellini, A. Dewaele, M. Mezour, P. Loubeyre, G. Morard, Melting of iron at Earth's inner core boundary based on fast X-ray diffraction, Science 340 (2013) 464.
- [2] C.W. Bale, P. Chartrand, S.A. Decterov, G. Eriksson, K. Hack, R. Ben Mahfoud, J. Melançon, A.D. Pelton, S. Petersen, FactSage thermochemical software and databases, Calphad J. 62 (2002) 189–228.
- [3] R. Boehler, Temperatures in the Earth's core from melting-point measurements of iron at high static pressures, Nature 363 (1993) 535–536.
- [4] J.M. Brown, McQuenn R.G, The equation of state for iron and the Earth's core. Advances in Earth and Planetary Sciences, vol. 12. High-Pressure Research in Geophysics, edited by S. Akimoto, M.H. Manghani. pp. 611–623.
- [5] E. Brosh, G. Makov, R.Z. Shneck, Application of CALPHAD to high pressures, Calphad 31 (2) (2007) 173–185.
- [7] A.S. Buono, D. Walker, The Fe-rich liquidus in the Fe–FeS system, Geochim. Cosmochim. Acta 75 (2011) 2072–2087.
- [8] A.J. Campbell, C.T. Seagle, D.L. Heinz, G. Shen, V.B. Prakapenka, Partial meltingin the iron-sulfur system at high pressure: a synchrotron X-ray diffraction study, Phys. Earth Planet. Inter. 162 (2007) 119–128.
- [9] L. Chudinovskikih, R. Boehler, Eutectic melting in the system Fe–S to 44 GPa, Earth Planet. Sci. Lett. 257 (2007) 97–103.
- [10] R. Dasgupta, A. Buono, G. Whelan, D. Walker, High-pressure melting relations in Fe-C-S systems: implications for formation, evolution, and structure of metallic cores in planetary bodies, Geochim. Cosmochim. Acta 73 (2009) 6678–6691.
- [12] A.M. Dziewonski, D.L. Anderson, Preliminary reference Earth model, Phys. Earth Planet. Inter. 25 (1981) 297–356.
- [13] Y. Fei, E. Brosh, Experimental study and thermodynamic calculations of phase relations in the Fe-C system at high pressure, Earth Planet. Sci. Lett. 408 (2014) 155–162.
- [14] Y. Fei, C.M. Bertka, The interior of Mars, Science 308 (2005) 1120–1121.
- [15] Y. Fei, C.M. Bertka, L.W. Finger, High-pressure iron-sulfur compound Fe<sub>3</sub>S<sub>2</sub>,

and melting relations in the system Fe–FeS, Science 275 (1997) 1621–1623.

- [16] Y. Fei, C.T. Prewitt, H.K. Mao, C.M. Bertka, Structure and density of FeS at highpressure and high temperature and the internal structure of Mars, Science 268 (1995) 1892–1894.
- [17] Y. Fei, J. Li, C.M. Bertka, C.T. Prewitt, Structure type and bulk modulus of Fe3S, a new iron-sulfur compound, Am. Mineral. 85 (2000) 1830–1833.
- [18] Y. Fei, Y. Wang, L. Deng, Melting relations in the Fe-C-S system at highpressure: implications for the chemistry of the cores of the terrestrial planets. Lunar and Planetary Science Conference, 2007, vol. 38, pp. 1231–1232.
- [20] D. Gubbins, Guy Masters, F. Nimmo, A thermochemical boundary layer at the base of Earth's outer core and independent estimate of core heat flux, Geophys. J. Int. 174 (2008) 1007–1018.
- [21] S. Kamada, E. Ohtani, H. Terasak, S. Takeshi, M. Miyahara, Y. Ohishi, N. Hirao, Melting relationships in the Fe–Fe<sub>3</sub>S up to the outer core conditions, Earth Planet. Sci. Lett. 359–360 (2012) 26–33.
- [22] A. Karbasi, S.K. Saxena, R. Hrubiak, The thermodynamics of several elements at high pressure, Calphad 35 (2011) 72–81.
- [23] E. Konigsberger, G. Eriksson, A new optimization routine for ChemSage, Calphad 19 (2) (1995) 207.
- [24] V. Kress, Thermochemistry of sulfide liquids: I. The system O–D–Fe at 1 bar, Contrib. Mineral. Petrol. 127 (1997) 176–186.
- [25] E.A. Kraut, G.C. Kennedy, New melting law at high pressures, Phys. Rev. Lett. 16 (1966) 608–609.
- [26] Lei Liu, Yoshio Kono, Curtis Kennev-Benson, Wenge Yang, Yan Bi, Guoyin Shen, Chain breakage in liquid sulfur at high pressures and high temperatures, Phys. Rev. B 89 (2014) 174201.
- [27] J. Li, J.Y. Fei, H.K. Mao, K. Hirose, S.R. Shieh, Sulfur in the Earth's inner core, Earth Planet. Sci. Lett. 193 (2005) 509–514.
- [28] J. Li, Y. Fei, Experimental constraints on core composition Treatise Geochem. TGC2: 00214, 2014.
- [29] O.T. Lord, M.J. Walter, R. Dasgupta, D. Walker, S.M. Clark, Melting in the Fe–C system to 70 GPa, Earth Planet. Sci. Lett. 284 (2009) 157–167.
- [30] G. Morard, D. Andrault, D. Antonqngeli, J. Bouchet, Properties of iron alloys

under the Earth's core conditions, C. R. Geosci. 346 (5) (2014) 130–139.

- [31] E. Ohtani, A.E. Ringwood, W. Hibberson, Composition of the core II. Effect of high pressure on solubility of FeO in molten iron, Earth Planet. Sci. Lett. 71 (1984) 94–103.
- [32] I.E. Paukov, E.Y. Tonkov, D.S. Mirinskii, Phase diagram ofsulfur under high pressure, Dokl. Akad. Nauk SSSR 164 (1965) 588–589.
- [33] A.D. Pelton, S.A. Degterov, G. Eriksson, C. Robelin, Y. Dessureault, The modified quasichemical model I-binary solutions, Metall. Mater. Trans. B 31B (2000) 652–659.
- [34] J.P. Poirier, Light elements in the Earth's core: a critical review, Phys. Earth Planet. Inter. 85 (1994) 319.
- [35] N. Saunders, A.P. Miodownik, CALPHAD: A Comprehensive Guide, Pergamon Press, London, 1988.
- [36] S.K. Saxena, Thermodynamics of Rock-forming Crystalline Solutions, Springer-Verlag, New York, 1973.
- [37] S.K. Saxena, R. Hrubiak, Mapping the nebular condensates and the chemical composition of the terrestrial planets, Earth Planet. Sci. Lett. 393 (2014) 113–119.
- [38] S.K. Saxena, G. Eriksson, Thermodynamics of iron at extreme pressures and temperatures, Phys. Chem. Solids 84 (2015) 70–74.
- [40] D.R. Stull, H. Prophet, JANAF Thermochemical Tables, U.S. Department of Commerce, Washington. Cp Fitted by CRCT, Montreal, 1985.
- [41] S. Urakawa, K. Someya, H. Terasaki, et al., Phase relationships and equations of state for FeS at high pressures and temperatures and implications for the internal structure of Mars, Phys. Earth Planet. Inter. 143–144 (2004) 469–479.
- [42] T.M. Usselman, Experimental approach to the state of the core: 1. The liquidus relations of the Fe-rich portion of the Fe–Ni–S system from 30 to 100 kb, Am. J. Sci. 275 (1975) 278–290.
- [43] P. Waldner, A. Pelton, Thermodynamic modeling of the Fe–S system, J. Phase Equilib. Diffus. 26 (2005) 23–27.
- [44] D. Walker, O.T. Lord, M.J. Walter, S.M. Clark, X-ray absorption contrast images of binary chemical reactions, Chem. Geol. 260 (2008) 211–220.