Supporting Information for

Density and sound velocity of liquid Fe–S alloys at Earth's outer core conditions

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Text S1. The accuracy of Murnaghan EOS

The accuracy of Murnaghan (M) EOS is tested by comparison with third-order Birch-Murnaghan (3^{rd}-BM) (Murnaghan 1944; Birch 1947) and Vinet (V) EOS (Rose et al. 1983; Vinet et al. 1987) (see Eq.S1 and Eq.S2). We find the isothermal density and bulk modulus of liquid Fe calculated using M, 3^{rd}-BM and V EOS are very close (see Fig.S1 and Fig.S2). Note that 3^{rd}-BM and V EOS are derived for solids. The fitted $K_{T_0}^{'}$ values of V EOS vary in large uncertainty up to 9.0 (see Table S), while the experimental $K_{T_0}^{'}$ values are approximately 4.0. Some works use $K_{T_0}^{'}=4$ directly in fitting. In this work, we chose Murnaghan EOS with simple format and high accuracy to describe the isothermal *P*–*V* relations. The $K_{T_0}^{'}$ takes a reasonable value between 3 and 4. The third-order Birch-Murnaghan EOS is expressed as (Murnaghan 1944; Birch 1947)

$$P=\frac{3}{2}K_{T_0}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}}-\left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left\{1+\frac{3}{4}\left(K_{T_0}^{'}-1\right)\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}}-1\right]\right\}, \quad (1)$$

while Vinet EOS is (Rose et al. 1983; Vinet et al. 1987)

$$P=3K_{T_0}\left(\frac{V}{V_0}\right)^{-\frac{2}{3}}\left[1-\left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right]\exp\left\{\frac{3}{2}\left(K_{T_0}^{'}-1\right)\left[1-\left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right]\right\}, \quad (2)$$

K_{T_0} is isothermal bulk modulus at zero pressure and temperature T_0, and $K_{T_0}^{'}$ is the derivative of K_{T_0} over pressure.

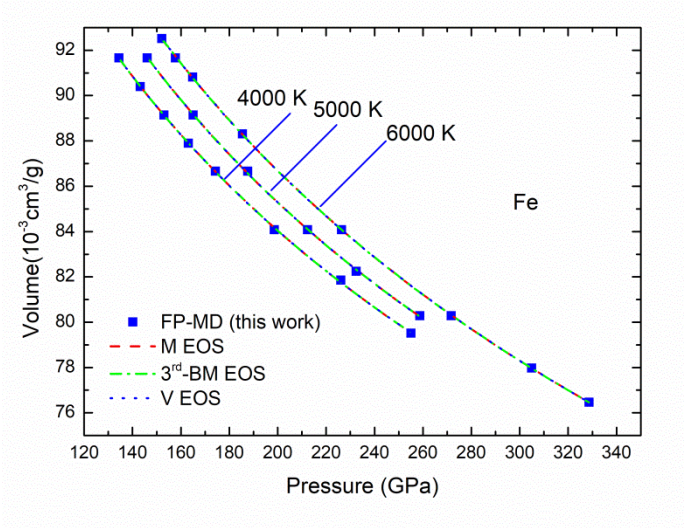

Fig. S1. The *P*–*V* relations from Murnaghan (M), third-order Birch-Murnaghan (3rd-BM) and Vinet (V) EOS. Symboles represents the *P*–*T*–*V* data from first-principles molecular dynamics (FP-MD) simulations.

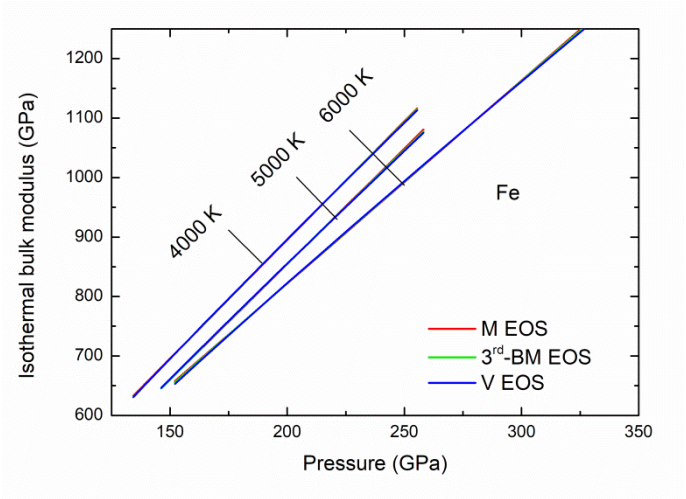

Fig. S2. The comparison of isothermal bulk modulus derived from Murnaghan (M), third-order Birch-Murnaghan (3rd-BM) and Vinet (V) EOS.

Table S1 The parameters of different EOS for liquid Fe–S alloys. M, 3rd-BM and V EOS represent Murnaghan, third-order Birch-Murnaghan and Vinet EOS, respectively.

	parameters	V_0 (10^{-3}cm^3/g)	K_{T0} (GPa)	K_{T0}'	e_0 (K^{-1})	g
M EOS	Fe	146.096	137.956	3.418	–6.19078110e–05	–1.98031245e–01
	Fe–5.5wt.%S ($Fe_{98}S_{10}$)	157.0206	117.791	3.458	–7.52390247e–05	1.57137821e–01
	Fe–11.5wt.%S ($Fe_{88}S_{20}$)	168.212	107.376	3.405	–7.16445460e–05	6.14492125e–02
	Fe–18.1wt.%S ($Fe_{78}S_{30}$)	191.730	75.145	3.463	–7.61060968e–05	1.46282058e–01
3rd-BM EOS	Fe	156.287	83.891	4.654	−6.16719151e−05	–1.81986834e–01
	Fe–5.5wt.%S ($Fe_{98}S_{10}$)	170.652	65.187,	4.801	−7.63012936e−05	1.58483633e−01
	Fe–11.5wt.%S ($Fe_{88}S_{20}$)	184.078	57.849	4.735	−7.11706581e−05	4.33988913e−02
	Fe–18.1wt.%S ($Fe_{78}S_{30}$)	224.381	28.021	5.127	−7.79706973e−05	1.47696297e−01
V EOS	Fe	180.022	29.730	6.709	−6.07089434e−05	−1.68489475e−01
	Fe–5.5wt.%S ($Fe_{98}S_{10}$)	206.037	17.028	7.166	−7.87508737e−05	1.60547774e−01
	Fe–11.5wt.%S ($Fe_{88}S_{20}$)	233.566	11.297	7.356	−7.19841049e−05	4.45033210e−02
	Fe–18.1wt.%S ($Fe_{78}S_{30}$)	339.859	1.735	8.664	−8.29881919e−05	1.48750884e−01

Note: the parameters fitted based on the reference temperature 6000 K, and γ = 1.5.

Text S2. The uncertainty of measured pressure

Block average method is a simple method to find the statistic errors in molecular dynamics simulations. After the simulation system has reached its equilibrium (Fig. S), we statistically average the pressure values from the start time to the end of the simulation to get the mean value $\langle A \rangle_{sim}$.

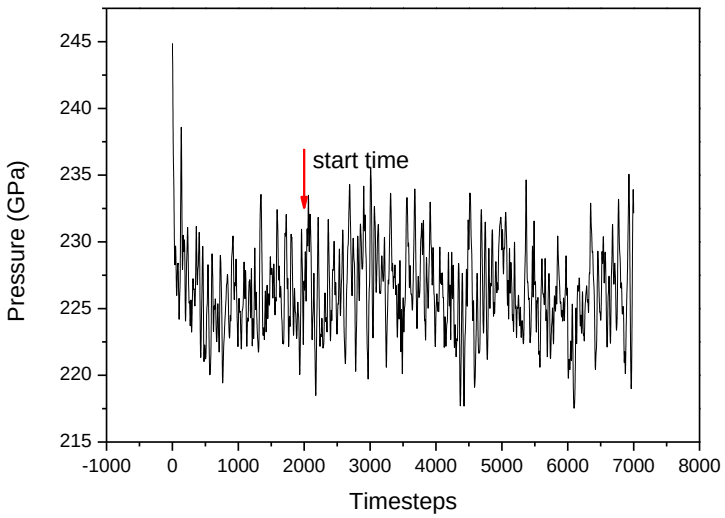

Fig. S3 Equilibration of MD data

Total timesteps M (from 2000 to 7000 step) are divided by n blocks with τ length, so $M = n\tau$. Average of each block is calculated by

$\langle A \rangle_b = \frac{1}{\tau} \sum_{i=1}^{\tau} (A_i - \langle A \rangle_{sim})^2$,

As the block length τ increased, block average is expected to be uncorrelated. In the limit,

$\sigma^2(\langle A \rangle_b) = \frac{1}{n} \sum_{i=1}^{n} (\langle A_b \rangle - \langle A \rangle_{sim})^2$.

The limit value for obtaining the statistic inefficacy can be calculated as

$s = \lim_{\tau \to \infty} \frac{\tau \sigma^2(\langle A \rangle_b)}{\sigma^2(A)}$, where $\sigma^2(A) = \frac{1}{M} \sum_{i=1}^{M} (A - \langle A \rangle_{sim})^2$.

When the limiting value s is found, the standard deviation of the obtained average $\langle A \rangle_{sim}$ can be calculated from

$\sigma(\langle A \rangle_{\mathrm{sim}}) \approx \sigma(\mathrm{A}) \sqrt{\frac{s}{M}}$, as displayed in Fig. S.

The uncertainty of pressure in this work is about 0.35 GPa.

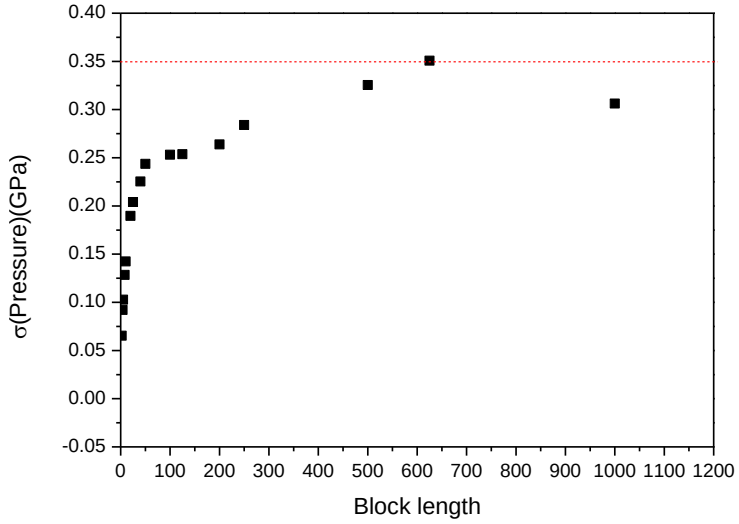

Fig. S4 Pressure uncertainty estimation for MD simulation

Text S3. The calculation of αK_T by first-principles MD method.

On the basis of *P–T–V* data from first-principles MD simulation, we calculate thermal expansion coefficient using the relation $\alpha K_T = \left(\frac{\partial P}{\partial T}\right)_V$. In this work, the calculated αK_T are listed in Table.S.

Table.S2 Calculated $\boldsymbol{\alpha K_T}$ using first-principles *P–T–V* data for Fe–S alloys.

T (K)	Fe (GPa/K)	$Fe_{98}S_{10}$ (GPa/K)	$Fe_{88}S_{20}$ (GPa/K)	$Fe_{78}S_{30}$ (GPa/K)
4000	0.011620	0.013281	0.013388	0.013603
5000	0.011668	0.012639	0.013324	0.012317
6000	0.011715	0.011997	0.013261	0.011030
7000	—	0.011354	0.013198	—

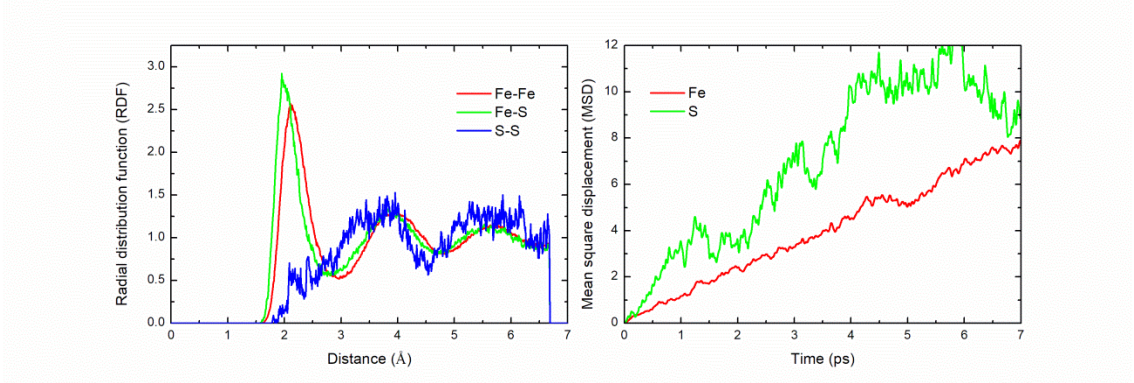

Fig. S5. The radial distribution functions (RDF) of Fe–Fe, Fe–S and S–S pairs and mean square displacement (MSD) of Fe, S atoms of liquid Fe–5.5 wt.% S at P = 222.5 GPa and T = 6000 K.

References

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