

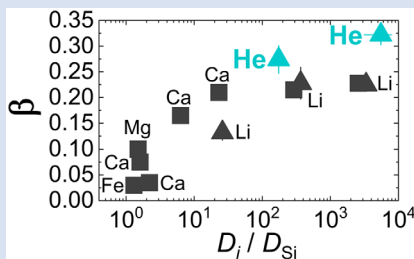
## Diffusional fractionation of helium isotopes in silicate melts

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doi: 10.7185/geochemlet.2128

### Abstract



Estimating Helium (He) concentration and isotope composition of the mantle requires quantifying He loss during magma degassing. The knowledge of diffusional He isotope fractionation in silicate melts may be essential to constrain the He loss. Isotopic mass dependence of He diffusion can be empirically expressed as  $D^3\text{He}/D^4\text{He} = (4/3)^\beta$ , where  $D$  is the diffusivity of a He isotope. However, no studies have reported any  $\beta$  values for He in silicate melts due to technical challenges in both experiments and computations. Here, molecular dynamics simulations based on deep neural network potentials trained by *ab initio* data show that  $\beta$  for He in albite melt decreases from  $0.355 \pm 0.012$  at 3000 K to  $0.322 \pm 0.019$  at 1700 K.  $\beta$  in model basalt melt takes a smaller value from  $0.322 \pm 0.025$  to  $0.274 \pm 0.027$  over the same temperature range.

Based on our results, we suggest using  $D^3\text{He}/D^4\text{He}$  values of  $1.097 \pm 0.006$  and  $1.082 \pm 0.008$  in natural rhyolite and basalt melt, respectively, to interpret measured He concentration and isotope composition of natural samples.

Received 26 April 2021 | Accepted 31 August 2021 | Published 11 October 2021

### Letter

Noble gases are known to be chemically inert, which means that their compositions were not altered by chemical or biological processes over the Earth's history. Only physical processes such as diffusion, adsorption, or ion implantation may cause significant elemental and isotopic fractionations (Moreira, 2013). The inert behaviour combined with the existence of both radiogenic and non-radiogenic isotopes for each noble gas provides powerful tools for constraining mantle degassing history and identifying long lived heterogeneities within the mantle (Behrens, 2010; Moreira, 2013; Moreira and Kurz, 2013). However, measured noble gas isotope ratios in mid-ocean ridge basalts (MORB) and oceanic island basalts (OIB) are often difficult to interpret due to possible fractionations that happen in magma degassing (Moreira and Kurz, 2013).

Magma degassing occurs in a closed or open system. The changes of noble gas isotope compositions during closed system degassing are determined by equilibrium isotope fractionation between noble gases dissolved in the melt and noble gases in the gas phase. In comparison, magma degassing in an open system may be diffusion controlled (Watson, 2017) and diffusion can fractionate isotopes considerably even at magmatic temperatures (e.g., Richter et al., 1999; Watkins et al., 2017). Diffusional separation of isotopes can be expressed as (Richter et al., 1999):

$$\frac{D_i}{D_j} = \left(\frac{m_j}{m_i}\right)^\beta \quad \text{Eq. 1}$$

where  $D_i$  and  $D_j$  are diffusion coefficients of two isotopes whose masses are  $m_i$  and  $m_j$  and  $\beta$  is a dimensionless empirical parameter. The knowledge of  $\beta$  for noble gases in silicate melts is

essential to interpret noble gas isotope ratios. However, no experiments have studied diffusional fractionation of noble gas isotopes in high temperature silicate melts. The results from previous diffusion experiments using silicate glasses (Shelby, 1971; Trull and Kurz, 1999) may not be extrapolated to the cases in silicate melts, although silicate glasses are widely regarded as proper structural analogues of silicate melts. The reason is that the dynamics of silicate networks in high temperature melts help open and close paths for noble gas diffusion, which may play a key role in determining diffusional isotope fractionation (Behrens, 2010; Watkins et al., 2017). Additionally, it is known that the diffusivities of noble gases show non-Arrhenius behaviour around the glass transition temperature (Behrens, 2010; Amalberti et al., 2016), which may imply a change in diffusion mechanism and thus influence diffusional isotope fractionation.

First principles molecular dynamics (FPMD) simulations are reliable to calibrate  $\beta$  in liquids (Luo et al., 2020), but the high computational cost makes them unsuitable to deal with trace elements (e.g., noble gases and Li). A recently developed technique called deep potential molecular dynamics (DPMD) simulations (Wang et al., 2018; Zhang et al., 2018), which is based on potentials trained by deep neural networks using *ab initio* data and is orders of magnitude faster than FPMD with comparable *ab initio* accuracy, has been successfully applied to predict  $\beta$  for Li in silicate melts (Luo et al., 2021). Here we perform DPMD simulations to study diffusional He isotope fractionation in albite and model basalt melts at 3000, 2200, and 1700 K around zero pressure. The major technical improvement in this study is that the deep potential generator (DP-GEN) (Zhang et al., 2020) is used to achieve a concurrent learning procedure and to obtain a representative training data set in a rigorous way (Supplementary Information).

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Albite and model basalt melts (excess Ca to compensate Fe) are close analogues of natural rhyolite and basalt melts, respectively. One He atom is added to the albite melt containing 8 NaAlSi<sub>3</sub>O<sub>8</sub> (104 atoms) and the model basalt melt containing Ca<sub>9</sub>Mg<sub>6</sub>Al<sub>6</sub>Si<sub>18</sub>O<sub>60</sub> (99 atoms), respectively. We conduct the simulations at 3000 K for 1 nanosecond (ns) with a time step of 0.5 femtosecond (fs) and at 2200 and 1700 K for 4 ns with a time step of 1.0 fs. Each simulation is repeated five times with different initial configurations. The accuracy of DPMD simulations is validated by comparing the predicted energies (Fig. S-1), forces (Fig. S-2), and radial distribution functions (Fig. S-3) with those calculated from FPMD simulations. To derive a reliable  $\beta$  from the linear fitting of  $\log D$  vs.  $\log M$  based on Equation 1, we use two pseudo-isotopes with masses  $M^* = 1$  and 2 g/mol, in addition to the two natural He isotopes (<sup>3</sup>He and <sup>4</sup>He). The self diffusivities of the four He isotopes are calculated using the Einstein relation (Einstein, 1956):

$$D_{\text{He}} = \lim_{t \rightarrow \infty} \frac{\langle |\vec{r}(t + t_0) - \vec{r}(t_0)|^2 \rangle_{\text{He}}}{6t} \quad \text{Eq. 2}$$

where  $\vec{r}(t)$  represents the particle trajectories and  $\langle \dots \rangle_{\text{He}}$  denotes average mean square displacement (MSD) over time from different time origins  $t_0$ . The average value over the five independent simulations and the corresponding confidence interval ( $\pm 2$  s.e.) on the diffusivities are reported. The finite size effect on the diffusivities of He isotopes is insignificant within error after considering the correction relation proposed by Yeh and Hummer (Yeh and Hummer, 2004).

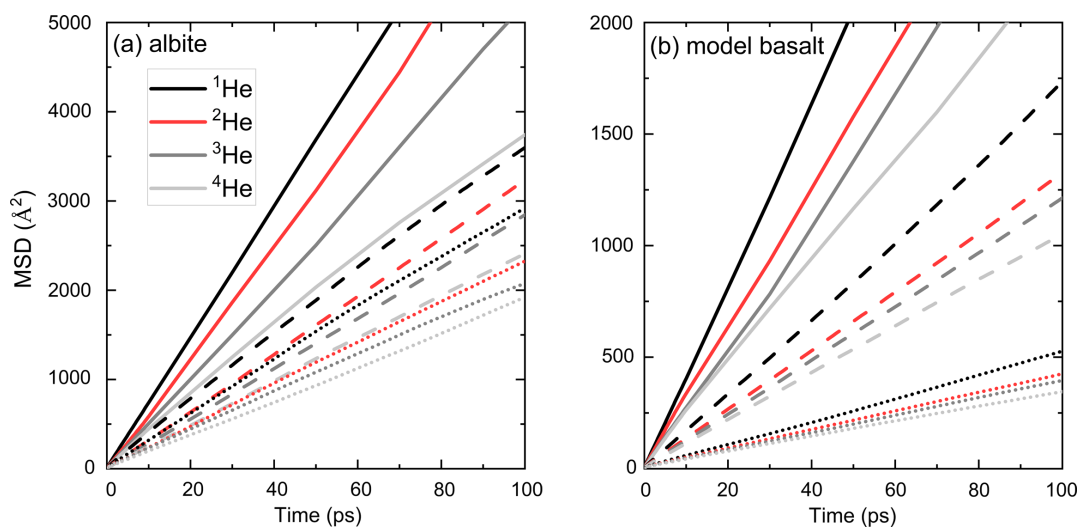
In Figure 1, linear MSD-time curves indicate that the diffusion of He isotopes was sampled well. All MSD curves for the four He isotopes at each condition are clearly separated. As suggested in previous studies (e.g., Bourg and Sposito, 2007; Luo *et al.*, 2020), only the first part of MSD curves in the diffusive regime (9–10 picoseconds (ps), 20–40 ps, and 50–100 ps at 3000, 2200, and 1700 K, respectively) is used to approximate the infinite time limit in Equation 2. We find that He diffuses much faster in albite than in model basalt melts, consistent with the trend found in glasses (Behrens, 2010). Calculated diffusion coefficients of He isotopes display a negative correlation with mass and a positive correlation with temperature

in both albite and model basalt melts (Table S-1, Fig. 2a). The temperature dependence of diffusivities is fit to the Arrhenius relation:

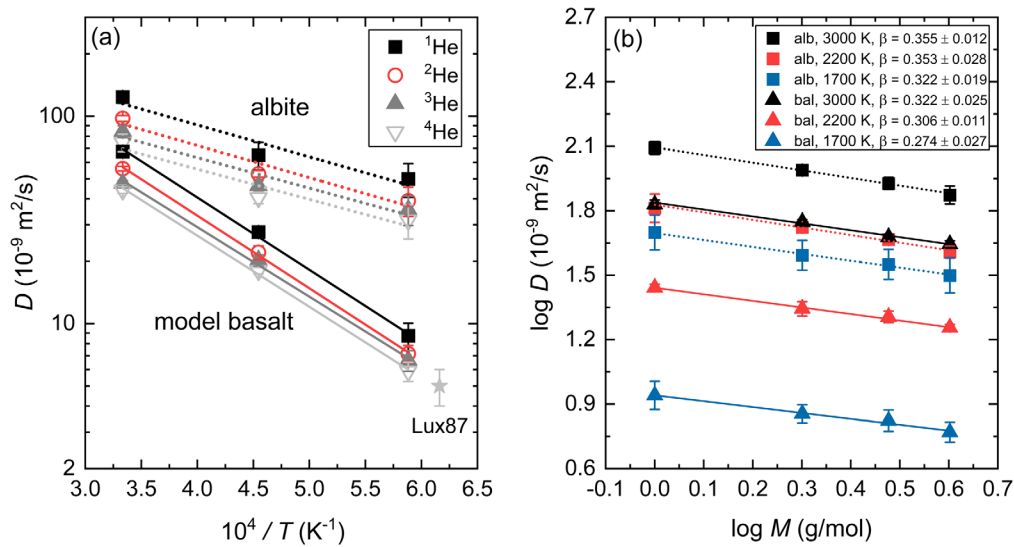
$$D_{\alpha} = D_{0\alpha} \exp \left[ \frac{-E_{\alpha}}{RT} \right] \quad \text{Eq. 3}$$

where  $\alpha$  represents a He isotope. The predicted pre-exponential factor ( $D_{0\alpha}$ ) and activation energy ( $E_{\alpha}$ ) appear to decrease with increasing isotopic mass of He (Fig. S-4). The predicted diffusivity for <sup>4</sup>He in model basalt melt at 1623 K is  $4.81 \times 10^{-9}$  m<sup>2</sup>/s, which agrees well with the experimental value of  $5 \times 10^{-9}$  m<sup>2</sup>/s in a tholeiitic melt (Lux, 1987) and the computational result from classical MD in a MORB melt (Guillot and Sator, 2012), although it is unclear why an experiment reported a much lower value of  $0.28 \times 10^{-9}$  m<sup>2</sup>/s in model basalt melt at 1673 K (Amalberti *et al.*, 2018).  $E_{\alpha}$  for <sup>4</sup>He in albite and model basalt melts are  $27.9 \pm 7.6$  and  $65.8 \pm 2.4$  kJ/mol, respectively. No experiments have reported activation energy for He diffusion in silicate melts. The experimental activation energies for He diffusion in albite and basalt glasses at much lower temperatures (398–673 K) are  $31.7$  (Shelby and Eagan, 1976) and  $83 \pm 4$  kJ/mol (Kurz and Jenkins, 1981), respectively. The smaller activation energies predicted by FPMD simulations compared to experimental results have been extensively reported (Karki *et al.*, 2018). The very different temperature ranges explored in simulations and experiments may account for the discrepancy. It is worth stressing that He diffusion in albite melt shows a small non-Arrhenius behaviour (Fig. 2a).

The linear correlation of  $\log D$  with  $\log M$  in Figure 2b is consistent with the empirical Equation 1 proposed by Richter *et al.* (1999). The calculated  $\beta$  in albite melt decreases from  $0.355 \pm 0.012$  at 3000 K to  $0.322 \pm 0.019$  at 1700 K. In comparison,  $\beta$  in model basalt melt takes a smaller value from  $0.322 \pm 0.025$  to  $0.274 \pm 0.027$  over the same temperature range. The smaller  $\beta$  value in model basalt than in albite melt is the same as that observed in the case of Li, which makes sense as both He and Li diffuse faster in rhyolitic than in basaltic melt due to higher ionic porosity of rhyolitic melt. The decreasing trend of  $\beta$  with temperature in silicate melts around zero pressure has been reported in the simulations of diffusional Mg and Li isotope fractionation (Luo *et al.*, 2020, 2021). An assumed linear regression fit to  $\beta$  vs.  $T^{-1}$  yields relationships:  $\beta = (0.397 \pm 0.017)$



**Figure 1** Mean square displacement (MSD) of He isotopes (<sup>1</sup>He, <sup>2</sup>He, <sup>3</sup>He, <sup>4</sup>He) as a function of time in (a) albite and (b) model basalt melts at 3000 (solid lines), 2200 (dashed lines), and 1700 K (dotted lines) around zero pressure.



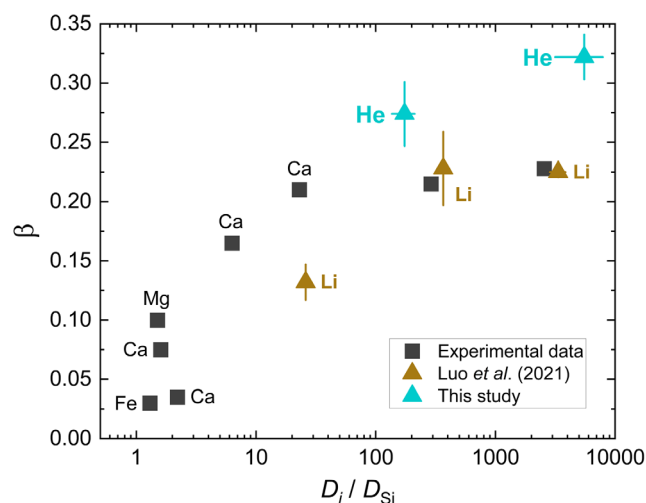
**Figure 2** (a) Diffusion coefficients of He isotopes ( $^1\text{He}$ ,  $^2\text{He}$ ,  $^3\text{He}$ ,  $^4\text{He}$ ) as a function of temperature in albite and model basalt melts around zero pressure. The experimental data (Lux87) for the diffusivity of He in a tholeiitic melt is from Lux (1987). (b) Log-log plot of the diffusivities of He isotopes in albite (alb) and model basalt (bal) melts as a function of isotopic mass at different temperatures around zero pressure.

$-(0.012 \pm 0.004) \times 10^4/T$  in albite melt and  $\beta = (0.389 \pm 0.021) - (0.019 \pm 0.005) \times 10^4/T$  in model basalt melt. The stronger temperature dependence of  $\beta$  for Li in model basalt than in albite melt is also observed here for He. Based on the predicted  $\beta$  values, a drop of temperature by 300 K (1700–1400 K in basaltic melt or 1400–1100 K in rhyolitic melt) results in a negligible decrease ( $\sim 0.7\%$ ) of  $D^3\text{He}/D^4\text{He}$  value. Thus, we suggest that using the data at 1700 K,  $D^3\text{He}/D^4\text{He}$  values of  $1.082 \pm 0.008$  in model basalt melt and  $1.097 \pm 0.006$  in albite melt, are accurate enough when dealing with diffusional fractionation of He isotopes in natural silicate melts at shallow depths of the present day Earth.

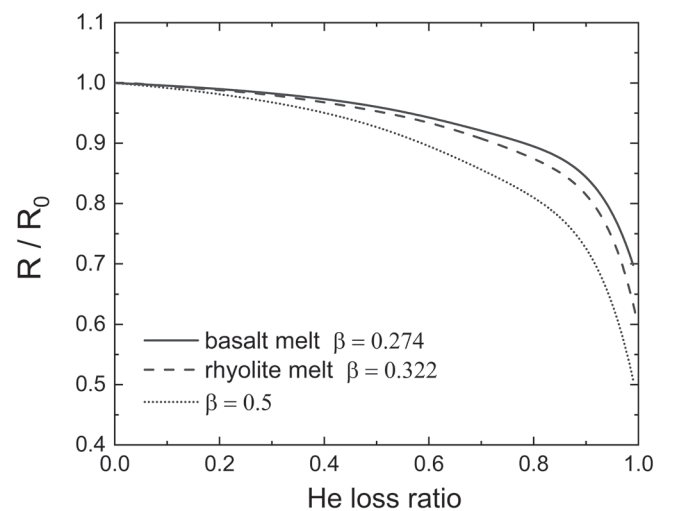
It has been proposed that  $\beta$  positively correlates with solvent normalised diffusivity ( $D_i/D_{\text{Si}}$ ), implying that cations that are easier to decouple from the silicate matrix exhibit a larger diffusional isotope fractionation (Watkins *et al.*, 2011, 2017). Note

that Luo *et al.* (2020, 2021) stressed that this positive correlation only works at a constant or narrowly defined temperature range as  $\beta$  in silicate melts is found to decrease with decreasing temperature while  $D_i/D_{\text{Si}}$  increases. The correlation of  $\beta$  for He with  $D_{\text{He}}/D_{\text{Si}}$  at 1700 K broadly follows the previous positive trend (Fig. 3). The value of  $D_{\text{He}}/D_{\text{Si}}$  is  $\sim 5525 \pm 2378$  in albite melt, much larger than the value of  $\sim 174 \pm 37$  in model basalt melt. However, it seems that the overall relationship between  $\beta$  and  $D_i/D_{\text{Si}}$  becomes less defined even at a narrow temperature range when data for different elements in different melt systems are considered (Fig. 3). This could be attributed to different extents of compositional dependence of both  $\beta$  and  $D_i/D_{\text{Si}}$ . More data are needed to further explore this issue.

Helium is the fastest diffusing species in natural silicate melts (except  $\text{H}_2$  which is easily oxidised) and there is a positive correlation between diffusivity and  $\beta$  at fixed temperatures. Thus, it is fair to say that the overall range of  $\beta$  for different elements in natural silicate melts is  $\sim 0\text{--}0.32$ . The largest  $\beta$  value is given by He isotope diffusion in rhyolitic melt, which is still much lower



**Figure 3** Relationship of  $\beta$  with solvent normalised diffusivity ( $D_i/D_{\text{Si}}$ ). Experimental data is from Richter *et al.* (2003, 2009), Watkins *et al.* (2009, 2011), and Holycross *et al.* (2018). Computational results of Li at 1800 K are from Luo *et al.* (2021). All data shown here are for the relatively narrow temperature range 1623–1800 K, except one data point from Holycross *et al.* (2018).



**Figure 4**  $(^3\text{He}/^4\text{He})/(^3\text{He}/^4\text{He})_0$  as a function of He loss ratio for different  $\beta$  values.

than the value of 0.5 in the case of ideal gas. Given measured He isotope ratios of geological samples (rocks, minerals, glasses, or melt inclusions) that went through diffusive degassing at the magmatic stage, a smaller  $\beta$  value means that the samples must have lost more He than previously thought.

For example, reducing an initial  $^3\text{He}/^4\text{He}$  ratio by 10 % requires 60 % gas loss for  $\beta$  equal to 0.5, but 73 % loss for  $\beta$  of 0.322 in rhyolite melt and 77 % loss for  $\beta$  of 0.274 in basalt melt (Fig. 4, Supplementary Information). Our reported  $\beta$  values are useful for quantitatively estimating He loss during magmatic degassing and trace back He concentration and isotope composition of magma source region.

## Acknowledgements

The research is supported by the Strategic Priority Research Program (B) of Chinese Academy of Sciences (XDB18010104) and National Science Foundation (EAR 1764140 and 2001074). High-performance computing resources were provided by Louisiana State University.

Editor: Anat Shahar

## Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2128>.



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Cite this letter as: Luo, H., Karki, B.B., Ghosh, D.B., Bao, H. (2021) Diffusional fractionation of helium isotopes in silicate melts. *Geochem. Persp. Let.* 19, 19–22.

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