Self-diffusion coefficient and sound velocity of Fe-Ni-O fluid: implications for the stratification of Earth’s outer core

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Abstract

It is experimentally reported that the stratified layer atop Earth's outer core is hundreds of kilometers thick with a maximum sound velocity reduction of 0.3% relative to the preliminary reference Earth model. However, why the sound velocity atop the outer core is reduced remains theoretically unclear. In this paper, the Ni and vital light O in the outer core were both considered to have implications for the stratification of Earth's core, including the stratification thickness and the sound velocity profile. Ab initio molecular dynamics simulations were performed on the Fe-Ni-O fluid under the conditions of Earth's outer core, and the self-diffusion coefficients and ion-ion dynamic structure factors were calculated. The self-diffusion coefficient of O is \((19.56 \pm 0.83) \times 10^{-9} \text{ m}^2\text{s}^{-1}\) at the core-mantle boundary. Combining the diffusion equation with the time evolution of the O self-diffusion coefficient, the calculated stratification thickness at present is 194.7 km. The calculated ion-ion dynamic structural factors indicate that the sound velocity in the outmost outer core near the stratified layer is 7.86 km/s. These results show that Fe-Ni-O is a possible composition of the stratified layer atop the outer core featuring an appropriate thickness and a reduced sound velocity, thereby shedding light on the dynamic behavior of Earth's core.

Full Text

The stratified layer underneath the core-mantle boundary (CMB) has a lower sound velocity\(^1,2\) than the corresponding values in the preliminary reference Earth model (PREM)\(^3\), and its thickness is approximately 200 km\(^4\) to 300 km\(^2,5\). Studies have suggested that this stratification is caused by light elements\(^2\) that may have been expelled from the inner core or diffused from the mantle\(^6\). However, mixtures comprising iron and light elements may increase sound velocity\(^7\), and the thickness of the stratification derived from the diffusion equation in a previous paper was only 60–70 km\(^6\). Hence, a theoretical explanation for the 200–300-km-thick stratification atop the outer core with a reduced sound velocity remains elusive.

The stratification in the outer core is both thermal and compositional in nature\(^8\). In terms of subadiabatic stratification, the addition of Ni decreases the thermal conductivity by approximately 10%, whereas the Ni effect on the thermal stratification is limited\(^9\). The thickness of the compositional stratification was calculated to be 60–70 km from the self-diffusion coefficient of O in Fe-O fluid\(^6\). In this early analytical model, the self-diffusion coefficient of light O was considered to be \(3 \times 10^{-9} \text{ m}^2\text{s}^{-1}\). However, ab initio results indicate that the self-diffusion coefficient of pure Fe is approximately \(6 \times 10^{-9} \text{ m}^2\text{s}^{-1}\). O has an anomalously large self-diffusion coefficient in Fe-O fluid under CMB conditions: \(9 \times 10^{-9} \text{ m}^2\text{s}^{-1}\) at 4581 K and 136 GPa, \(50 \times 10^{-9} \text{ m}^2\text{s}^{-1}\) at 3829 K and 136 GPa\(^12\), and \(~22 \times 10^{-9} \text{ m}^2\text{s}^{-1}\). Although the O concentration is only 1.6–3.8 wt.% in the outer core and O does not exist in the inner core\(^14\), O is essential for compositional convection\(^15\) and partitions much more strongly than do S and Si from the inner core.
to the outer core. In addition, the results of nuclear resonance inelastic X-ray scattering demonstrate that Fe enrichment in (Mg,Fe)O has the potential to explain the large velocity drop at the base of the mantle\(^ {16}\).

With increasing computational capabilities, \textit{ab initio} molecular dynamics can yield accurate adiabatic sound velocities, which can be calculated from equations of state (EOSs)\(^ {7}\) or dynamic structural factors\(^ {17}\). Sound velocity calculations show that liquid Fe with O has a fast sound velocity, while liquid Fe with Ni has a slow sound velocity\(^ {7}\). Considering both the stratification thickness and the sound velocity, a system comprising Fe and Ni as the basic components and O as a potential light element, i.e., Fe-Ni-O ternary liquid, should be explored. After calculating the self-diffusion coefficients and adiabatic sound velocity of Fe-Ni-O fluid, we find that Fe-Ni-O fluids only weakly attenuate seismic waves and exhibit thick compositional stratification.

We utilized advanced \textit{ab initio} molecular dynamics and calculated the time evolution of different particle configurations with the main aim of determining the compositional stratification thickness and the stratification characteristics. On the one hand, the self-diffusion coefficients D were calculated by the velocity autocorrelation function, and the thickness of the stratified layer was calculated from the diffusion equation and restricted boundary condition. On the other hand, the ion-ion dynamic structure factor S(q,\(\omega\))\(^ {17}\) was calculated from the Fourier transform of the particle distribution. Then, the adiabatic sound velocity \(V\) for ion acoustic modes was determined as the slope of the dispersion relation.

The calculated self-diffusion coefficients of the Fe-Ni-O fluid at the pressures beneath the CMB (Figure 1 (a)) and at the inner core boundary (Figure 1 (b)) are of the same order as the previous \textit{ab initio} simulation results\(^ {11-13,18,19}\). At CMB pressures, the self-diffusion coefficient of O ranges from \((15.28\pm0.65)\times10^{-9}\) m\(^2\)s\(^{-1}\) at 3500 K to \((27.13\pm1.18)\times10^{-9}\) m\(^2\)s\(^{-1}\) at 5500 K; in contrast, the self-diffusion coefficient of Fe ranges from \((6.74\pm0.34)\times10^{-9}\) m\(^2\)s\(^{-1}\) at 3500 K to \((13.56\pm0.73)\times10^{-9}\) m\(^2\)s\(^{-1}\) at 5500 K. The self-diffusion coefficients of Fe and Ni are very small under different temperature and pressure conditions, and the self-diffusion coefficient of Ni is slightly lower than that of Fe. The Ni effect on the thermal conductivity of liquid Fe is also quite limited\(^ {9}\). Fe and Ni are nearly adjacent in the periodic table and have a similar electron occupation types, which may explain their similar properties.

The above shows that Fe-Ni-O fluid has an anomalously high self-diffusion coefficient of O, which is consistent with the self-diffusion coefficient of Fe-O fluid\(^ {12,13}\). This may originate from the low atomic mass of O, which always corresponds to ease of movement within the fluid. This anomalous self-diffusion coefficient was recently explained by structural\(^ {13}\) and electronic\(^ {12}\) analyses. The higher self-
The compositional stratification atop the outer core is caused by the diffusion of light O\textsuperscript{6}. In the stratified layer, the O concentration distribution \( C(r, t) \) varies radially and satisfies the diffusion equation. In the convective region, the O concentration is homogeneous, and the contributions of O to the outer core originate from both the inner core and the mantle. The thickness of the compositional stratification is calculated by the diffusion equation with the time evolution of the O self-diffusion coefficient \( D(t) \), which is considered by combining the temperature-dependent self-diffusion coefficient \( D(t) \) and cooling rate at the CMB \( \frac{dT_c}{dt} \). The thermal conductivity of Fe-Ni fluid shows that it is subadiabatic on top of the outer core, and the age of the inner core and the CMB temperature \( T_c(t) \) are collected\textsuperscript{9}. From the time evolution of \( T_c(t) \), the temperature-dependent equilibrium concentration \( C_{eq}(T) \) and self-diffusion coefficient \( D(T) \) are transformed into the time evolution of \( C_{eq}(T) \) and \( D(t) \).
Ion-ion dynamic structure factors were calculated from the traces of particles from \textit{ab initio} molecular dynamics simulations, and the dispersion relationship of the collective excitations was determined by analyzing the positions of the side peaks. The resulting slope of the dispersion relation for small wave vectors is the adiabatic sound velocity. The ion-ion dynamic structure factors and dispersion relationship of Fe-Ni-O fluid are presented in Figure 3(a) and (b). The adiabatic sound velocity of Fe-Ni-O fluid is 7.86 km/s at 4000 K and 136 GPa. The sound velocity of this Fe-Ni-O fluid at CMB pressure is highly sensitive to temperature and thus ranges from 9.29 km/s at 3500 K to 6.45 km/s at 5000 K; that is, the temperature effect on the sound velocity is nonnegligible. The ion-ion dynamic structure factors correspond to inelastic X-ray scattering experiments, where angle-dispersive X-ray diffraction (XRD) spectra can be converted into structure factors. The sound velocity of pure Fe is lower than 8.0 km/s at 136 GPa and 5000 K according to inelastic X-ray scattering measurements combined with shock-wave data based on the Mie-Grüneisen EOS\textsuperscript{14}.

Figure 4 shows the sound velocity of Fe-Ni-O fluid along the core's adiabatic gradient in comparison with PREM\textsuperscript{3} and experimental values\textsuperscript{1,2,14}. The sound velocity of the Fe-Ni-O fluid is lower than the PREM values (~8.05 km/s) but agrees well with the experimental results\textsuperscript{1,2}. As the O concentration is not a constant near the CMB, the shape of the velocity profile of the Fe-Ni-O fluid is different from the experimental profile (subfigure of Figure 4), which can be attributed to the ideal mixing of Fe-Ni and Fe-O fluids\textsuperscript{7}. The low velocity may originate from the Ni effects on the bulk modulus and density, as Ni plays an important role in slowing the sound velocity. The existence of an Fe-O or a Ni-O phase may also correspond to a low sound velocity\textsuperscript{16}. To further understand the nature of the stratification atop Earth's core, more \textit{ab initio} molecular dynamic simulations should be adopted to ascertain the self-diffusion coefficients and sound velocities of other possible Fe-Ni-X (X being another possible light element) fluids.

The thickness and sound velocity of the stratified layer provide fundamental seismic insights into Earth's core. From our \textit{ab initio} molecular dynamics simulations, for the first time, we derived the self-diffusion coefficients and adiabatic sound velocity of Fe-Ni-O fluid under the conditions of Earth's core. The \textit{ab initio} approach for calculating the self-diffusion coefficient and the dynamic structure factor represent complementary methods for determining the sound velocity with inelastic X-ray scattering measurements and seismic observation profiles of the stratification atop Earth's core. Hence, the use of \textit{ab initio} molecular dynamics to calculate the self-diffusion coefficients and adiabatic sound velocities of fluids reveals new pathways to study the compositional evolution of Earth's core.

In conclusion, the self-diffusion coefficient of O can reach \((19.56\pm0.83)\times10^{-9}\) m\(^2\)s\(^{-1}\) at the CMB. The compositional stratification thickness derived from the diffusion equation is 194.7 km in the present day,
whereas it was 285.1 km after the accretion of the inner core. The adiabatic sound velocity of the Fe-Ni-O fluid at the CMB is 7.86 km/s according to ion-ion dynamic structure factors. We report both the short-range and the long-range structures of Fe-Ni-O fluid to describe the dynamics of Earth's core. *Ab initio* molecular dynamics simulations concurrently show that the Fe-Ni-O fluid exhibits a large self-diffusion coefficient and low seismic velocity. These unique features of the Fe-Ni-O fluid might be responsible for the stratification structure of Earth's outer core. Ultimately, this paper provides new insights into the dynamics and evolution of Earth's core.

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**Methods**

The methods are available as a download in the supplementary files section.

**Figures**
Figure 1

Temperature-dependent self-diffusion coefficients (D₀, DFe, and DNi) of the Fe-Ni-O fluid at the (a) CMB and (b) inner core boundary. Our calculated results are dotted lines (D₀, DFe and DNi) in the figures. The labels with names denote the previously calculated results by Wijs11, Alfè18, Pozzo19, Ichikawa12, and Posner13 in Fe, FeO, and Fe-S-O fluids.
Figure 2

Time evolution of the compositional stratification \( s \) (km), time evolution of the O concentration at the CMB \( C_m(t) \), and the spatial distribution of the O concentration \( C(r, t=4.5 \text{ Ga}) \) at present.

Figure 3
Calculation of the (a) ion-ion dynamic structure factors and (b) dispersion relationship for the ion acoustic mode at 136 GPa and 4500 K. The dotted line in (b) is the linear fit of the adiabatic sound velocity.

Figure 4

Adiabatic sound velocity profile under the conditions of Earth's core. The red dotted line is the calculated profile for the Fe-Ni-O fluid. The shaded area is the stratification calculated from Figure 2, and ‘Fe exp.’14, ‘PREM’3, ‘Helffrich’2 and ‘Granero’1 denote reference data. The shaded area is the compositional stratification atop out core.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- FeNiOdiffvelMethod.docx