

First-Principles Calculation of $\text{Fe}_{1-x}\text{S}_x$ Liquid Alloys at Conditions of Earth's Outer Core

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Abstract

The composition and properties of the Earth's terrestrial outer core cannot be directly probed, however, indirect information of density and sound velocity from seismic measurements of the outer core, suggests that liquid iron is the most abundant element, alloyed with other lighter elements. Among these elements, sulphur has been suggested to be present. In this study, we investigate the effects of sulphur on the dynamical and structural properties of liquid Fe-S alloys with varying S content under conditions similar to those of Earth's outer core, providing a systematic atomic-scale characterization including structural, diffusion, and thermodynamic properties that has been largely absent from previous AIMD studies of this system. We examine compositions ranging from 0 to 14.9 wt% S (0 to 23.4 at% S). Our results demonstrate that the compressional wave velocity increases with sulphur concentration and pressure, with pressure having a more pronounced effect. We find that both Fe and S have similar diffusion coefficients at all concentrations studied. Our findings suggest that a concentration of S ranging between 10.2 and 11.4 wt%S could account for the density of the Earth's core but not for its sound velocity. This discrepancy indicates that sulphur cannot be the only light element present in the Earth's core. This dataset constrains the density-velocity mismatch with a full P-T grid and provides a self-consistent binary reference for ongoing work on ternary Fe-S-X systems.

INTRODUCTION

The most direct information about Earth's outer core (density and sound velocity for instance) comes from global seismic studies and radial velocity profile range, notably those in their Preliminary Reference Earth Model (PREM)¹ and the AK135-F model².

The outer core is the second innermost layer of the Earth, after the inner core. Different studies indicate that: 1) the outer core is liquid, 2) its mass density increases with depth from ~ 9.9 to $\sim 12.2 \text{ Mg/m}^3$ between 2900 km and 5146 km³, and 3) the inner and outer core (solid and liquid respectively) at the inner-outer core boundary or IOCB exhibits a density difference of $\Delta \rho \approx 0.85 \text{ Mg/m}^3$ ⁴. Taking into consideration these different properties, Fe is the main element present in the core, with an estimated $\sim 10 \text{ wt}\%$ additional amount of light elements. This is used to explain the density of the liquid outer core, which is substantially lower than that of pure iron^{5,6,7,8,9}. The presence of light elements such as carbon (C), hydrogen (H), oxygen (O), sulfur (S) and silicon (Si) has been suggested, based on their abundance in the solar system and their affinity with the metallic phase.^{10,11,12,13} Among these elements, S is a leading candidate as an important light element in the core, because it is a siderophile and moderately volatile element.^{14,15} However, the exact composition of the Earth's core is currently unknown.

To elucidate the most satisfactory concentration of these elements, experimental techniques such as Laser-Heated Diamond Anvil Cell (LH-DAC) and shock-wave experiments (SW) at pressures and temperatures between 130–330 GPa and 3000–6000 K respectively. Using these methods, any authors reproduced results of density and sound velocity (ρ , v_p) for concentrations of S in the range of 5 to 14 wt%S.^{16,17,18}

Besides geophysical observations, geochemical imprint of the early planetary metal-silicate differentiation have been used as a tool to understand the composition of Earth's core and it is an ongoing topic of scientific discussions.^{19,20,21,22,23} Previous studies by Dreibus¹⁹ proposed a sulfur content of 1.7wt% in the core, while more recent work by Mahan²⁴ constrained this value to 6.3 wt%S when the pressure dependence of Zn partitioning between metal and silicate is considered. Zinc, a moderately volatile element, has been used as an indicator of volatile depletion and evaporation in planetary materials. However, emerging research suggests that a fraction of the zinc budget in differentiated planetary bodies, including Earth, may reside in the core due to its slight affinity for the metallic phase, particularly at high temperatures.²³

Complementary to experimental works, the use of computational modelling methods allows materials properties to be studied at pressure and temperature conditions relevant to the core.^{25,26,27,28} Among the most common methods are those based on density functional theory (DFT) and *ab initio* molecular dynamics (AIMD), which have facilitated the study of Fe-S liquid alloys at core conditions.^{29,30,31,32} Using AIMD methods, Umemoto³² asserted that a concentration of 14.4 wt%S reproduces the values of (ρ , v_p) given by PREM for the liquid outer core. Badro et al.³¹ performed AIMD calculations at conditions of the IOCB suggesting a concentration of 10.3 wt%S in the outer core. Finally, Umemoto et al.³³ found that ~ 13-15wt%S with other light elements such as ~ 0.8-1.1wt%H, ~ 8-10wt%O, or ~ 9-11wt%Si, that reproduce the values of (ρ , v_p) of the liquid outer core. While the experimental and theoretical estimates for sulfur content yield IOCB values comparable to the PREM model, inconsistencies remain between the two approaches, as detailed in the Supplementary Information (SI).

Several theoretical and experimental studies have investigated the mechanical, structural, and thermodynamic properties of pure iron and its alloys.^{15,16,34,35} Using AIMD methods, Ichikawa et al.^{28,36}, Fu et al.³⁷ and Xu et al.³⁸ studied the density and sound velocity of Fe-S alloys under outer core conditions and also proposed an adiabatic temperature profile. However, to the best of our knowledge, previous AIMD studies of Fe-S liquid alloys have focused primarily on the equation of state and PREM comparison, without providing a systematic characterization of the atomic-scale structural and dynamical properties – including radial distribution functions, coordination numbers, diffusion coefficients, and viscosity – as a function of S concentration across the full outer core P-T range. Such a characterization is essential for understanding the microscopic origin of the density and velocity anomalies attributed to light element incorporation, and for constraining transport properties relevant to core dynamics.

In this context, we aim to use AIMD computational methods to systematically investigate the change of energy (E) - pressure (P) - volume (V) - Temperature (T) for Fe-S liquid alloys with S concentrations ranging from 0 to 14.9 wt%S under the pressure and temperature conditions of the Earth's outer core. Our work is intended to understand the effect that pressure and S concentration have on the structural, dynamics and thermal properties of these alloys, providing a systematic dataset that is directly transferable to more complex, multicomponent liquid metal systems. We establish thermal equations of state (EoS) for these Fe-S alloys and calculate thermodynamical properties, as well as density and sound velocity profiles.

These properties allow us to constrain the amount of S present in the outer core that agrees with the values reported by PREM. This binary dataset also provides a self-consistent reference baseline for the growing body of work on ternary Fe-S-X systems. The composition of the outer core is of relevance for building geophysical and geochemical models for the understanding of the Earth's core.

RESULTS

Dynamical and Structural properties of Fe-S alloys

The effects of sulphur incorporation on the structural properties of Fe-S liquid alloys can be illustrated in the partial radial distribution functions (RDF) at IOCB conditions, as shown in Fig. 1a. It can be seen that the incorporation of S from 0 wt% to 14.9 wt% S, carries several effects within the liquid structure. Firstly, an increase in S concentration causes the average Fe-S distance decrease from 2.1 to 1.9 Å when concentration is increased to its maximum of 14.9wt% S (see Fig. 1a). This distance reduction is related to the tendency of the Fe-S bond to be more covalent than the Fe-Fe bond leading therefore, to shorter Fe-S bond distances.^{39,40} The average distance values reported in this work are comparable with the values for $d_{\text{Fe-Fe}} = 2.08 \text{ Å}$ and $d_{\text{Fe-S}} = 1.94 \text{ Å}$ ¹⁶ at similar core conditions. Furthermore, because S is lighter than Fe and the substitution produces little change in liquid volume, replacing Fe with S is expected to lower the mass density, favouring an increase in P wave velocity as will be shown later. Additionally, the substitution of Fe by S atoms in the alloy has the consequence of decrease (increase) the $C_{\text{Fe-Fe}}$ ($C_{\text{Fe-S}}$) partial coordination number as seen in Fig. 1b. However, the total coordination given by $C_{\text{Fe-Fe}} + C_{\text{Fe-S}}$ remains almost constant, suggesting that S atoms substitute readily by Fe atoms within the molten system. Calculations for the Fe-Fe and Fe-S partial RDFs, as well as the total radial distribution function, can be found in the Supplementary Information (SI).

The effect of pressure on partial RDFs is smaller than that due to the concentration of S (see Fig. 1a and Fig. 1b), where the Fe-S average bond distance decreases with pressure while the coordination number increases. The average bond distance changes by approximately 3% with increasing pressure in the Fe-S radial distribution functions at the highest studied concentration. Furthermore, the effect of pressure is weaker compared to that of the S concentration. The diffusion properties of ions in the liquid system are detailed in the Supplementary Information.

Equation of State for FeS liquid

In Table 1 we show the fitted parameters obtained for several $\text{Fe}_{1-x}\text{S}_x$ alloys at a reference condition of 0 GPa and 7000 K³⁴. The linear increase from 1.37 to 1.43 of γ with S concentration has been suggested previously for these alloys^{35,45} and it might be due to a change of vibrational properties on the structure with the presence of S⁴⁶. The P, V data set of liquid $\text{Fe}_{1-x}\text{S}_x$ was used to analyse the EoS between 4000K and 7000K (Fig. 2). To obtain the EoS, only data from systems that remained liquid at a given P and V

were used. This was controlled by monitoring the simulation through the estimation of the MSD. In addition, we have used the melting curve of pure iron reported by Alfè *et al*^{26,14} as a reference.

Table 1
Fitted parameters for the E_{th} -P-V-T relationship obtained from AIMD calculations and the model discussed using equations (1) to (5)

Parameters	Fe ³⁴	Fe-pure	8.6wt%S	10.6wt%S	14.9wt%S
$V_o \left(\backslash \text{AA}^3 / atom \right)$	17.87	16.74	17.97	18.24	18.93
$K_{T_o} (GPa)$	24.6	24.46	18.00	17.00	14.75
γ_o	6.65	6.64	6.65	6.65	6.66
a	1	1.00	0.99	1.00	1.10
b	0.35	0.33	0.4149	0.4149	0.4
e_o	3.14×10^{-5}	1.90×10^{-5}	3.5×10^{-5}	4.00×10^{-5}	5.00×10^{-5}
g	-0.4	-0.44	-0.4	-0.44	-0.444

Thermodynamic properties for Fe-S liquid alloys

The thermodynamic properties of liquid Fe-S alloys, including density and isothermal bulk modulus obtained from the EoS are shown in Figs. 3 and 4, and Grüneisen parameter, thermal expansion coefficient, and isobaric heat capacity in Supplementary information. We first compare our isothermal density results for pure Fe (see Fig. 3a) with those from previous experimental and theoretical works. The density of our liquid iron at a pressure of 260 GPa and ~ 6000K, is 12.30 Mg/m³ close to the values of 12.46 Mg/m³³⁴ and 12.30 Mg/m³³⁷. This highlighting the strong agreement of our density results, showing deviation ranging from 0% to 1.3% compared to these findings under similar temperature and pressure conditions. This good agreement demonstrates that the methodology by Ichikawa *et al*³⁴ initially used for Fe melts and implemented here for FeS liquid alloys to obtain the P-V-T equation of state, is appropriate for studying the composition of the Earth's core. The isothermal densities in Fig. 3 also show as a general trend that the density decreases with increasing temperature and S content, this is consistent

with the previous results found^{17,32,33,37}. Our findings for iron and sulphur alloys provide several conclusions. Our concentration of 14.9 wt%S (see Fig. 3d) exhibits lower density values compared to PREM, in contrast to the results presented by Umemoto *et al*^{32,33}. On the other hand, a concentration close to 10.6 wt%S is found (see Fig. 3c), following the approaches of Badro *et al*³¹ that reproduce the density of the liquid core at a temperature above 6000 K. However, this does not provide a comprehensive explanation for the composition of the outer core, as this temperature does not align with the hypothesis of a temperature above 5000 K suggested by other authors for the Inner Core Boundary (ICB)^{15,16}. Our results give a concentration close to 10.6 wt%S as the most likely to reproduce the PREM data.

The calculated K_T are displayed in Fig. 4. In the case of pure Fe, these values are consistent with those reported in previous literature.^{6,8,47}

We can use the information obtained above in order to calculate isentropic equations of state, which allow for the comparison of our results with the geophysical profile of the outer core¹. In order to obtain isentropic equations of state from our work, we have used the same methodology described by Ichikawa *et al*³⁴ and the geothermal profile.^{26,48,49,50,51} Using this methodology, we found a Grüneisen parameter for pure Fe at 0 GPa of $\gamma = 1.9$ (Table 1), which is comparable with the values of 1.52–1.38^{16,34}. Furthermore, our model shows that an addition of sulphur from 0 wt%S to 14.9 wt%S leads to a ~ 6% change in the Grüneisen parameter for pressures in the range of the outer core, which suggests that this parameter is weakly dependent on the S content. (See SI)

The derivative functions of the EoS are obtained using the thermodynamic definitions of

$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{K_T}{V}$ for the isothermal bulk modulus and $K_S = (1 + \alpha \gamma T)K_T$ for the adiabatic bulk modulus where α is the thermal expansivity coefficient as a function of pressure (See SI).

We notice an increase in the thermal expansivity coefficient as a function of temperature. However, no significant changes can be observed as a function of composition for the alloys studied. Under the conditions of the IOCB, finding values ranging from $0.7 \times 10^{-5} K^{-1}$ for pure Fe to $1.4 \times 10^{-5} K^{-1}$ for a FeS alloy with a maximum S concentration of 14.9 wt%S. These values are in the lines with previous works on pure Fe, which reported values of $1.05 \times 10^{-5} K^{-1}$ ³⁴ and $1.0 \times 10^{-5} K^{-1}$ ⁶. Furthermore, LH-DAC experiments at 202GPa and 5200K indicate an average value of $9.13 \times 10^{-6} K^{-1}$ ⁶ for pure Fe, which is lower than the values obtained in this work.

The isobaric heat capacity (See SI) can be obtained from the expression $C_P = C_V (1 + \alpha \gamma T)$ where

$C_V = \left(\frac{\partial E_{th}}{\partial T}\right)_V$ is the isochoric heat capacity. C_p increases with temperature and concentration. In particular, there is a $5 - 7 J / (K \bullet mol)$ rise in C_p between pure iron and an alloy containing 8.6 wt% of S. This behaviour helps the core to retain heat, maintaining the core in a liquid state.

DISCUSSION

Compressional sound velocity (also called P wave velocity) in a liquid state is defined as:

$$v_p = \sqrt{\frac{(1+\alpha \gamma T)K_T}{\rho}} \quad (1).$$

The results of Eq. (1) are shown in Fig. 5. From these results we can see that at conditions of the CMB and IOCB our model shows a maximum rise in sound velocity of 6% when the S concentration is increased to 14.9wt%S. This small effect of the concentration on the sound velocity can be explained by the low concentration and small effect of S on the vibrational properties of these alloys at high pressure. The behaviour of v_p as a function of S concentration follows a linear trend where the velocity increases as S content within the melt increases and in good agreement with the model proposed by Badro *et al.*⁵² and that can be written as:

$$v_p = \frac{v_{Fe}v_{Fe-S}}{(1-x)v_{Fe}+x \bullet v_{Fe-S}} \quad (2),$$

where x is the Fe volume fraction. Additionally, we illustrate the behaviour of mass density as a function of S concentration. Our results show a linear relationship, similar to the one suggested by Badro *et al.*⁵². For this, we used a relationship that incorporates the linear terms from the relation proposed by Morard *et al.* (2018) but now for high-pressure systems, and it follows the form:

$$\rho_o(X_s) = \rho_{Fe-o} + C \bullet X_s$$

3

where X_s represents the S concentration ranging from $0 \leq X_s \leq 14.9wt\%S$, ρ_{Fe-o} is the pure iron mass density, C is constant. A fitting of Eq. (3) using the data displayed in Fig. 6a yields a $C = -0.0841 \text{ Mg/m}^3 \bullet (wt\%S)^2$. When comparing with the PREM density on the liquid side of the IOCB, it is observed that the concentration of S has a value between $\sim 10.2 \text{ wt\%S}$ and $\sim 11.4 \text{ wt\%S}$, and temperatures in the range of 6000K and 5000K, consistent with the studies by Huang *et al.*¹⁷. This S concentration reproduces the composition of the IOCB under conditions close temperature of 4850 K⁴⁸ and 5400 K⁴⁹. In the event that the hypothetical temperature of the IOCB is close to 7000 K, the concentration of S must not be lower than $\sim 8.7wt\%S$.

The adiabatic profile along the geotherm is given by $T = T_{ICB} \left(\frac{\rho}{\rho_{ICB}} \right)^\gamma$ where T_{ICB} and ρ_{ICB} are the temperature and density at the conditions of the outer-inner core boundary, ρ and γ the density and Grüneisen parameter obtained from the analysis used for the EoS. It is clear that the adiabatic profile depends on the values of T_{ICB} taken as a reference. Figure 6b shows an adiabatic density profile taken at several T_{ICB} values of reference (4850, 5400, 6350 and 7100 K). Using this information, we can predict the most likely S concentration at the T_{ICB} used. Our calculations show that at a $T_{ICB} = 4850 \text{ K}$ the corresponding S concentration to match the values reported by PREM for their density profile is 11.5 wt%. With $T_{ICB} = 5400 \text{ K}$ it is 10.8 wt%S and with 6350 K and 7100 K, these values are 9.6 wt%S and 8.6 wt% respectively.

We have used these values to obtain the density and sound velocity profiles along the geotherm as shown in Fig. 6c and 6d. Reference values show that a concentration between $\sim 8.6\text{wt}\%S$ and $\sim 10.6\text{wt}\%S$ are most in agreement with PREM. However, since the results for this concentration cannot match density and sound velocity results simultaneously, it suggests that a third element should be present in the core. Recent work investigated the concentration of light elements, including oxygen (O) and magnesium (Mg), in binary alloys with Fe^{38,53}. These results provide a relevant reference framework for subsequent modelling and analysis of ternary alloy systems. The presence of ternary alloys has been previously suggested, with elements such as O and Si proposed as potential light components in the core alongside S^{33,43,54}. Recently, values of 9.0 wt%Si and 3.0 wt%Si must be present as a third element in the outer core to match the PREM results¹⁷. In addition to ternary systems, not much is said about the possibility of having metal alloys composed of Fe-Si-S-O, and further studies to determine sound velocity and density of these systems are needed.

METHODS

The calculations in this work are based on density functional theory as implemented in the VASP code developed by Kresse *et al.*^{55,56}. The exchange and correlation energy contributions have been represented using the generalized-gradient-approximation (GGA) approach in the version for solids (called PBE-sol)⁵⁷. The electronic wave functions were expanded on a plane wave basis with a maximum cutoff energy of 520 eV, which guarantees convergence in energy and forces up to 2 meV and 1 meV/Å-atom respectively (see SI for information on convergence tests). Pseudopotentials of the projector augmented wave type were used for Fe and S, with an electronic configuration of valence states $3s^23p^63d^64s^2$ and $3s^23p^4$, respectively^{55,58}. Sampling in the Brillouin zone was performed at Γ point.

To determine the P-V-T EoS of Fe-S liquid alloys, the total internal energy (E) and total pressure (P) we use the methodology proposed by Ichikawa *et al.*³⁴. AIMD calculations are performed within the NPT ensemble using a Nosé-Poincaré thermostat⁵⁹ and a Parrinello-Raman barostat⁶⁰. All systems were thermodynamically equilibrated at outer core pressure conditions (130–330 GPa) and temperatures of 4000 K, 5000 K, 6000 K and 7000 K for a minimum time of 2 ps, which has been shown to be enough to obtain thermal equilibration in these molten alloys⁴⁶. Production runs were performed in an NVT ensemble for all studied concentrations at volumes and temperatures displayed in Table 2, using a Nosé-Hoover thermostat^{61,62} for a total of at least 10 ps. All molecular dynamics calculations were carried out using 128 atoms systems and with an integration timestep of 1 fs. Magnetic effects are negligible at the pressure and temperature conditions of this work and therefore were not included in the calculations⁴⁶.

Table 2
Obtained pressure values (in GPa) for the set of ab-initio calculations performed in this work at a given temperature and volume. * Correspond to P–V calculations in which the system was found to be non-liquid and were therefore excluded from the estimation of the equation of state (EoS) properties.

Pure Iron					
V (Å ³ /atom)	7.03	7.42	7.81	8.20	8.59
T(K)					
4000	269.7*	208.9*	168.6*	135.11*	106.8*
5000	273.7*	226.4*	182.8*	146.2*	115.5
6000	297.7	239.2	191.7	154.2	123.3
7000	309.3	249.3	200.48	162.4	130.9
Fe – 8.6wt%S					
4000K	261.4	209.7	171.5	135.9	107.9
5000K	274.9	227.8	182.6	145.4	116.7
6000K	295.5	237.7	191.2	154.5	125.4
7000K	305.5	246.6	199.6	162.8	132.2
Fe – 10.6wt%S					
4000K	273.4	216.5	171.5	136.9	108.2
5000K	284.1	226.9	182.3	146.3	117.4
6000K	294.8	236.8	191.2	154.9	125.0
7000K	305.1	245.9	200.4	163.8	133.2
Fe – 14.9wt%S					
4000K	274.5	217.1	172.7	137.9	110.2
5000K	285.7	227.5	182.8	147.0	119.2
6000K	297.2	238.0	192.8	157.4	128.3
7000K	304.9	247.5	202.1	164.9	136.2

We have computed the pure iron endmember (Fe₁₂₈) and have selected the following concentrations for the Fe-S alloy systems: 8.6 wt%S (Fe₁₁₀S₁₈), 10.6 wt%S (Fe₁₀₆S₂₂), and 14.9 wt%S (Fe₉₈S₃₀). The selection of these concentrations has been based on estimates of the maximum range of S content in Earth's core.^{1,2,15,16,17,31,32,63} To check for size effects and structural properties convergence, we have compared results to calculations using supercells of 256 atoms at the same P and T conditions obtaining similar

results. For all calculations, we verified that the system remains in a liquid state over the entire duration of the simulation by calculating the mean square displacement (MSD) $\langle r^2(t) \rangle = \langle r_f^2(t_f) - r_i^2(t_i) \rangle$. MSD slopes were used to estimate diffusion coefficients. Only P-V data corresponding to liquid alloys were considered for the equation-of-state analysis, excluding simulations in which crystallization or the formation of frozen structures occurred at any point during the simulation time.

Pressure variation as a function of density for each S concentration and several isotherms, was studied by calculating the E-P-V-T relationship using a Mie-Grüneisen Model⁶⁴:

$$P(\rho[V], T) = P_{T_o}(\rho[V]) + \Delta P_{th}(\rho[V], T),$$

4

where the total pressure is the sum of the pressure at a reference temperature $P_{T_o}(\rho[V])$ plus a contribution, $\Delta P_{th}(\rho[V], T)$, depending only on temperature. The third order Birch-Murnaghan equation of state (EOS) was used to fit the data for each isotherm:

$$P(\rho[V]) = \frac{3K_{oT}}{2} \left[\left(\frac{\rho}{\rho_{oT}} \right)^{\frac{7}{3}} - \left(\frac{\rho}{\rho_{oT}} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} (K'_{oT} - 4) \left[\left(\frac{\rho}{\rho_{oT}} \right)^{\frac{2}{3}} - 1 \right] \right\},$$

5

where K_{oT} is the isothermal bulk modulus, K'_{oT} is the first derivative as a function of pressure, and ρ_{oT} is the isothermal density, all at $P = 0$.

The thermal pressure $\Delta P_{th}(\rho[V], T)$ can be expressed by the variation of the internal thermal energy ΔE_{th} between T and T_o ⁶⁵:

$$\Delta P_{th}(\rho[V], T) = \frac{\gamma(V)}{V} \Delta E_{th}(V, T),$$

6

where $\gamma(V)$ is the total Grüneisen parameter and ΔE_{th} the variation of the internal thermal energy. These two quantities can be obtained from our calculations using the expressions³⁴:

$$\gamma(V) = \gamma_o \left\{ 1 + a \left[\left(\frac{V}{V_o} \right)^b - 1 \right] \right\}$$

7

and

$$\Delta E_{th}(V, T) = 3nR \left[(T - T_o) + e_o \left(\frac{V}{V_o} \right)^g (T^2 - T_o^2) \right],$$

8

where n is the number of atoms per formula unit and R is the constant for the ideal gases. These equations require the knowledge of six parameters (V_o , K_{T_o} , K'_{T_o} , γ_o , a , b , e_o , and g) to be estimated. We use as a reference temperature the lowest temperature ($T_o = 4000$ K) to constrain the reference isothermal as tightly as possible in the broad P-T range.

The use of the methodology of Ichikawa *et al.*³⁴ in this work allows the calculation of total internal energy, total pressure, and temperature through AIMD, and the acquisition of fitting constants associated with EOS and second-order polynomials. This enables the calculation of thermodynamic properties such as thermal expansivity, Grüneisen parameter, and adiabatic bulk modulus, which are difficult to obtain using other methods.

The fitting carried out using an EOS model derived from our results and including a variation on the bulk modulus enables to describe the liquid density behaviour at different S concentration and to the values of sound velocity under the same P and T conditions. With this information, the S concentration best approximating the observations of global seismic tomography can be established.

CONCLUSIONS

We have used computer modelling methods to study the effect of S on the structural and dynamical properties of Fe-S alloys under the pressure and temperature conditions of the outer core of the Earth, providing a systematic atomic-scale dataset across the full outer core P-T range. Increasing the sulphur concentration in the iron liquid alloy gradually increases the number of S atoms in the first solvation shell of Fe and, therefore, the number of more covalent Fe-S bonds. These modifications affect the structural properties of the materials. However, the diffusion coefficients of iron and sulphur show no dependence on concentration but a strong dependence on pressure. Our results indicate that an Fe-S alloy with a sulphur concentration of between ~ 10.2 wt%S to ~ 11.4 wt%S show close densities to the PREM model, over the entire pressure range of the outer core of the Earth. This finding falls in the range of previous theoretical estimations (i.e. 10.3 wt%S and 14.4 wt%S)^{31,34} and is relatively close to the experimental estimate of 10.8 wt%S.¹⁷ However, the sulphur concentration is not consistent with the PREM sound velocities at the bottom of the Earth's outer core at this concentration and much lower sulphur concentrations (lower than 8.6 wt%S) would be needed to mimic the sound velocity of the PREM model. Future work accounting for the presence of other light elements would be needed to discuss the hypothesis of a stratified outer core, for which the present binary dataset provides a self-consistent reference baseline.

Declarations

Author Contribution

A.D.M. and C.P. designed the study, I.C. and A.D.M. carried out the simulations, A.D.M., A.M.E., M.B., G.M. and C.P. analyzed and discussed results. A.D.M and C.P, wrote the manuscript. All authors reviewed the manuscript.

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Data Availability

All data supporting the findings of this study are available within the paper and its Supplementary Information.

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Figures

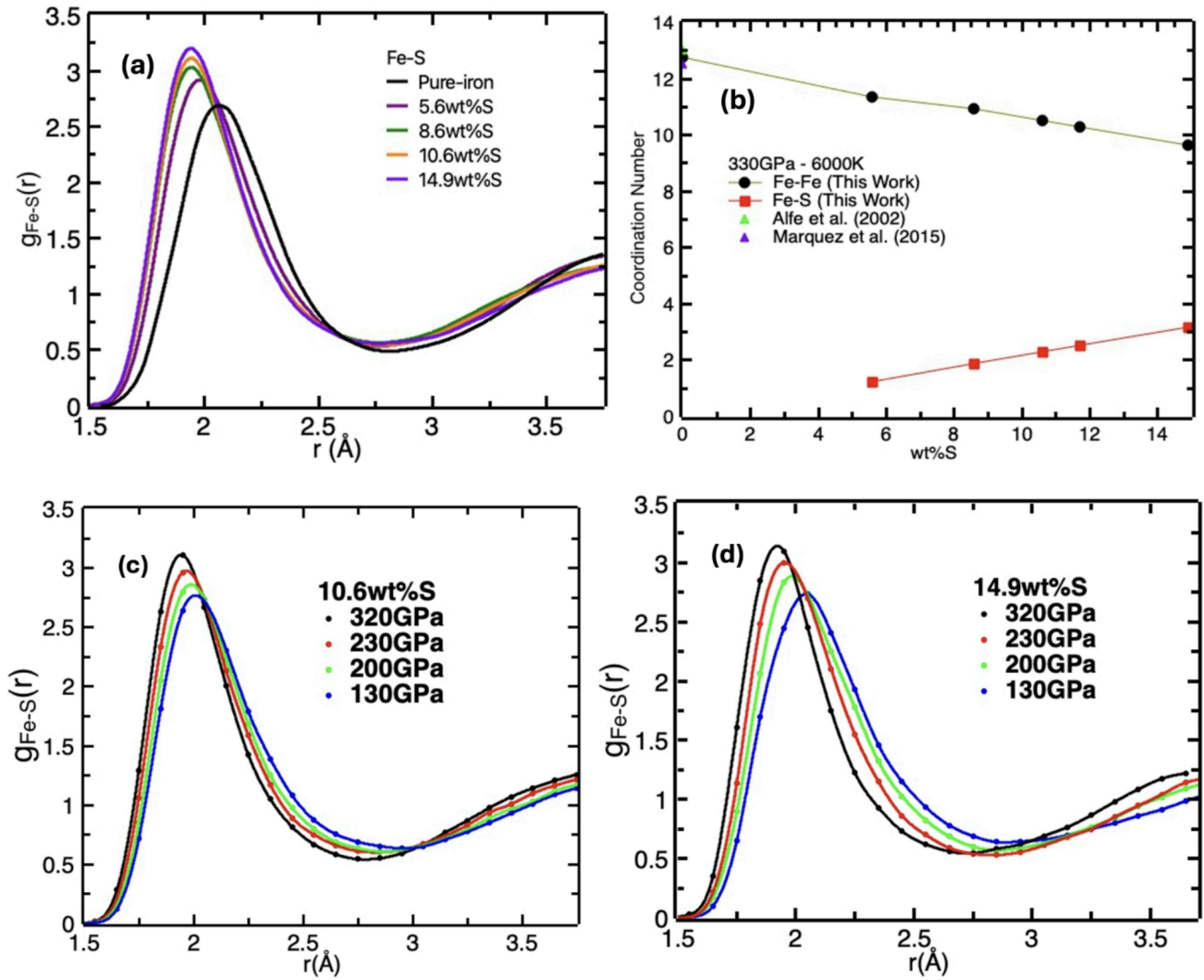


Figure 1

a) Partial radial distribution functions for all the studied alloys at 330 GPa and 6000 K. b) Fe-Fe and Fe-S atomic coordination number for all the studied alloys as a function of sulfur concentration at IOCB conditions (330 GPa, 6000 K). Upper triangles correspond to pure iron theoretical studies^{14,67} at IOCB conditions. c) Effect of pressure on the FeS alloys structure: correspond to the radial distribution function for Fe-S at concentration of 10.6 wt%S at 6000 K. d) 14.9 wt%S, at 6000 K.

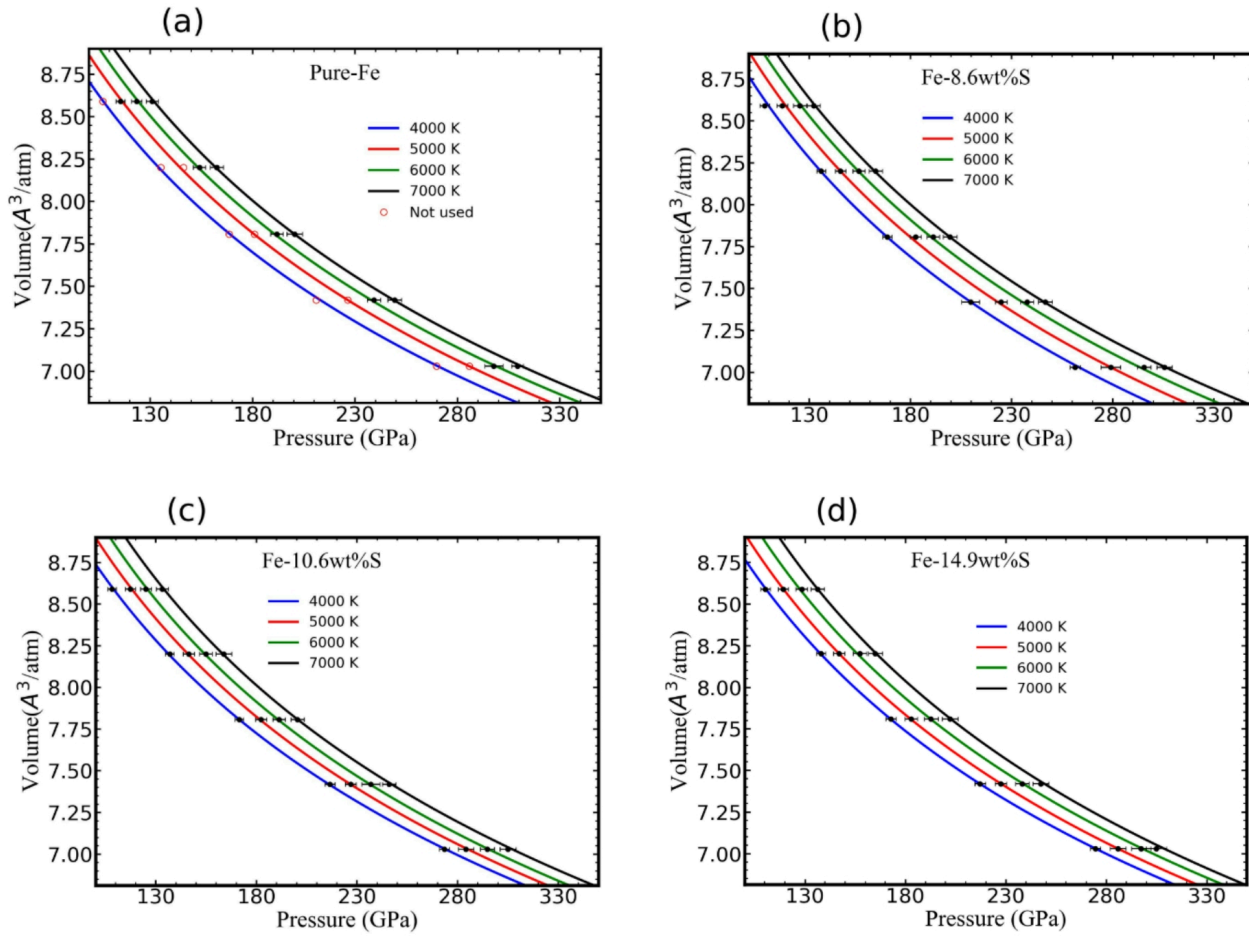


Figure 2

EOS of P-V-T data of iron, 8.6wt%S, 10.6wt%S and 14.9wt%S liquid at core's conditions between 130 at 330 GPa and 4000K at 7000K obtained from AIMD. Filled black circles and open red circles represent, respectively, the P and T conditions above and below the melting temperature of each alloy.

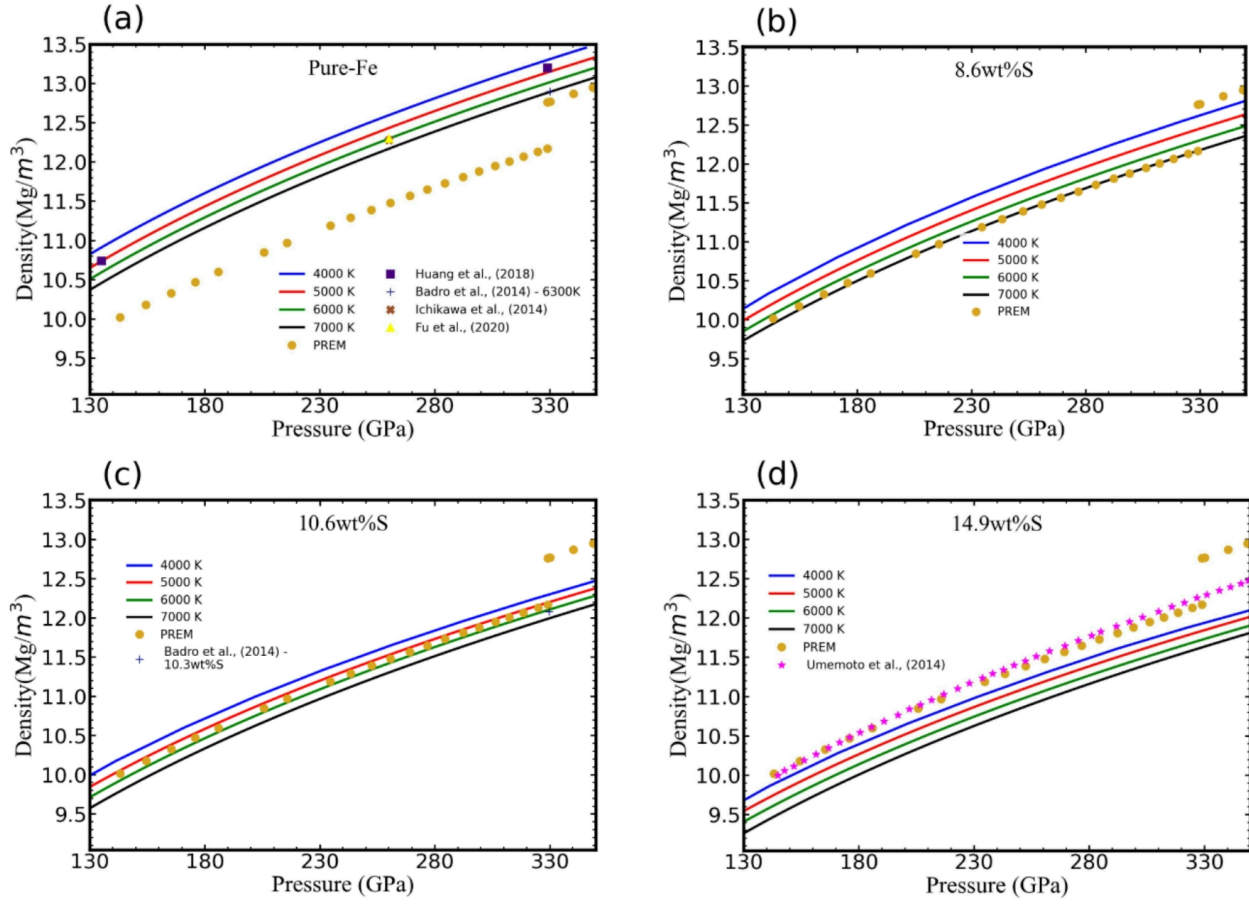


Figure 3

Mass density of Fe-S alloys as a function of pressure for S concentrations of 0wt%S, 8.6wt%S, 10.6wt%S and 14.9wt%S. Comparison data taken at 6000 K³², 6150 K¹⁷ and ranging between 4300 K and 6300 K³¹ are included when available.

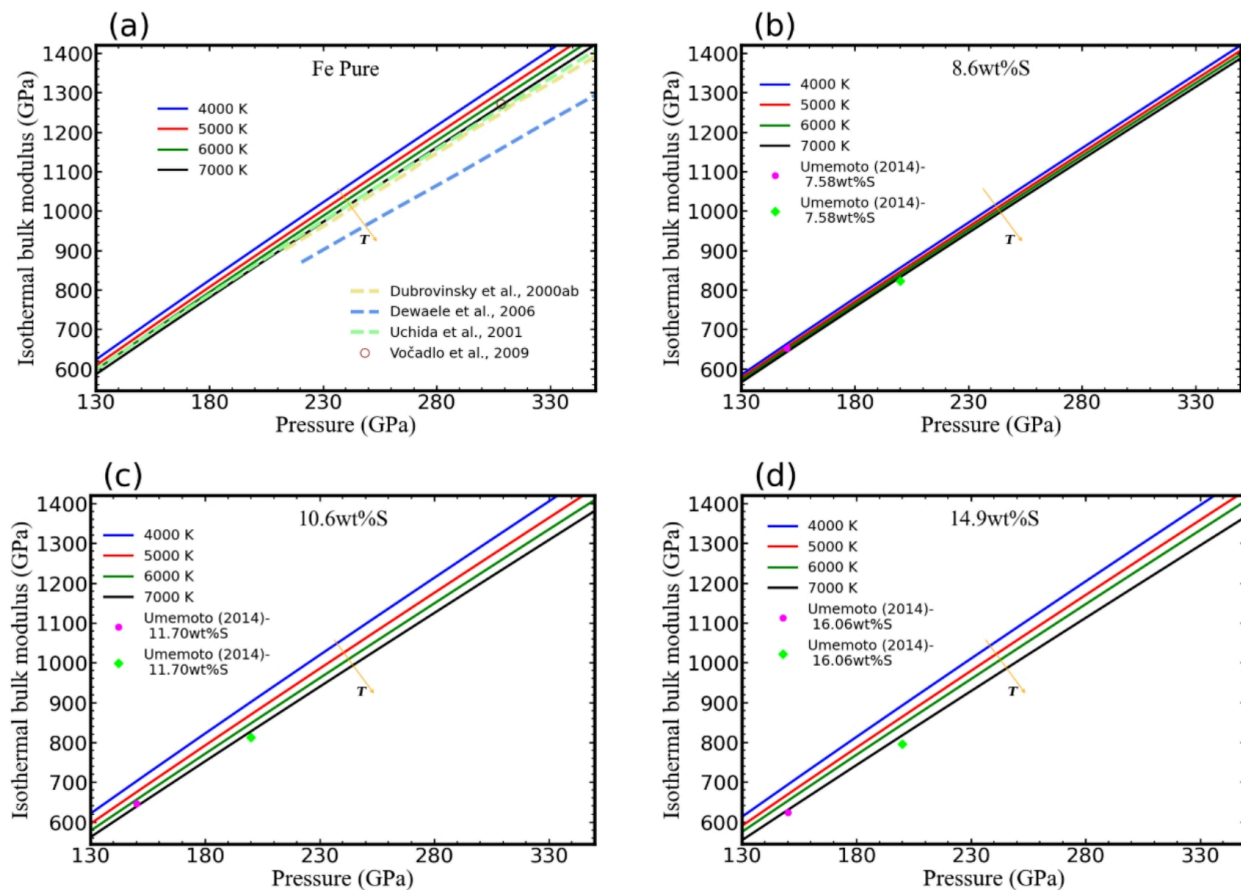


Figure 4

Isothermal Bulk modulus of Fe-S alloys as a function of pressure and temperature for 0wt%S, 8.6wt%S, 10.6wt%S and 14.9wt%S.

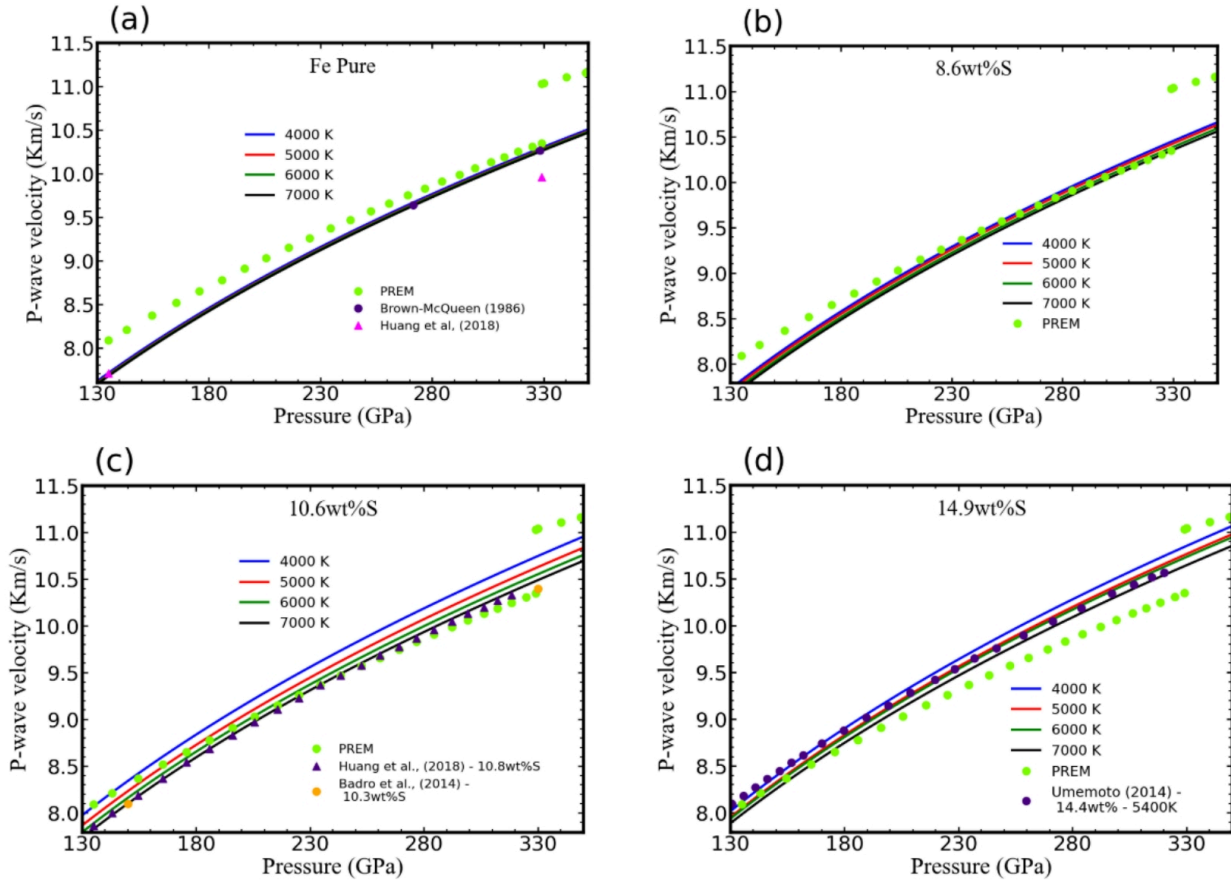


Figure 5

Sound velocity (v_p) of Fe-S alloys as a function of pressure for 0wt%S, 8.6wt%S, 10.6wt%S and 14.9wt%S.

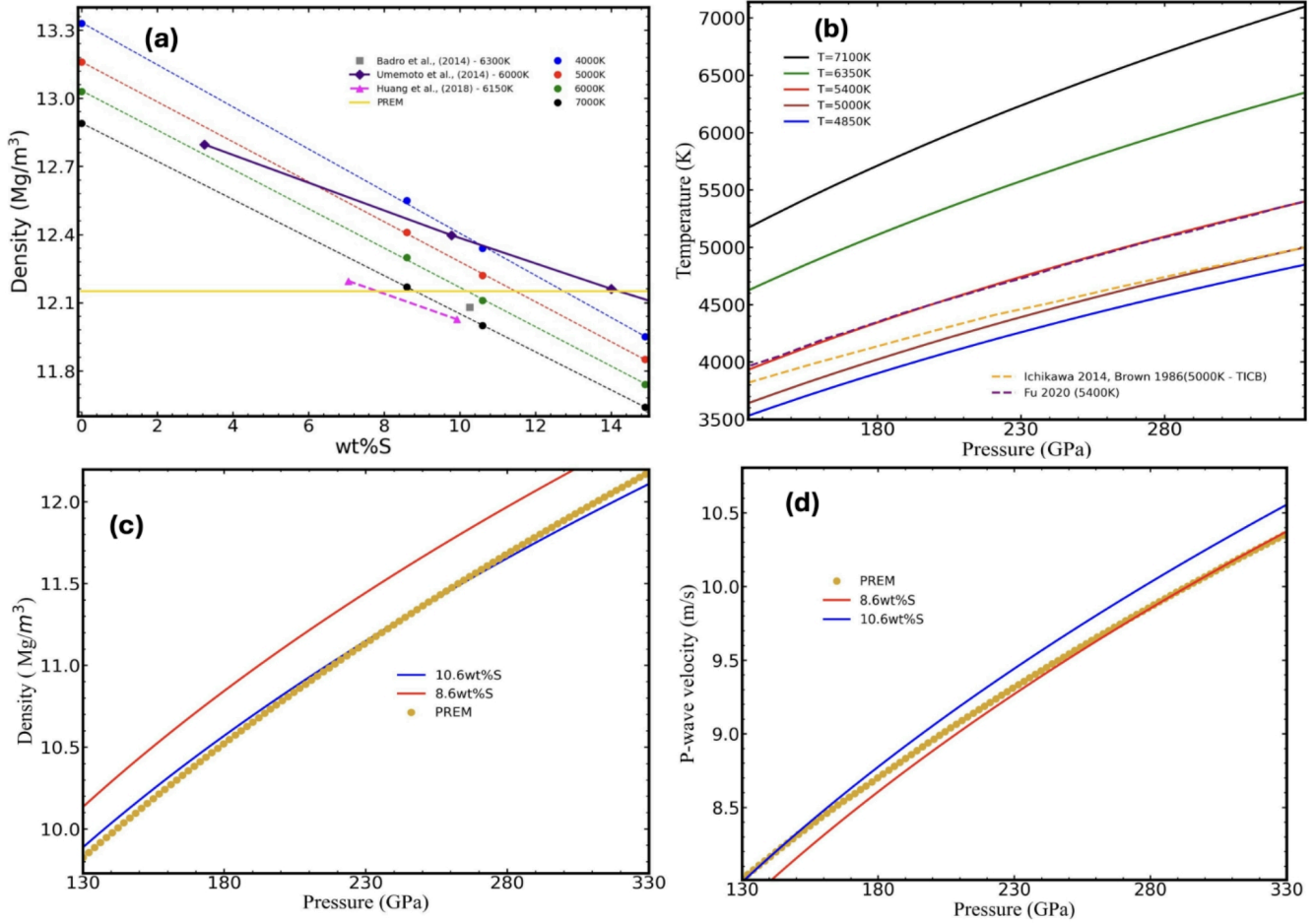


Figure 6

a) Density curves fitted for different sulfur concentrations and different temperature at IOCB pressure. This work is compared to previous experimental¹⁷ and theoretical results^{31,32} as well as the PREM model. b) Adiabatic temperature profile in the outer core. To obtain these results, we have used the expression , with reference temperatures (T_{IOCB}) corresponding to the results of previous works such as 4850 K⁴⁸, 5000 K³⁴, 5400 K^{37,49}, 6350 K^{26,50}, and 7100 K⁵¹. Our geotherms were obtained using variable Grüneisen modulus values with pressure, behaved similarly to the curves of the cited authors, except for a slight discrepancy at pressures close to the CMB. c) Adiabatic density of the 8.6wt%S and 10.6 wt%S alloy along the geotherm, obtained from a thermal correction to the isothermal EoS. It can be observed that our concentration of 10.6wt%S largely reproduce the density of the outer core from the CMB to the IOCB. However, in d) an 10.6wt%S concentration does not fully reproduce the sound velocity along PREM, indicating that an Fe-S alloy does not completely explain the composition of the Earth's outer core.

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