Density and sound velocity of liquid Fe-S alloys at Earth’s outer core $P$-$T$ conditions

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**Abstract**

Pressure-temperature-volume ($P$-$T$-$V$) data on liquid iron-sulfur (Fe-S) alloys at the Earth’s outer core conditions (~136 to 330 GPa, ~4000 to 7000 K) have been obtained by first-principles molecular dynamics simulations. We developed a thermal equation of state (EoS) composed of Murnaghan and Mie-Grüneisen-Debye expressions for liquid Fe-S alloys. The density and sound velocity are calculated and compared with Preliminary Reference Earth Model (PREM) to constrain the S concentration in the outer core. Since the temperature at the inner core boundary ($T_{ICB}$) has not been measured precisely (4850–7100 K), we deduce that the S concentration ranges from 10–14 wt% assuming S is the only light element. Our results also show that Fe-S alloys cannot satisfy the seismological density and sound velocity simultaneously and thus S element is not the only light element. Considering the geophysical and geochemical constraints, we propose that the outer core contains no more than 3.5 wt% S, 2.5 wt% O, or 3.8 wt% Si. In addition, the developed thermal EoS can be utilized to calculate the thermal properties of liquid Fe-S alloys, which may serve as the fundamental parameters to model the Earth’s outer core.

**Keywords:** Earth’s outer core, liquid Fe-S alloy, first-principles molecular dynamics, sound velocity, equation of state

**Introduction**

The composition of the Earth’s outer core at pressures from 136 to 330 GPa and temperatures from 4000 to 7000 K (Dziewonski and Anderson 1981; Koči et al. 2007; Alfè 2009) remains controversial. The direct geophysical data are from measurements of the speed of seismic wave propagation. Understanding the geodynamics in the outer core requires the thermal properties of its composition. According to Birch’s reports (Birch 1952), the outer core is mainly composed of Fe. However, the Preliminary Reference Earth Model (PREM) (Dziewonski and Anderson 1981) indicates that pure Fe is much denser than the substance in the outer core and has a lower sound velocity. It is argued that there must exist some light elements (e.g., sulfur, silicon, oxygen, carbon, and hydrogen) to decrease the density and increase sound velocity (Poirier 1994; Hirose et al. 2013; Badro et al. 2015; Litasov and Shatskiy 2016; Umemoto and Hirose 2020). The presence of light elements does reduce the density of ferroalloy, but not the sound velocity of each component matches the PREM data. The type of light elements is still pending.

Owing to its siderophile nature, sulfur (S) is considered as a major light element in the Earth’s outer core (Huang et al. 2011; Kawaguchi et al. 2017). The concentration of S is typically predicted by comparing the density and sound velocity of liquid Fe-S alloy with PREM data. So far, many efforts have been done in experiments. Huang and coauthors (Huang et al. 2011, 2018) measured the density and sound velocity of liquid Fe$_{52}$S$_{25}$Ni$_{23}$ and Fe$_{50}$O$_{2}$S$_{25}$ up to 208 GPa and Fe-11.8 wt% S up to 214.4 GPa through the shock-wave experiment and predicted the maximum S content was around 10 wt%. A similar experiment estimated the S concentration of 2 wt% (Zhang et al. 2016). Using laser-heated diamond-anvil cells, Kawaguchi et al. measured the sound velocity of Fe$_{57}$Ni$_{2}$S$_{25}$ and Fe$_{50}$Ni$_{2}$S$_{25}$ up to 58 GPa and 2480 K, and proposed the amount of S was 5.8–7.5 wt% (Kawaguchi et al. 2017). Since most experimental $P$-$T$-$V$ data (Sanloup et al. 2002; Badro et al. 2007; Jing et al. 2014; Kuskov and Belashchenko 2016) were obtained at pressures and/or temperatures below the outer core conditions, the values at higher $P$-$T$ were usually extrapolated using Birch’s law (Badro et al. 2007). The validity of Birch’s law at extremely high temperatures is questionable (Lin et al. 2005). In brief, due to technical challenges in dynamic and static high-pressure measurements, the exact S concentration in the Earth’s outer core is far from reaching a consensus.

As a remedy, theoretical calculations have been utilized to determine the S concentration (Alfè and Gillan 1998; Alfè et al. 2002a; Badro et al. 2014; Umemoto et al. 2014; Bazhanova et al. 2017). Since some theoretical calculations were performed at 0 K, the temperature effects on thermal pressure were often neglected or approximated (Bazhanova et al. 2017). Ignoring the temperature impact at extreme conditions leads to erroneous pressure-volume ($P$-$V$) relations. Therefore, first-principles molecular dynamics (FP-MD) simulations are suitable to study the $P$-$T$-$V$ relations, namely, equation of state (EoS). By applying the EoS, density and sound velocity can be obtained. Actually, the thermal EoS for liquid Fe has been reported (Vočadlo et al. 2003; Bouchet et al. 2013; Ichikawa et al. 2014; Wage and Steinle-Neumann 2019), but it is rare for liquid Fe-S alloys. The latter plays a central role in predicting the S concentration...