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Plate tectonic cycling modulates Earth's $^{3}He/^{22}Ne$ ratio

Nick Dygert[1,2*], Colin R.M. Jackson[3,4], Marc A. Hesse[1], Marissa M. Tremblay[5,6,7], David L. Shuster[5,6], Jesse T. Gu[1]

[1]Department of Geological Sciences, Jackson School of Geosciences, University of Texas at Austin, Austin TX 78712

[2]Planetary Geosciences Institute, Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, Knoxville TN 37996

[3]Geophysical Laboratory, Carnegie Institution for Science, Washington DC 20015

[4]National Museum of Natural History, Smithsonian Institution, Washington DC 20560

[5]Department of Earth and Planetary Science, University of California, Berkeley, Berkeley CA 94720

[6]Berkeley Geochronology Center, Berkeley, CA 94709

[7]Now at the Scottish Universities Environmental Research Centre, East Kilbride, Scotland G75 0QF

*Corresponding author.

Email: ndygert1@utk.edu
Current phone: 1-865-974-6022
Present mailing address: Nick Dygert
Department of Earth and Planetary Sciences
University of Tennessee, Knoxville
1621 Cumberland Avenue
602 Strong Hall
Knoxville, TN 37996

Abstract

The ratio of ^{3}He and ^{22}Ne varies throughout the mantle. This observation is surprising because ^{3}He and ^{22}Ne are not produced in the mantle, are highly incompatible during mantle melting, and are not recycled back into the mantle by subduction of oceanic sediment or basaltic crust. Our new compilation yields average ^{3}He/^{22}Ne ratios of 7.5±1.2 and 3.5±2.4 for mid-ocean ridge basalt (MORB) mantle and ocean island basalt (OIB) mantle sources respectively. The low ^{3}He/^{22}Ne of OIB mantle approaches planetary precursor ^{3}He/^{22}Ne values; ~1 for chondrites and ~1.5 for the solar nebula. The high ^{3}He/^{22}Ne of the MORB mantle is not similar to any planetary precursor, requiring a mechanism for fractionating He from Ne in the mantle and suggesting isolation of distinct mantle reservoirs throughout geologic time. New experimental results reported here demonstrate that He and Ne diffuse at rates differing by one or more orders of magnitude at relevant temperatures in mantle materials. We model the formation of a MORB mantle with an elevated ^{3}He/^{22}Ne ratio through kinetically modulated chemical exchange between dunite channel-hosted basaltic liquids and harzburgite wallrock beneath mid-ocean ridges. Over timescales relevant to mantle upwelling beneath spreading centers, He may diffuse tens to hundreds of meters into wallrock while Ne is effectively immobile, producing a mantle lithosphere regassed with respect to He and depleted with respect to Ne, with a net elevated ^{3}He/^{22}Ne. Subduction of high ^{3}He/^{22}Ne mantle lithosphere throughout geologic time would generate a MORB source with high ^{3}He/^{22}Ne. Mixing models suggest that to preserve a high ^{3}He/^{22}Ne reservoir, MORB mantle mixing timescales must be on the order of hundreds of millions of years or longer, that mantle convection has not been layered about the transition zone for most of geologic time, and that Earth's convecting mantle has lost at least 96% of its primordial volatile elements. The most depleted, highest $^{3}He/^{22}Ne$ mantle may be best preserved in the lower mantle where relatively high viscosities impede mechanical mixing.

Keywords: $^{3}He/^{22}Ne$; noble gas; dunite channel, kinetic fractionation; diffusion; mantle lithosphere

1. Introduction

^{3}He and ^{22}Ne are not produced in the mantle or fractionated by partial melting, and neither isotope is recycled back into the mantle by subduction of oceanic basalt or sediment (e.g., Heber et al., 2007; Hilton et al., 2002; Jackson et al., 2013a; Staudacher and Allègre, 1988; Tucker and Mukhopadhyay, 2014). Thus, it is a surprise that large ^{3}He/^{22}Ne variations exist within mantle-derived rocks and that by inference; the mantle has a net elevated ^{3}He/^{22}Ne ratio compared to volatile-rich planetary precursor materials such as the solar nebula, chondritic meteorites, iron meteorites and achondrites (Fig. 1, Graham, 2002; Harper and Jacobsen, 1996; Honda and McDougall, 1998; Ott, 2002). ^{3}He/^{22}Ne ratios may preserve a unique record of mantle evolution, provided mechanisms for fractionating He from Ne in the mantle are understood.

Previous work (Graham 2002; Honda and McDougall, 1998) and the updated compilation presented in this manuscript (Fig. 1; Supplementary Table 1) show that the mid-ocean ridge basalt (MORB) mantle source has distinctly higher ^{3}He/^{22}Ne compared to ocean island basalt (OIB) sources (7.5±1.2 and 3.5±2.4 respectively; see the electronic supplement for a description of our methods). The low ^{3}He/^{22}Ne of OIBs approaches chondritic (~1) and solar nebula values (~1.5), whereas the high ^{3}He/^{22}Ne of the MORB mantle is not similar to solar sources or any known family of meteorites. Such a high ^{3}He/^{22}Ne ratio for MORB mantle requires a mechanism for fractionating He from Ne in the mantle and suggests isolation of distinct mantle reservoirs during Earth's evolution.

The current model for forming a mantle heterogeneous in ^{3}He/^{22}Ne invokes fractionation from magma ocean degassing (Honda and McDougall, 1998; Tucker and Mukhopadhyay, 2014). He is ~2× more soluble than Ne in peridotitic melt (e.g., Iacono-Marizano et al., 2010);

degassing a magma ocean to form a primitive atmosphere would elevate the ^{3}He/^{22}Ne of the magma ocean. In a best-case scenario under equilibrium conditions, a degassing event roughly doubles the ^{3}He/^{22}Ne of the magma ocean. Subsequent degassing events can only further fractionate mantle ^{3}He/^{22}Ne ratios if there is atmospheric blow-off prior to the next period of magma ocean-atmosphere equilibration.

Primordial sources of He and Ne have ^{3}He/^{22}Ne ratios of ~1.5 (e.g., Harper and Jacobsen, 1996; Mahaffy et al., 1998; Ott, 2002; Trieloff and Kunz, 2005). Thus, accounting for ^{3}He/^{22}Ne ratios above 10 (e.g., Fig. 1, Graham, 2002; Honda and McDougall, 1998; Tucker and Mukhopadhyay, 2014) requires >2 magma ocean degassing events affecting the MORB mantle, and complete atmospheric blow-off prior to each magma ocean event. If He is rapidly lost from the atmosphere, as is the case today, between magma oceans, subsequent atmosphere-magma ocean equilibration would lead to a decreased ^{3}He/^{22}Ne ratio in the mantle, rather than the proposed increase.

Here we explore the possibility that elevated ^{3}He/^{22}Ne ratios relate to diffusion kinetics of He and Ne. It has long been known that He, Ne, and heavier noble gases have high-temperature diffusivities that differ by orders of magnitude in igneous materials (e.g., Behrens, 2010; Baxter, 2010 and references therein), providing the potential for kinetic fractionation of He from Ne in the mantle. The importance of kinetic fractionation for producing isotopic and trace element variations has been investigated previously (e.g., Albarède, 2008; Barford et al., 1999; Dygert et al., 2016; Hart, 1993; Hofmann and Hart, 1978; Kenyon, 1990; 1993; Spiegelman and Kenyon, 1992). Kinetic fractionation has been invoked to explain noble gas systematics in basalts that may be consistent with disequilibrium melting (e.g., Burnard, 2004; Burnard et al., 2004; Yamamoto et al., 2009). Here, instead of focusing on mantle melts, we evaluate how differences in He and Ne diffusivities can affect the compositions of mantle melting residues. We model the formation of an elevated and variable ^{3}He/^{22}Ne MORB source through kinetically modulated chemical exchange between dunite channel-hosted basaltic liquids and harzburgite wallrock beneath mid-ocean ridges. We demonstrate that kinetic fractionation of He and Ne will occur as basaltic liquids migrate through upwelling mantle, a process known to occur within Earth for billions of years. Our model predicts observed correlations between ^{3}He/^{22}Ne ratios and indices of depletion, including La/Sm, and the Rb-Sr and Sm-Nd isotope systems. It requires the entire high ^{3}He/^{22}Ne source to have fluxed through the global mid-ocean ridge system at least once, effective mantle mixing timescales of 0.4 Gyr or longer, and suggests that convection of the MORB mantle across the transition zone has dominated throughout geologic time.

1.1 Melt transport in dunite channels

Tabular bodies of olivine (dunites) are observed in ophiolites and interpreted to form a tree-root like network of high-porosity pathways called dunite channels. Dunite channel networks are thought to efficiently focus and extract mantle melts produced by adiabatic decompression melting beneath mid-ocean ridges (Fig. 2; Kelemen et al., 1995; 1997). Channelization necessarily juxtaposes dunite-hosted basaltic melts against harzburgitic melting residues (e.g., Liang et al. 2010; Schiemenz et al., 2010; Spiegelman et al., 2001; Spiegelman and Kelemen, 2003). Field observations demonstrate that dunite-hosted basaltic melts and adjacent harzburgite wallrock are not in chemical equilibrium (e.g., Dygert et al., 2016; Kelemen et al., 1992; 1995; Suhr et al., 2003), which inevitably leads to some amount of diffusive exchange (e.g., Burnard, 2004; Burnard et al., 2004; Kenyon, 1990; 1993; Spiegelman and

Kenyon, 1992). The extent of diffusive interaction between the dunite-hosted basaltic melt and adjacent wallrock depends on the effective diffusion rate of the element in the wallrock.

2. He and Ne diffusion rates in mantle materials

2.1 Measurements

Helium is significantly lighter and smaller than Ne and is therefore expected to diffuse faster than Ne in silicate melts and minerals at mantle temperatures. Relatively high He diffusivity would lead to kinetic fractionation of He from Ne (and heavier noble gases) in harzburgite wallrock around dunite channels. Despite the clear expectation for faster He diffusion than Ne, reported Arrhenius relationships for He and Ne are highly scattered. Measurements of Ne and He diffusion rates in mantle-relevant materials are summarized in Figure 3; lattice diffusion in olivine is shown in Fig. 3a, diffusion in silicate glasses is shown in Fig. 3b, grain boundary diffusion is shown in Fig. 3c. These studies comprise a variety of experimental approaches including first-principles calculations (Wang et al., 2015), high-pressure gas-soaking (Cherniak et al., 2014) and implantation degassing experiments (Cherniak and Watson, 2012; Cherniak et al., 2014), bulk degassing of natural and proton irradiated materials (Blard et al., 2008; Burnard et al., 2015; Futagami et al., 1993; Gourbet et al., 2012; Shuster et al., 2004; Tolstikhin et al., 2010; this study), and glass membrane (Frank et al., 1961; Swets et al., 1961), bubble shrinkage (Frischat and Oel, 1965; Wendler et al., 1995), and desorption experiments (Mulfinger and Scholze, 1962). An unrepeated preliminary experiment conducted at a single temperature on a superliquidus basaltic melt suggests $D_{He} > D_{Ne}$ (Lux, 1987). A recent study on CMAS glass and superliquidus melt found $D_{He} > D_{Ar}$ at a temperature of 1300ºC, but a He diffusion rate significantly slower than previous work (Alamberti et al., 2018). Here we adopt an assumption common to the noble gas literature (e.g. Gonnermann and Mukhopadhyay, 2007; Weston et al., 2015), that Arrhenius relations for He and Ne diffusion rates in simple silicate glasses can be extrapolated to mantle temperatures to approximate high-temperature diffusion in basaltic melts (green squares, Fig. 3d).

Data summarized in Fig. 3 collectively suggest that while measured diffusion rates vary among references for a particular element, Ne diffuses one or more orders of magnitude more slowly than He in mantle minerals and melts at mantle-relevant temperatures (Fig. 3d). A notable exception is the study of Gourbet et al., 2012 (green line, Fig. 3a), which measured bulk diffusion of Ne in proton-irradiated olivine using a step-heating technique. Gourbet et al. (2012) observed Ne diffusion rates orders of magnitude faster than other work (Cherniak et al., 2014; Futagami et al., 1993), and found that Ne and He diffuse at similar rates at high temperature.

To evaluate the discrepancy among measurements of Ne diffusion in olivine, we conducted a new bulk degassing experiment on a single crystal fragment from the batch of proton-irradiated San Carlos olivine previously investigated by Gourbet et al., 2012. We selected a grain with relatively few inclusions and cracks (Supplementary Figure S1), in contrast to grains investigated by Gourbet et al., 2012 (see their Supplementary Figure S2a). ^{3}He and ^{21}Ne were analyzed simultaneously during degassing, allowing us to directly compare their diffusivities throughout the experiment. Bulk degassing data were interpreted assuming a spherical geometry using equations presented in Fechtig and Kalbitzer (1966). Results are shown in Fig. 4 and Supplementary Figure S2; experimental, analytical and interpretive methods are discussed in detail in the Electronic Supplement. Except for some final He steps (collected after >99% degassing and barely above the instrumental detection limit, unfilled red circles, Fig. 4), all data collected while temperatures were well resolved are included in our analysis for both He and Ne.

The experiment yields activation energies of 122.1±5.1 kJ/mol for He and 168.6±8.8 kJ/mol for Ne. An effective spherical olivine radius of 330μm gives Arrhenius preexponentials of $8.80 \times 10^{-7}{}^{+7.89\times10^{-7}}_{-4.16\times10^{-7}}$ for He and $1.25 \times 10^{-6}{}^{+1.70\times10^{-6}}_{-7.21\times10^{-7}}$ for Ne. In that He diffuses significantly faster than Ne at all experimental temperatures, our results are consistent with the work of Futagami et al. (1993) and Cherniak et al. (2014). However, we observe high-temperature Ne diffusion rates orders of magnitude more rapid than either of these previous studies (compare thick blue and magenta lines, Fig. 3a). The cause of the discrepancy is unknown, but it could be related to differences in analytical and/or experimental methods, data interpretation, or the presence of optically unobservable diffusive fast paths or multiple diffusion domains in the relatively large olivine crystal fragment we analyzed (e.g., cracks, c.f. Cherniak et al., 2014). The latter is not supported by our He data, which agree well with diffusivities given by other recent studies (Fig. 3a; Blard et al., 2008; Cherniak and Watson, 2012; Shuster et al., 2004; Tolstikhin et al., 2010; Wang et al., 2015). We note that unlike prior work, our Ne activation energy is greater than that of He, consistent with diffusion compensation theory (e.g., Hoffman, 1980; Winchell 1969).

2.2 Pathways for diffusive exchange between dunite channels and wallrock

To model kinetic fractionation of He from Ne around dunite channels, we must consider which diffusive mechanisms produce the largest flux of noble gases into harzburgite wallrock. Diffusion of Ne along grain boundaries has not been measured, but recent work suggests He and Ar diffusion along olivine grain boundaries is slower than olivine lattice diffusion when grain boundary Arrhenius relations are extrapolated to mantle temperatures (Fig. 3c; Burnard et al., 2015; Delon et al., 2018). We assume Ne behaves similarly.

Diffusion through a network of interconnected melt at the dunite channel-wallrock interface would facilitate diffusive exchange, as noble gas diffusion in melts is assumed to be $\gtrsim 2$ orders of magnitude faster than in the olivine lattice (compare Figs 3b and 3a), and noble gases are highly soluble in melts relative to minerals (e.g., Heber et al., 2007; Jackson et al., 2013a). However, numerical simulations suggest the melt fraction around dunite channels may be at or below the "permeability threshold", i.e., the minimum melt fraction needed to produce an interconnected melt network (if such a threshold exists). Melt suction into the lower reaches of dunite channels creates a compacting boundary layer (CBL) around channels with a very low melt fraction (Liang et al., 2010; Schiemenz et al., 2010), and melt-rock reaction at the dunite channel-wallrock interface consumes latent heat, producing a cold thermal boundary layer around the channel (e.g. Katz and Weatherly, 2012). In the models presented below, we test cases where the CBL is impermeable, and cases where it has low but finite permeability. We also explore how different CBL thicknesses affect the efficiency of fractionation of He from Ne in dunite channel wallrock.

3. A model for kinetic fractionation of He from Ne in the mantle

A schematic illustrating our model setup is shown in Fig. 5, which is similar to Kenyon (1990). The simulation domain is divided into three adjacent segments: harzburgite wallrock, a CBL with a relatively low melt fraction, and a dunite channel. The contact between the dunite channel and CBL is the origin in the horizontal (*x*) dimension. In all simulations the width of the simulation domain is 100m, the dunite channel is 5m wide; the width of the CBL varies as *l*. We assume melt upwells in the wallrock at a rate of 4cm/y and use the wallrock-hosted melt as our reference frame. Melt in the dunite channel advects 50× faster than melt in the wallrock owing to its higher permeability (e.g., Kelmen et al., 1997). There is no lateral advection of melt; diffusion in the vertical (*z*) dimension is neglected. The composition of material in the dunite channel is given by

$$\frac{\partial C_c}{\partial t} + V_c \frac{\partial C_c}{\partial z} = D_c \frac{\partial^2 C_c}{\partial x^2} \qquad (1),$$

where D_c is the effective diffusion rate in the channel and V_c is the velocity of the channel melt in the *z* direction. The composition of the CBL is given by

$$\frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial x^2} \qquad (2),$$

where D_b is the effective diffusion rate in the boundary layer. The composition of the harzburgite wallrock is given by

$$\frac{\partial C_w}{\partial t} = D_w \frac{\partial^2 C_w}{\partial x^2} \qquad (3),$$

where D_w is the effective diffusion rate in the wallrock. Compositions at the channel-CBL interface and CBL-harzburgite wallrock interface and are fixed by equilibrium constants

$$C_b(x = 0) = K_{cb} C_c(x = 0) \qquad (4),$$

$$C_w(x = -l) = K_{bw} C_b(x = -l) \qquad (5),$$

where K_{cb} is the bulk channel-CBL partition coefficient, and K_{bw} is the bulk CBL-wallrock partition coefficient, which depend on the relative phase proportions across these contacts *(effectively the melt fractions, as we treat noble gases as perfectly incompatible in silicate minerals*). Effective diffusion coefficients are given by

$$D_i = \frac{\varphi_i}{\sqrt{2}} D_{melt} + (1 - \varphi_i) D_{solid} \qquad (6),$$

where φ_i is the melt fraction and diffusion in melt is scaled to correct for the tortuous matrix topology. In a second series of simulations we test cases where the CBL is impermeable; in those simulations, D_b is fixed at olivine volume diffusion rates. In all simulations, diffusion coefficients are calculated assuming a constant temperature of 1300°C.

The maximum upwelling distance assumed (70km) is the minimum height of the melting column beneath mid-ocean ridges suggested by isotopic and trace element evidence for garnet stability at the base of the MORB source melting region (c.f. Kelemen et al., 1997, and references therein). This establishes the total time for upwelling of the wallrock melt (1.75 Myr). Initial concentrations of ^{3}He and ^{22}Ne in the wallrock are assumed to be 0, consistent with a few percent of near-fractional melting of the mantle before formation of dunite channel networks, and the very low partition coefficients of noble gases in mantle minerals (~10^{-4}, Heber et al., 2007; Jackson et al., 2013a). The initial ^{3}He/^{22}Ne in the channel is 1.5; for the purpose of studying the kinetic fractionation process concentrations are arbitrary but assumed to be 0.075 ppm for ^{3}He, and 0.05 ppm for ^{22}Ne in the channel (bulk). Equations 1, 2 and 3 are solved numerically using a Crank-Nicholson finite difference method. The solver was tested against the exact solution to a constant surface diffusion problem (Supplementary Fig. S3) and found to be in excellent agreement.

4. Results

Diffusion profiles produced in representative simulations testing different He and Ne diffusivities are shown in Fig. 6 for a series of time steps; simulation assumptions are detailed in the figure caption. In general, ^{3}He concentrations decrease in the dunite-hosted melt as they increase in the wallrock; ^{22}Ne concentrations increase in the wallrock (and decrease in the channel) much more slowly. The simulations suggest that kinetic fractionation may efficiently modulate the ^{3}He/^{22}Ne of the depleted mantle within diffusive length scales around dunite channels beneath mid-ocean ridges. We emphasize that heavier noble gases will not be fractionated from one another by melt migration because of their slower diffusivities.

Dunite channels are thought to form a repeating network of dunite-wallrock units in triangular melting regions beneath mid-ocean ridges (Fig. 2a; also see Supplementary Figure S4). Material in the melt triangle ultimately becomes lithosphere as it cools and advects away from the ridge axis due to corner flow. To estimate He and Ne concentrations and the average ^{3}He/^{22}Ne of the depleted mantle lithosphere, we input our simulation results into a melt triangle model assuming a 45-45-90 geometry and triangle depth of 70km directly beneath the ridge axis. Asthenospheric mantle forms new lithosphere that advects laterally away from the ridge axis as it crosses the solidus owing to conductive cooling. The upwelling rate is assumed to be uniform across the base of the triangle; melting columns near the corners of the triangle experience less upwelling than columns near the center because they are cooled and rotated into the direction of seafloor spreading at greater depths. When a parcel of mantle reaches the lithosphere-asthenosphere boundary, it "freezes in" some fraction of trapped melt; here we assume 0.2% melt is frozen in the dunite, CBL and wallrock (e.g., Sundberg et al., 2010). Depending on the choice of diffusion coefficients, CBL thickness, and diffusive pathway (i.e., permeable vs. impermeable CBL), our models produce a regassed mantle lithosphere with a ^{3}He/^{22}Ne ratio ~2-6× greater than the initial source value (Fig. 7a) and noble gas concentrations ~2-3 orders of magnitude below initial source values (Fig. 7b;c).

Oceanic lithosphere eventually passes through subduction zones where it can form a high ^{3}He/^{22}Ne MORB source, provided high ^{3}He/^{22}Ne mantle lithosphere is not fully degassed after subduction. The mantle's *heavy* noble gas (Ar-Xe) budget appears to be dominated by a recycled atmospheric component likely related to subduction of hydrothermally altered slab (e.g., Holland

and Ballentine, 2006; Parai and Mukhopadhyay, 2015; Smye et al., 2017), but recycling of an atmospheric *light* noble gas (He-Ne) component has not had a demonstrable impact on mantle budgets. Because atmospheric ^{3}He/^{22}Ne in sediment and altered basalt is ~0, if surface-influenced portions of subducting slabs did not lose atmospheric Ne and He in subduction zones, the MORB source would have a lower ^{3}He/^{22}Ne than primordial sources (e.g., Tucker and Mukhopadhyay, 2014). Shallow regions of subducting lithosphere presumably lose noble gases and other volatiles from pore fluids (Sumino et al., 2010) and hydrous phases (Jackson et al., 2013b; Kendrick et al., 2011; 2018) owing to cracking, heating and prograde metamorphism (e.g., Chavrit et al., 2016; Holland and Ballentine, 2006; Staudacher and Allègre, 1988; Smye et al., 2017). Isotopic, lithologic, and geospeedometric evidence suggests hydration beneath oceanic spreading centers is limited to approximately the upper km of the mantle section (Dygert and Liang, 2015; Dygert et al., 2017; Gregory and Taylor, 1981; Rospabe et al., 2017). Seismic reflection-refraction data suggest hydration of old lithospheric slabs is restricted to the upper 10km of mantle lithosphere (e.g., Han et al., 2016; Van Avendonk et al., 2011). Thus, it is reasonable to expect that most mantle lithosphere that passes through subduction zones is not hydrated, and that mantle-derived noble gases in thick lithospheric slabs pass through subduction zones, allowing them to impart their high ^{3}He/^{22}Ne signature on the convecting mantle.

5. A MORB mantle mixing model

Regassed mantle has He concentrations ~2-3 orders of magnitude lower than undegassed mantle that did not experience partial melting and kinetic fractionation beneath mid-ocean ridges (Figs. 7b,c). Thus, equal mixtures of undegassed and diffusively regassed mantle will have ^{3}He/^{22}Ne similar to undegassed mantle. In order to form a MORB source with high ^{3}He/^{22}Ne, most of the MORB mantle must have cycled through the global mid-ocean ridge system at least once, and mantle mixing must be sufficiently slow to produce a large reservoir of unmixed, regassed mantle. Volumetrically smaller mixtures of regassed and undegassed mantle may form low ^{3}He/^{22}Ne component within the MORB source.

Here we adopt the methodology of Gonnermann & Mukhopadhyay (2009) (their analytical box model) to consider the formation of a high ^{3}He/^{22}Ne MORB source. This model differs from their numerical simulations in two fundamental ways: (1) we make no attempt to model the evolution of the OIB source, which we consider to have been partially isolated from the MORB source throughout geologic time (e.g., Caracausi et al., 2016; Mukhopadhyay, 2012; Mundl et al., 2017; Pető et al., 2013; Rizo et al., 2016), (2) we do not consider or advocate for a lower mantle that is isolated from the upper mantle. On the contrary, our results suggest that the MORB source has dominated the volume of the upper and lower mantle throughout geologic time (see Section 8).

Within the MORB source there are high and low ^{3}He/^{22}Ne reservoirs made up of components. The low ^{3}He/^{22}Ne reservoir is composed of "undegassed" component that experiences some mixing with subducted, high ^{3}He/^{22}Ne components; the high ^{3}He/^{22}Ne reservoir is composed of many "regassed" components that are partially consumed by mixing with low ^{3}He/^{22}Ne component,

$$\frac{M_d}{M_0} = \frac{N}{t}\int_0^t e^{(s-t)/\tau} ds \qquad (7).$$

M_d is the mass of depleted, high ^{3}He/^{22}Ne component produced at time s remaining in the MORB source at time t, M_0 is the initial mass of the MORB source, N is the number of MORB source masses processed through the global mid-ocean ridge system over time t, and τ is a characteristic mantle mixing timescale. Integrating over geologic time,

$$\frac{M_d}{M_0} = 1 - \frac{N}{t}\tau - \frac{N}{t}\tau e^{-t/\tau} \quad (8).$$

This model assumes that the MORB source was initially composed of a single body of primordial, low ^{3}He/^{22}Ne (~1.5) material that is consumed as high ^{3}He/^{22}Ne components are produced to form the high ^{3}He/^{22}Ne reservoir. The low ^{3}He/^{22}Ne reservoir in the MORB source melts preferentially because it is more fusible than the depleted, high ^{3}He/^{22}Ne reservoir (Fig. 8a).

Because He and Ne concentrations in regassed, high ^{3}He/^{22}Ne mantle are low, mixing between low and high ^{3}He/^{22}Ne components enlarges the low ^{3}He/^{22}Ne reservoir and shrinks the high ^{3}He/^{22}Ne reservoir. For a given N, a long τ produces a relatively large high ^{3}He/^{22}Ne reservoir; a short τ produces a relatively large low ^{3}He/^{22}Ne reservoir. Tradeoffs between characteristic mantle mixing timescales (τ) and the number of mantle masses fluxed through the global mid-ocean ridge system (N) are shown in Fig. 8b for cases where the MORB source is composed of 90±10% high ^{3}He/^{22}Ne reservoir. This large extent of degassing can be accounted for by 4-9 MORB source masses being cycled through the global mid-ocean ridge system (e.g., Coltice et al., 2009; Tolstikhin et al., 2014), which corresponds to a τ value range of ~0.4-1 Gyr (Fig. 8b). Smaller N values require longer characteristic mantle mixing timescales. MORB mantle mixing timescales have been constrained using pseudochrons within the Rb-Sr, Sm-Nd, and U-Pb isotopic systems (Donnelly et al., 2004); mantle mixing timescales derived from these pseudochrons are roughly consistent with τ values explored here (~0.3 Gyr vs. ~0.4-1 Gyr). In scenarios where MORB source mixing timescales are shorter, volatile extraction by volcanism is inefficient because volatile-poor components within the MORB source are homogenized with and dominated by more volatile-rich components (Fig. 8; Gonnermann and Mukhopadhyay, 2009). Thus, the long MORB source mixing timescales suggested by the ^{3}He/^{22}Ne system are corroborated by observed depletion of radiogenic Xe isotopes and ^{3}He relative to radiogenically produced ^{4}He in the MORB source (see below, e.g., Class and Goldstein, 2005; Coltice et al., 2009; Davies, 2011; Parai et al., 2015; Porcelli and Elliot, 2008; Tolstikhin et al., 2014; Tucker et al., 2012).

6. Consistency of our model with other noble gas systems and mantle dynamics

6.1 Constraints on MORB source degassing from long-lived Xe and ^{3}He/^{4}He systematics

For regassed, high ^{3}He/^{22}Ne mantle to be a significant reservoir within the MORB source, degassing of primordial volatiles from the MORB mantle must have been extensive (>96%) owing to the low overall gas contents of regassed mantle. Evidence for extensive degassing of primordial volatiles comes from recent studies that demonstrate the MORB mantle contains very little Pu-derived Xe compared to U-derived Xe. Because Pu-derived Xe was produced before U-derived Xe, this observation implies >99% degassing of the MORB source primordial volatile budget throughout geologic time (e.g., Tolstikhin et al., 2014; Tucker et al., 2012; Parai et al., 2015). Similar extents (>99%) of degassing are implied by estimates of initial mantle ^{3}He concentration and present-day MORB source ^{3}He/^{4}He systematics (e.g., Class and Goldstein, 2005; Porcelli and Elliot, 2008). Depending upon the isotopic system, estimates of timescales for achieving 99% MORB source degassing range from ~1.5Gyr to all of geologic time (e.g., Tolstikhin et al., 2014 and references therein). The Xe system suggests extensive early degassing followed by a longer period of more measured degassing. Extensive early degassing could have been produced by vigorous Hadean volcanism, potentially superimposed on degassing associated with a Moon-forming giant impact. However, provided that He was fractionated from Ne around dunite channels for most of geologic time, no impact-related degassing is required by our model.

6.2 Consistency of extensive MORB source degassing with dynamic models and Earth's ^{40}Ar budget

Canonical estimates of Earth's ^{40}Ar budget place ~50% of all ^{40}Ar atoms in the mantle (Hart et al., 1985; Allègre et al., 1996). Because ^{40}Ar is strictly produced by the decay of ^{40}K and ^{40}K has a 1.25 Gyr half-life, this implies >50% degassing of the mantle's primordial volatile component. Within a purely whole mantle convection model framework, 50% degassing of ^{40}Ar is achieved in dynamic models at ~60% to 93% primordial element degassing, depending on Earth's thermal history (Brandenburg et al., 2008; Phipps Morgan, 1998; van Keken and Ballentine, 1999). This range of primordial element degassing is less than the >96% required by the ^{3}He/^{22}Ne system within our model and the ^{3}He/^{4}He and Xe isotope systems. Within the dynamic models, higher MORB source primordial volatile degassing extents would be associated with 50% retention of ^{40}Ar if depth of melting scaled with mantle potential temperature and/or if a portion of the mantle ^{40}Ar budget were contained in a region separate from the MORB source (e.g., Ballmer et al., 2017; Kellog et al., 1999; Mukhopadhyay, 2012; Tolstikhin et al., 2006). Unambiguous evidence for mantle reservoirs isolated from the MORB source throughout geologic time is given by the isotopic systematics of OIBs (Caracausi et al., 2016; Mukhopadhyay, 2012; Mundl et al., 2017; Pető et al., 2013; Rizo et al., 2016), providing at least one "hidden reservoir" to balance Earth's ^{40}Ar budget. However, we note that uncertainties in the mantle ^{40}K budget are significant, potentially eliminating any need to host ^{40}Ar in hidden mantle reservoirs (e.g., Lassiter, 2004). Thus, the requirement for large extents of MORB source primordial volatile degassing is consistent with the ^{40}Ar distribution in the Earth.

6.3 MORB source ^{3}He/^{4}He and ^{4}He/^{40}Ar

The processes that cause kinetic fractionation of He from Ne around dunite channels in the MORB source will also fractionate He from U and Th. U and Th decay to produce ^{4}He; MORB melts and subcontinental lithospheric mantle have ^{3}He/^{4}He of $\lesssim 8R_A$ (R_A being the atmospheric ratio), far below the closed system value for a primitive mantle and suggesting long term depletion of ^{3}He relative to U+Th in the MORB source (e.g., Allègre et al., 1983; Day et al., 2005). Because U and Th diffusion rates are sluggish, our kinetic fractionation model would be expected to enrich the MORB mantle in ^{3}He relative to U+Th during melt migration beneath mid-ocean ridges, in apparent contradiction with a low ^{3}He/^{4}He MORB source. However, we invoke long-term subduction of oceanic crust along with high ^{3}He/^{22}Ne mantle lithosphere to form a high ^{3}He/^{22}Ne MORB source. Because U and Th are highly incompatible during mantle melting and the overwhelming majority of magmatic He is degassed, subducted lithosphere has a strongly elevated U+Th/He ratio. We modeled the evolution of ^{3}He/^{4}He in the depleted mantle assuming a fraction of U+Th in the subducted oceanic crust is mixed back into the high ^{3}He/^{22}Ne MORB source (Supplementary Figures S5a;d). Our models suggest the regassed high ^{3}He/^{22}Ne mantle quickly recovers the signature low ^{3}He/^{4}He ratio associated with the MORB source by production of ^{4}He (Supplementary Figure S5).

The ^{4}He/^{40}Ar ratio of the mantle is similar to or greater than values calculated assuming closed system accumulation of ^{4}He and ^{40}Ar due to the decay of U+Th and ^{40}K (e.g., Burnard, 2004; Honda and Patterson, 1999). Like He, U and Th, He may be expected to be fractionated from Ar around dunite channels owing to relatively sluggish diffusion of Ar in mantle materials, creating a high ^{4}He/^{40}Ar ratio regassed mantle that is inconsistent with some observations. However, the production rate of ^{4}He and ^{40}Ar (by U+Th and ^{40}K decay) is sufficiently fast such that the elevated ^{4}He/^{40}Ar of the regassed mantle is overwhelmed by decay of U+Th+K in the crustal component of the subducted slab. Models presented in Supplementary Figures S5b;e suggest that after a fractionation event, the high ^{3}He/^{22}Ne MORB source quickly recovers ^{4}He/^{40}Ar values consistent with observations.

7. Evidence for kinetic fractionation of ^{3}He from ^{22}Ne

The most convincing verification of our kinetic fractionation model would come from direct observation of noble gas concentration gradients around dunite channels in ophiolites. We believe direct observation is unlikely because (1) serpentinization upon exhumation of mantle lithosphere may overprint preexisting noble gas signatures (Kendrick et al., 2011; 2018; Sumino et al., 2010), and (2) subsolidus reequilibration should be rapid enough to homogenize diffusion profiles over timescales relevant to lithospheric cooling.

Evidence for kinetic fractionation may alternatively be observed in basalts and mantle xenoliths. Near-fractional partial melting of the mantle, concomitant with transport-produced kinetic fractionation, will form mantle sources depleted in incompatible trace elements (e.g., Johnson et al., 1990; Sobolev and Shimizu, 1993) with elevated ^{3}He/^{22}Ne. Parent isotopes are fractionated from daughter isotopes by mantle melting events, such that ancient, long-term depletion is recorded by radiogenic isotope ratios in abyssal peridotites unaffected by significant overprinting from melt impregnation (e.g., Mallick et al., 2014; Warren et al., 2009). Thus, we expect a correlation between ^{3}He/^{22}Ne and indices of long-term depletion such as radiogenic isotopes and incompatible trace element ratios. These correlations are observed within ^{87}Rb-^{87}Sr and ^{147}Sm-^{143}Nd isotope systems, and in La/Sm ratios in MORBs from around the world (Figure 9; also see Tucker and Mukhopadhyay, 2014).

Whether these trends represent mixtures of basalts from more and less depleted sources or simply variations in the extent of source depletion is uncertain. Preservation of La/Nd-^{3}He/^{22}Ne and radiogenic isotope-^{3}He/^{22}Ne correlations requires that basalts subducted along with high ^{3}He/^{22}Ne mantle lithosphere lose some of their enrichment before being mixed back into the MORB source (e.g., Gonnermann and Mukhopadhyay, 2009), likely to continental crust, or that basaltic crust is partly decoupled from mantle lithosphere during subduction. If unmodified lithosphere were subducted back into MORB mantle, then MORB mantle would not be net depleted and the correlations shown in Figure 9 would not be preserved.

Mantle peridotite xenoliths are typically residues of partial melting and unaltered specimens can be obtained for analysis. They may faithfully record kinetic fractionation of ^{3}He from ^{22}Ne (or the lack thereof) depending on their melting history. Available data on the noble gas abundances in peridotite xenoliths are limited, but exhibit ^{3}He/^{22}Ne systematics consistent with trends among basalts. Hotspot-sourced xenoliths (Fig. 1d) have relatively low ^{3}He/^{22}Ne, slightly elevated relative to their basaltic counterparts, as would be expected in a kinetic fractionation scenario. Subcontinental samples have greater variations in ^{3}He/^{22}Ne (Fig. 1e). Central European subcontinental lithospheric mantle (SCLM) is relatively low in ^{3}He/^{22}Ne and may be affected by a mantle plume (Builkin et al., 2005), but xenoliths from the Patagonian backarc have high and variable ^{3}He/^{22}Ne (Jalowitski et al., 2016). Peridotites from arc environments that experienced high extents of partial melting are expected to have high ^{3}He/^{22}Ne ratios owing to repeated or prolonged kinetic fractionation events, consistent with the Patagonian xenoliths. However, because ^{3}He/^{22}Ne in SCLM xenoliths may be overprinted by interaction with metasomatic fluids/magmas, it is not clear which volatile sources are represented in SCLM xenolith compositions. The picture is further muddied by estimates of SCLM ^{3}He/^{22}Ne from well gas data which suggest ratios of 0.1-1.9 (Ballentine, 1997). However, these well gases are from crustal reservoirs with small mantle-derived components. Our model predicts a secular increase in the average MORB source $^{3}He/^{22}Ne$ throughout geologic time. Thus, we may anticipate that ancient SCLM has a $^{3}He/^{22}Ne$ closer to Earth's primordial value than younger SCLM. We encourage additional efforts to characterize the systematics of SCLM $^{3}He/^{22}Ne$.

8. Implications

Because the MORB mantle has an elevated $^{3}He/^{22}Ne$, the entire MORB source must have experienced at least one melt extraction and kinetic fractionation event. According to our simulations, each event removes 96-99% of the He and 98-99.7 of the Ne from the mantle source (Figure 7). Subsequent melt extraction events will further deplete the MORB source. Thus, our models imply the MORB mantle is at least 96% degassed with respect to its primordial He and 98% degassed with respect to its primordial Ne, in agreement with previous estimates based on $^{3}He/^{4}He$ and Xe isotopes (e.g., Class and Goldstein, 2005; Davies, 2011; Porcelli and Elliott, 2008; Tolstikhin et al., 2014; Tucker et al., 2012). The near complete extraction of He and Ne likely extends to the full suite of Earth's primordial volatiles, given their similar behavior upon mantle melting (Aubaud et al., 2005; Heber et al., 2007; Jackson et al., 2013a; Keppler et al., 2003). This suggests that the primordial volatile content of the convecting mantle has been essentially lost to Earth's surface and that the modern volatile content of the mantle is dominated by recycling processes.

Kinetic fractionation around dunite channels may modulate the ratio of any relatively fast and slow diffusing element pairs in the depleted mantle (e.g., H/C, He/C, H/N, He/(U+Th)). H/C is high in the most H_2O depleted basalts (Hirschmann and Dasgupta, 2009), consistent with kinetic fractionation of light H from relatively heavy C around dunite channels. However, any element that is reintroduced to the mantle by subduction will have a more complicated cycling history than ^{3}He/^{22}Ne, i.e., kinetic fractionation of many element pairs may not be observable in the compositions of erupted basalts due to recycling and mixing.

Seismic tomography suggests subducted slabs pass through the mantle transition zone (e.g., Grand, 2002; Fukao and Obayashi, 2013; Kárason and van der Hilst, 2000), which must be balanced by complementary mass transport from the lower to upper mantle (e.g., Forte et al., 2010). The timing associated with the onset of mantle convection across the transition zone, however, is unclear (e.g., Allègre, 1997; Davies, 1995). Our model requires convection across the transition zone throughout geologic history so that the low ^{3}He/^{22}Ne ratios of undegassed lower mantle do not dominate the modern day convecting mantle. Because mixtures of undegassed and regassed mantle will have low ^{3}He/^{22}Ne ratios, the preservation and prevalence of the high ^{3}He/^{22}Ne MORB source suggests the regions of the lower mantle that participate in MORB mantle magmatism have already passed through the global mid-ocean ridge system at least once, i.e., mantle convection is not and has not been layered about the transition zone for most of geologic history. To preserve the high ^{3}He/^{22}Ne MORB source, exchange of noble gases between low ^{3}He/^{22}Ne, high ^{3}He/^{4}He reservoirs and the depleted mantle must be limited, as suggested by Xe and W isotope systematics (e.g., Caracausi et al., 2016; Mukhopadhyay, 2012; Mundl et al., 2017; Pető et al., 2013; Rizo et al., 2016). This does not preclude mass exchange of less volatile elements, or exchange of volatiles between subducted materials and the OIB and MORB sources (Parai and Mukhopadhyay, 2015). Lowest and highest ^{3}He/^{22}Ne MORB mantle components likely reside in the lower mantle, where high viscosities impede mechanical stirring.

If mixing is relatively rapid in the upper mantle, mixing timescales for the ^{3}He/^{22}Ne system predominantly reflect rates of mass exchange between the upper and lower mantle.

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FIGURE CAPTIONS

Figure 1. ^{3}He/^{22}Ne ratios of ocean island basalts (a), plume-influenced MORBs (b), MORBs (c), hotspot sourced mantle xenoliths (d), and subcontinental lithospheric mantle (e). ^{3}He/^{22}Ne for all samples are calculated using methods detailed in the electronic supplement. Data used to calculate ratios for subaerial samples are exclusively from crush steps in order to minimize any contribution from a cosmogenic component. Shown in parentheses are the standard deviation (mean) and median absolute deviation (median). Data source references are presented in the Electronic Supplement; the compilation is downloadable from the electronic repository. Sample localities are the following; OIBs: Galapagos, Samoa, Iceland, Reunion, Hawaii; plume-influenced MORBs: Azores, Discovery, Shona, East Pacific Rise, Galapagos Ridge, Southeast Indian Ridge; MORBs: Mid Atlantic Ridge; East Pacific Rise; Chile Ridge, Southwest Indian Ridge; hotspot sourced xenoliths: Hawaii, Mt. Cameroon, Kerguelen, Biu Plateau, Reunion, Samoa; subcontinental lithospheric peridotites: Szentbekalla (Hungary), Dreiser Weiher (Germany), Laguna Ana; Laguna Timone; Governador Gregores (Patagonia). In all cases, we deferred to the interpretations of our data sources to assign a sample type, which were assigned based on ^{3}He/^{4}He and radiogenic isotope ratios.

Figure 2. Schematic of a dunite channel network in a triangular melting region beneath a mid-ocean ridge (a). Arrows show paths of solid advection. Partial melts are focused and extracted in tabular dunite bodies (green). (b) Close-up showing dunite-wallrock relationships. Between the dunite and harzburgite wallrock is a compacting boundary layer with a low melt fraction. Note the harzburgite wallrock and dunite channel host melts with distinct compositions, in local equilibrium with their host matrix.

Figure 3. Measured rates of He and Ne diffusion in the olivine lattice (a) and silicate glasses (b); He diffusion along olivine aggregate grain boundaries (c); and relative diffusion rates of He and Ne as a function of temperature (d) for experiments from three laboratories. Glass data are extrapolated from lower temperature experimental observations through the glass-liquid transition, and are from simple compositional systems which may differ structurally from basaltic glasses.

Figure 4. An Arrhenius plot showing data collected in a bulk degassing experiment on a proton irradiated fragment of San Carlos olivine, and Arrhenius parameters inverted from the data. He and Ne data were collected simultaneously. We estimate an effective spherical radius of 330μm for this grain (see Supplementary Figure S4), yielding preexponentials of $8.80 \times 10^{-7}{}^{+7.89\times10^{-7}}_{-4.16\times10^{-7}}$ for He and $1.25 \times 10^{-6}{}^{+1.70\times10^{-6}}_{-7.21\times10^{-7}}$ for Ne.

Figure 5. Schematic illustrating our model setup. Vertical advection in the harzburgite wallrock and CBL is not shown as it provides a reference frame for our solutions. Total upwelling distance is 70km. Diffusion in the vertical dimension is neglected.

Figure 6. Representative results from simulations assuming different diffusion coefficients and a 6m thick compacting boundary layer. $^{3}He/^{22}Ne$ is the ratio of the regassed lithosphere after compaction of trapped melt to a residual value of 0.2% (see Section 4).

Figure 7. $^{3}He/^{22}Ne$ regassed in mantle lithosphere relative to its initial source value from simulations assuming a permeable compacting boundary layer (solid lines) and an impermeable layer (dashed lines) as a function of compacting boundary layer thickness (a). Average He (b) and Ne (c) concentrations in the mantle lithosphere relative to initial mantle source concentrations. The extent of depletion of the regassed mantle relative to its undegassed mantle source is estimated assuming a 10% extent of melting.

Figure 8. (a) Cartoon illustrating the formation of a high $^{3}He/^{22}Ne$ MORB source according to the model of Gonnermann and Mukhopadhyay, 2009 (Eqs. 7 & 8). The high $^{3}He/^{22}Ne$ reservoir, composed of many high $^{3}He/^{22}Ne$ components formed at different times, is produced by partial melting and kinetic fractionation of material originating from a primordial, low $^{3}He/^{22}Ne$ reservoir. Mixing between the low and high $^{3}He/^{22}Ne$ reservoirs shrinks the high $^{3}He/^{22}Ne$ reservoir and enlarges the low $^{3}He/^{22}Ne$ reservoir. If mixing is sufficiently slow, the high $^{3}He/^{22}Ne$ reservoir grows through time, as is shown here. (b) Tradeoff between the number of MORB source masses fluxed through the global mid-ocean ridge system (N) and the characteristic mantle mixing timescale (τ) needed to produce a MORB source composed of 90% of regassed, high $^{3}He/^{22}Ne$ mantle (solid line) according to Eq. 8. Dashed lines show cases with a MORB source composed of 10% more or less high $^{3}He/^{22}Ne$ mantle. The black box shows the range of permissible values according to Xe isotope systematics (e.g., Coltice et al., 2009; Tolstikhin et al., 2014).

Figure 9. Variations among $^{3}He/^{22}Ne$ and several indices of depletion; chondrite normalized La/Nd (a); $^{204}Pb/^{206}Pb$ (b); $^{144}Nd/^{143}Nd$ (c); $^{86}Sr/^{87}Sr$ (d). La/Nd, $^{144}Nd/^{143}Nd$, and $^{86}Sr/^{87}Sr$ show

good correlations between ^{3}He/^{22}Ne and extent of source depletion, consistent with our model which predicts that samples with the highest ^{3}He/^{22}Ne should be the most depleted. Data used to prepare this figure are presented in the electronic repository; references are listed in the Electronic Supplement.

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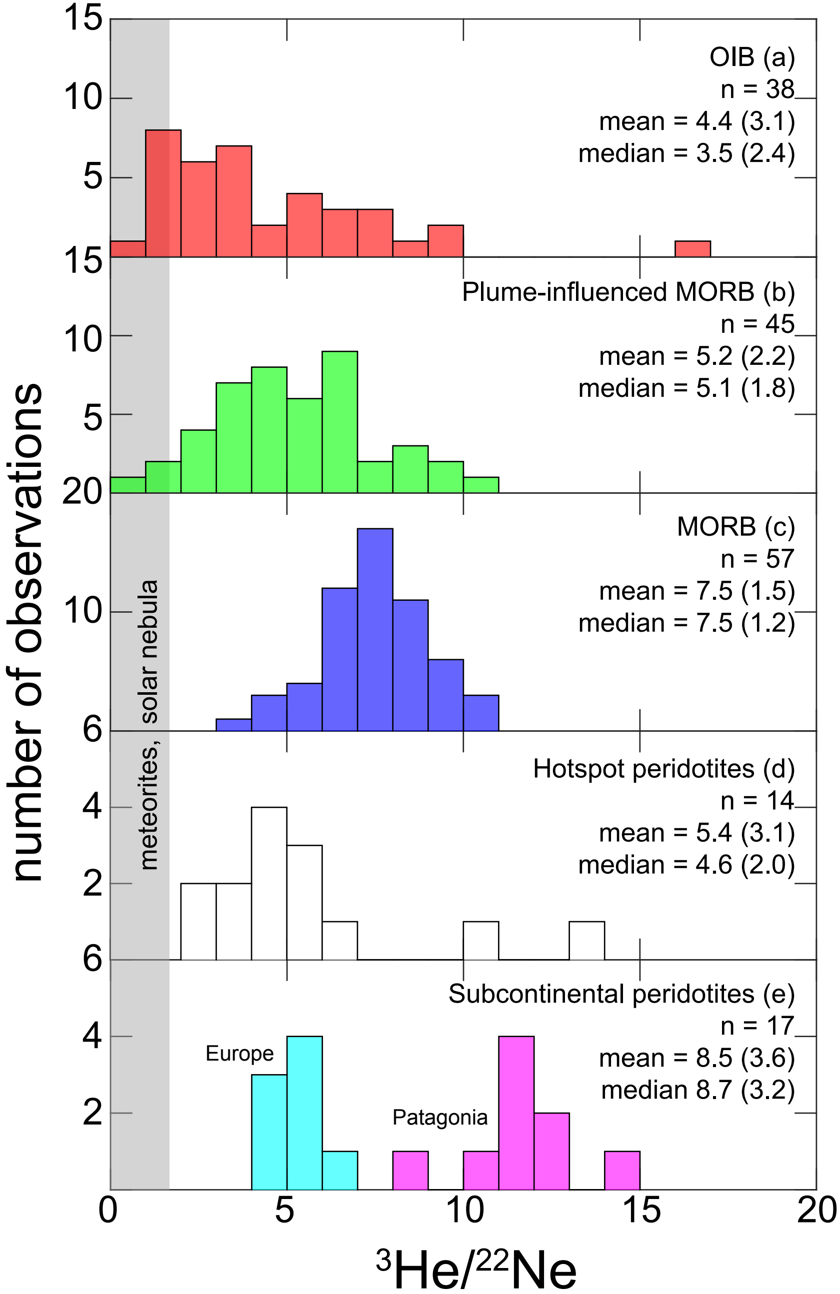
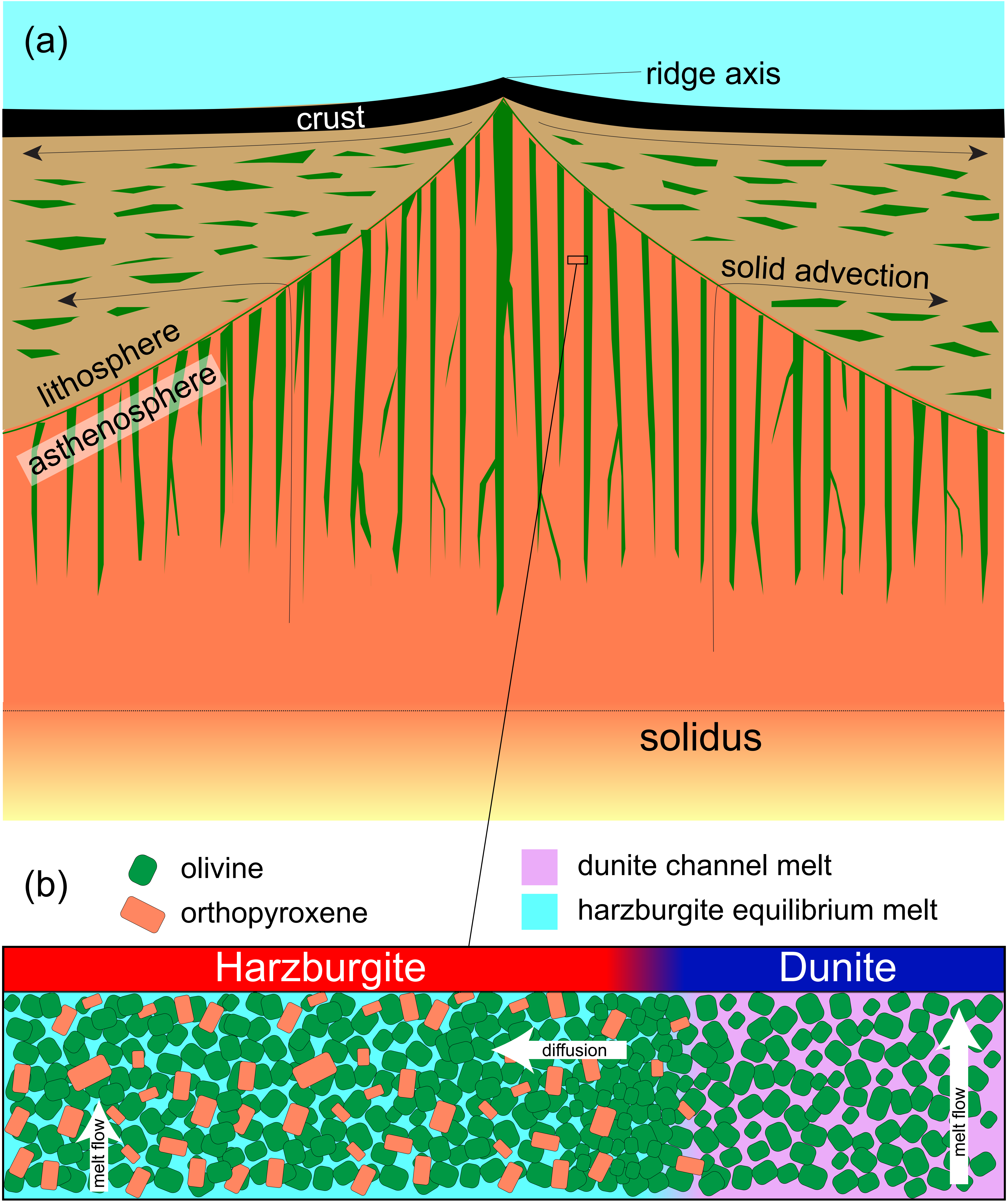
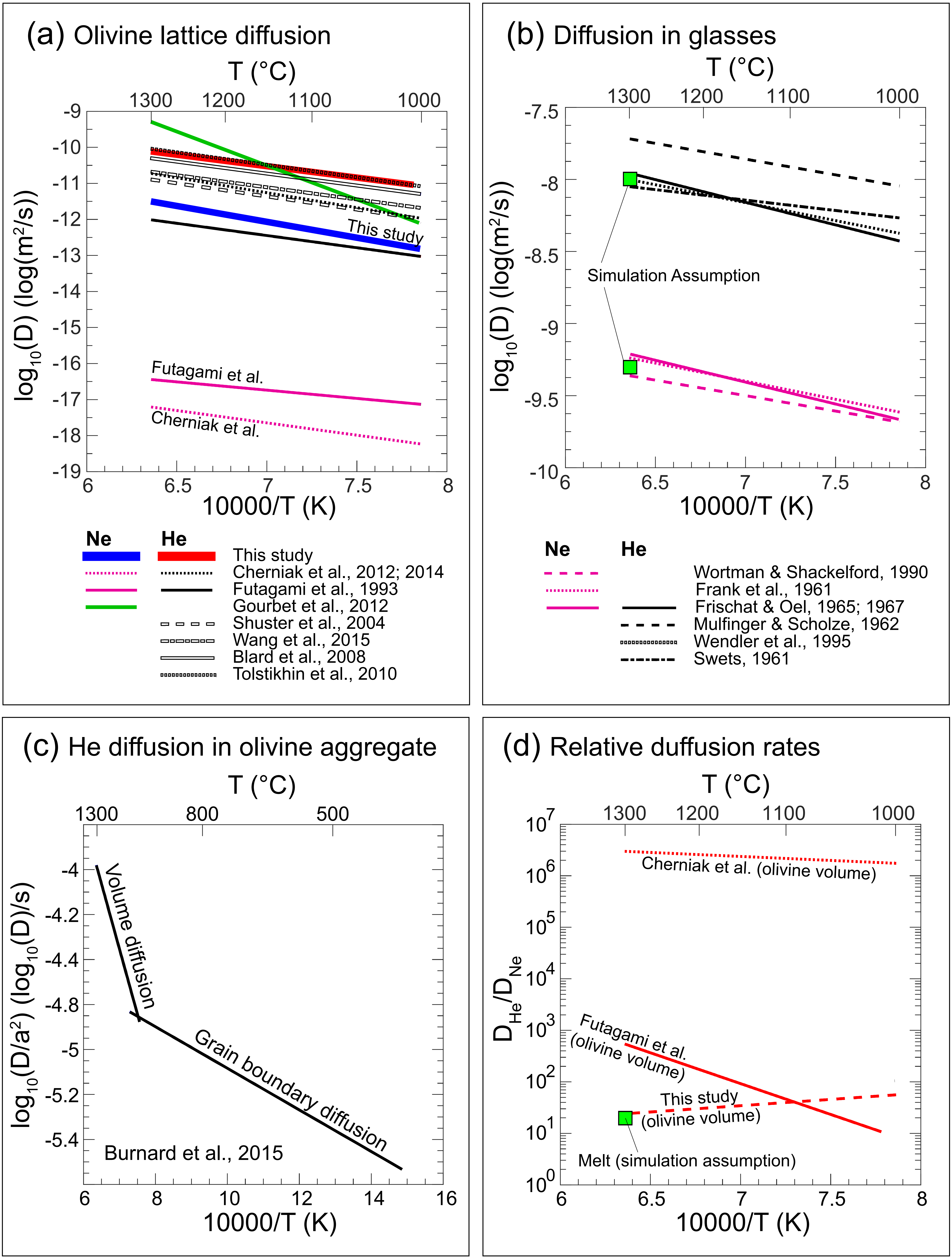
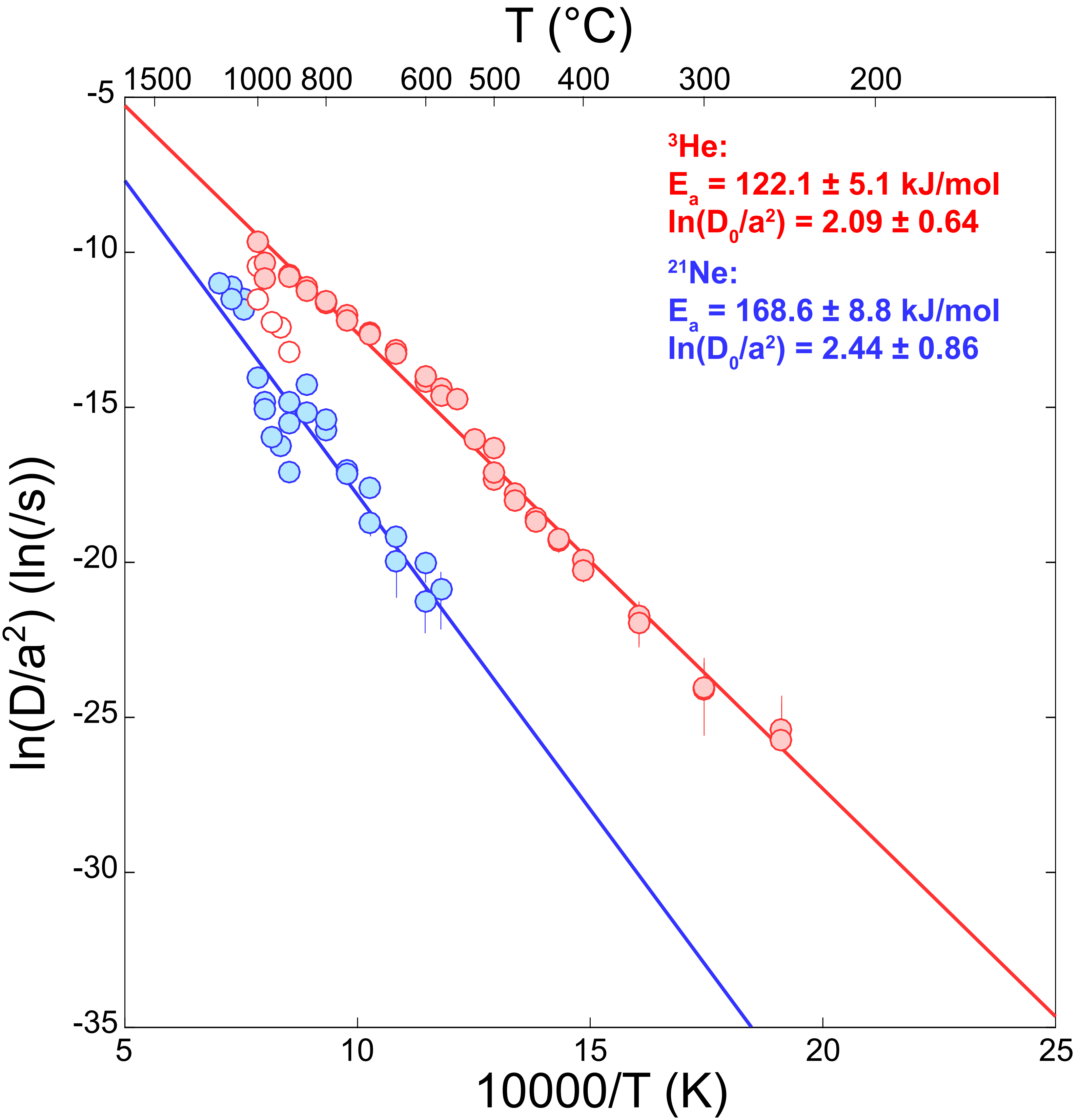
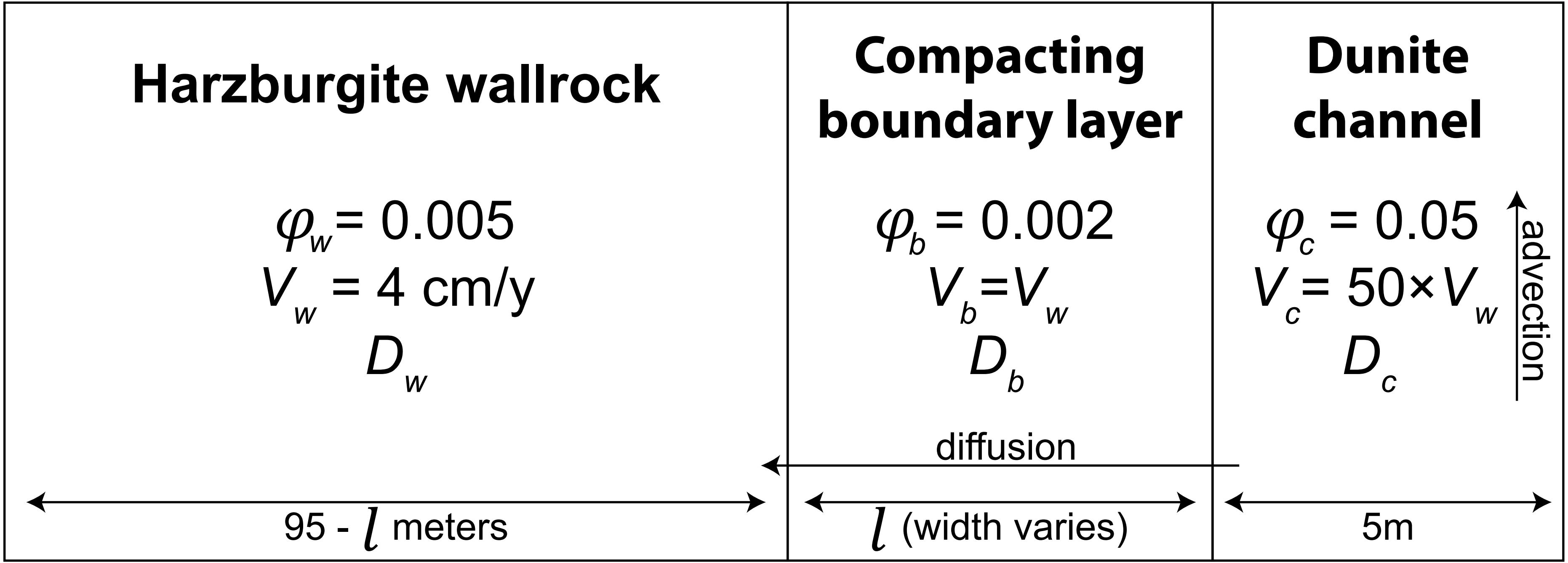
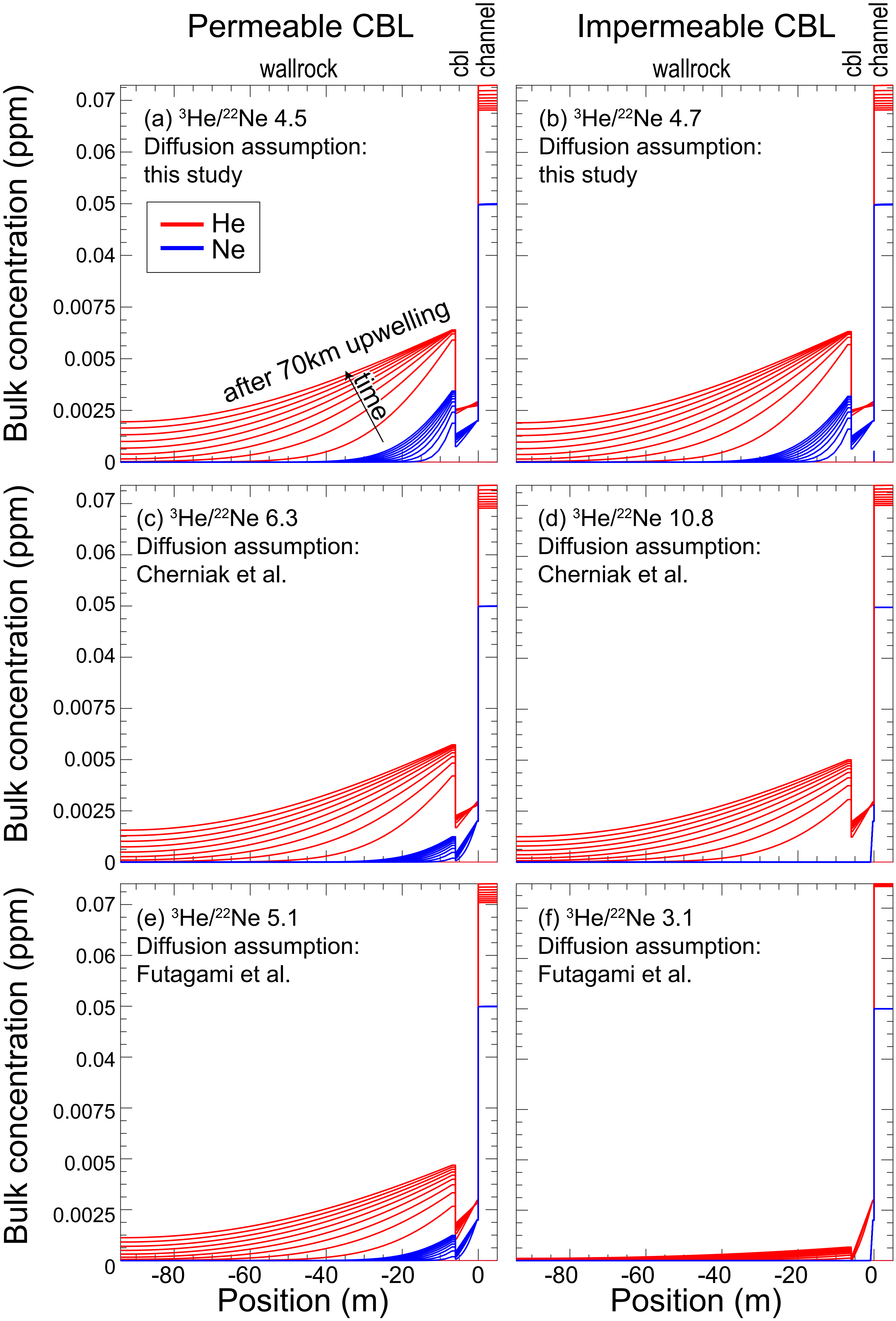

number of observations
OIB (a)
n = 38
mean = 4.4 (3.1)
median = 3.5 (2.4)
Plume-influenced MORB (b)
n = 45
mean = 5.2 (2.2)
median = 5.1 (1.8)
MORB (c)
n = 57
mean = 7.5 (1.5)
median = 7.5 (1.2)
Hotspot peridotites (d)
n = 14
mean = 5.4 (3.1)
median = 4.6 (2.0)
Subcontinental peridotites (e)
n = 17
mean = 8.5 (3.6)
median 8.7 (3.2)
Europe
Patagonia
meteorites, solar nebula
15
10
5
15
10
5
20
10
6
4
2
6
4
2
0
5
10
15
20
$^3He/^{22}Ne$

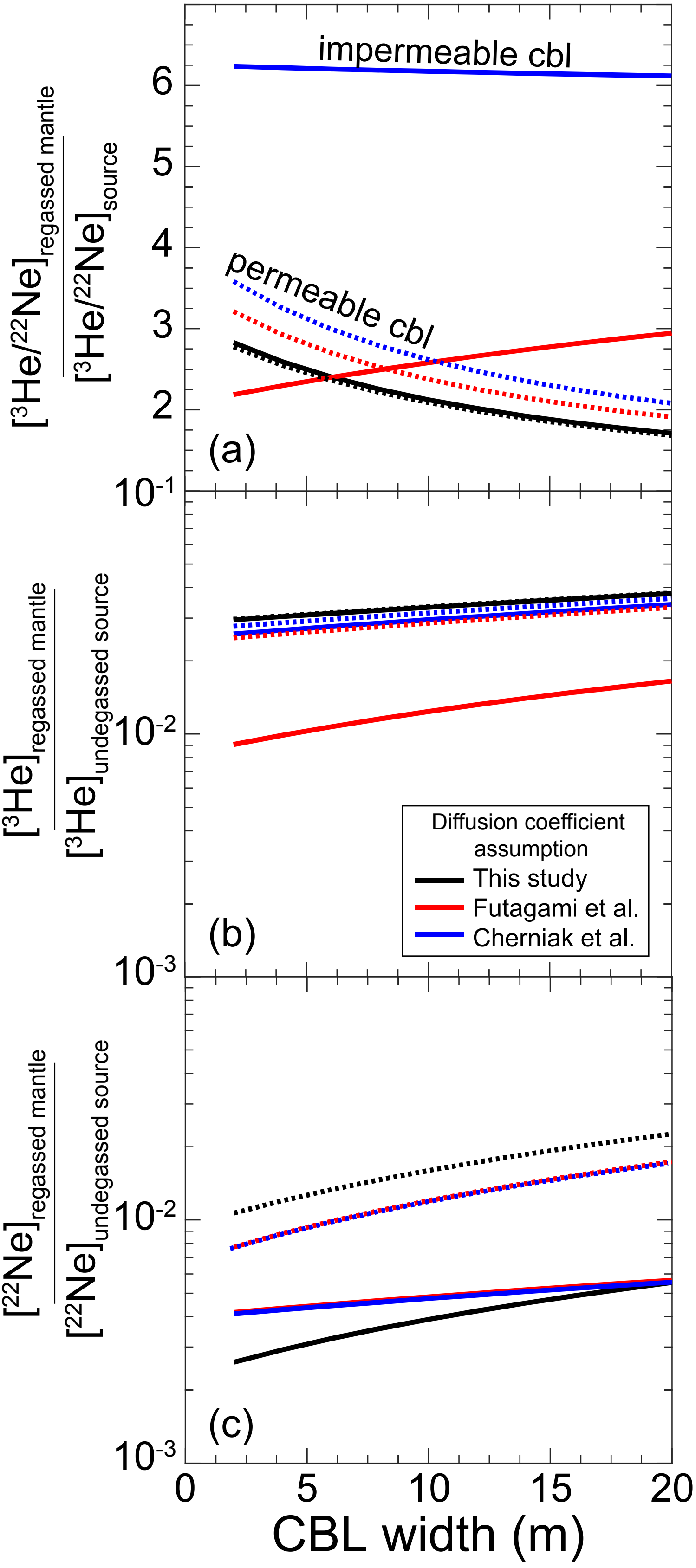

(a)
ridge axis
crust
solid advection
lithosphere
asthenosphere
solidus
(b)
olivine
orthopyroxene
dunite channel melt
harzburgite equilibrium melt
Harzburgite
Dunite
diffusion
melt flow
melt flow

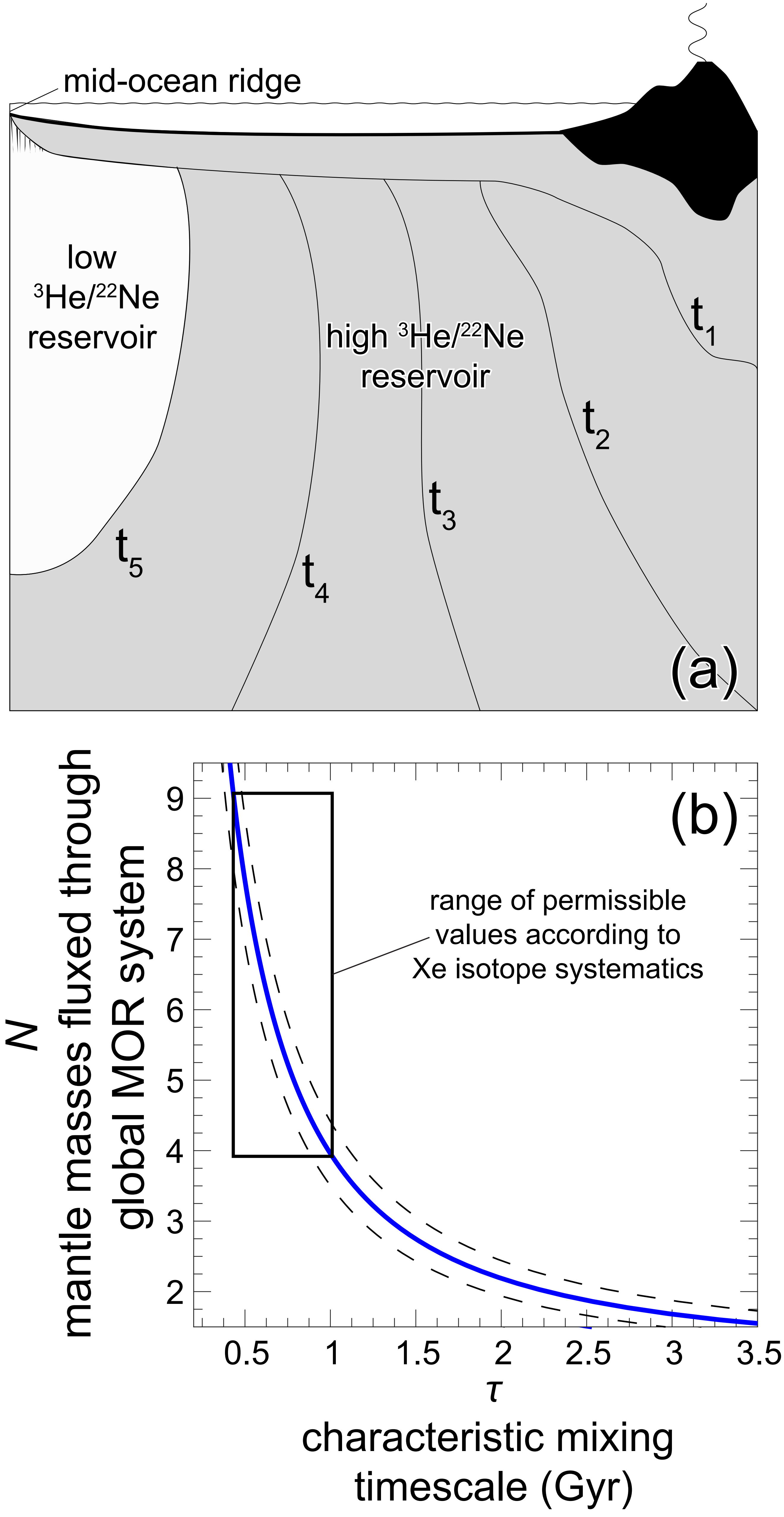

(a) Olivine lattice diffusion
T (°C)
1300
1200
1100
1000
$\log_{10}(D)$ (log(m²/s))
-9
-10
-11
-12
-13
-14
-15
-16
-17
-18
-19
This study
Futagami et al.
Cherniak et al.
6
6.5
7
7.5
8
10000/T (K)
Ne
He
This study
Cherniak et al., 2012; 2014
Futagami et al., 1993
Gourbet et al., 2012
Shuster et al., 2004
Wang et al., 2015
Blard et al., 2008
Tolstikhin et al., 2010
(b) Diffusion in glasses
T (°C)
1300
1200
1100
1000
$\log_{10}(D)$ (log(m²/s))
-7.5
-8
-8.5
-9
-9.5
-10
Simulation Assumption
6
6.5
7
7.5
8
10000/T (K)
Ne
He
Wortman & Shackelford, 1990
Frank et al., 1961
Frischat & Oel, 1965; 1967
Mulfinger & Scholze, 1962
Wendler et al., 1995
Swets, 1961
(c) He diffusion in olivine aggregate
T (°C)
1300
800
500
$\log_{10}(D/a^2)$ ($\log_{10}$(D)/s)
-4
-4.2
-4.4
-4.8
-5
-5.2
-5.4
Volume diffusion
Grain boundary diffusion
Burnard et al., 2015
6
8
10
12
14
16
10000/T (K)
(d) Relative duffusion rates
T (°C)
1300
1200
1100
1000
D_{He}/D_{Ne}
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
Cherniak et al. (olivine volume)
Futagami et al. (olivine volume)
This study (olivine volume)
Melt (simulation assumption)
6
6.5
7
7.5
8
10000/T (K)

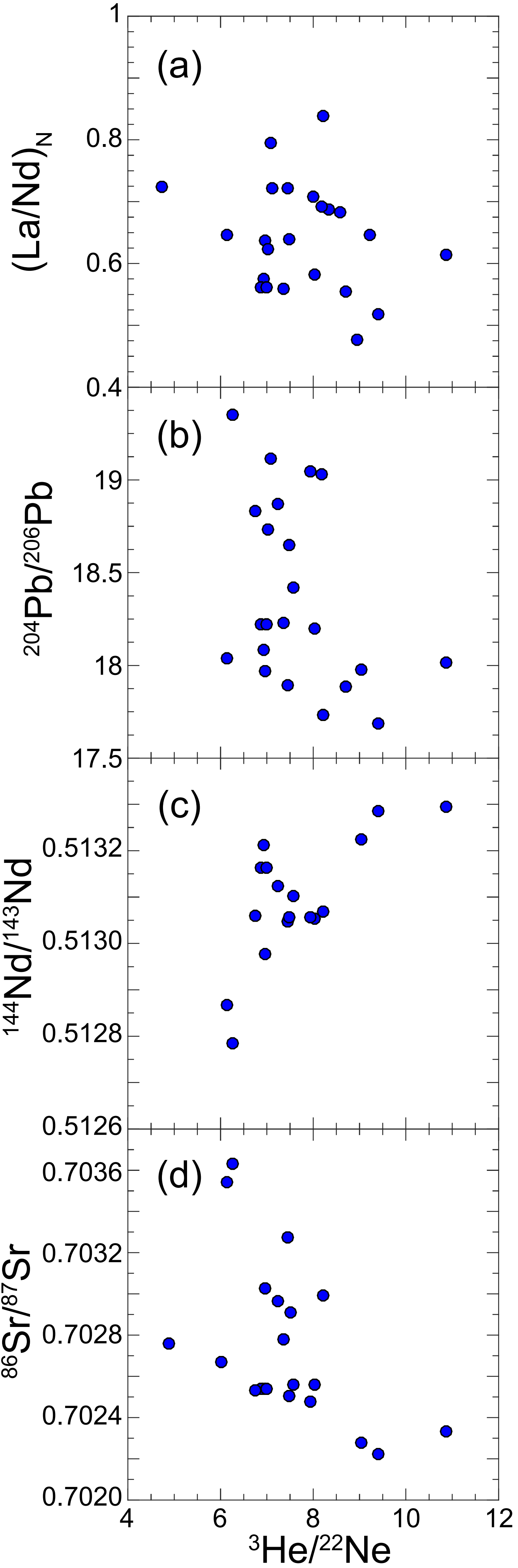

T (°C)
1500
1000
800
600
500
400
300
200
-5
-10
-15
-20
-25
-30
-35
ln(D/a²) (ln(/s))
5
10
15
20
25
10000/T (K)
³He:
Eₐ = 122.1 ± 5.1 kJ/mol
ln(D₀/a²) = 2.09 ± 0.64
²¹Ne:
Eₐ = 168.6 ± 8.8 kJ/mol
ln(D₀/a²) = 2.44 ± 0.86


Harzburgite wallrock
$\varphi_w = 0.005$
$V_w = 4$ cm/y
D_w
Compacting boundary layer
$\varphi_b = 0.002$
$V_b = V_w$
D_b
Dunite channel
$\varphi_c = 0.05$
$V_c = 50 \times V_w$
D_c
advection
diffusion
95 - l meters
l (width varies)
5m


Permeable CBL
Impermeable CBL
wallrock
cbl
channel
(a) ^{3}He/^{22}Ne 4.5
Diffusion assumption:
this study
He
Ne
after 70km upwelling
time
(b) ^{3}He/^{22}Ne 4.7
Diffusion assumption:
this study
(c) ^{3}He/^{22}Ne 6.3
Diffusion assumption:
Cherniak et al.
(d) ^{3}He/^{22}Ne 10.8
Diffusion assumption:
Cherniak et al.
(e) ^{3}He/^{22}Ne 5.1
Diffusion assumption:
Futagami et al.
(f) ^{3}He/^{22}Ne 3.1
Diffusion assumption:
Futagami et al.
Bulk concentration (ppm)
0
0.0025
0.005
0.0075
0.04
0.05
0.06
0.07
Position (m)
-80
-60
-40
-20
0


impermeable cbl
permeable cbl
[^{3}He/^{22}Ne]$_{\text{regassed mantle}}$ / [^{3}He/^{22}Ne]$_{\text{source}}$
6
5
4
3
2
(a)
10^{-1}
[^{3}He]$_{\text{regassed mantle}}$ / [^{3}He]$_{\text{undegassed source}}$
10^{-2}
(b)
10^{-3}
Diffusion coefficient assumption
This study
Futagami et al.
Cherniak et al.
[^{22}Ne]$_{\text{regassed mantle}}$ / [^{22}Ne]$_{\text{undegassed source}}$
10^{-2}
(c)
10^{-3}
0
5
10
15
20
CBL width (m)


mid-ocean ridge
low
^{3}He/^{22}Ne
reservoir
high ^{3}He/^{22}Ne
reservoir
t_1
t_2
t_3
t_4
t_5
(a)
(b)
N
mantle masses fluxed through
global MOR system
range of permissible
values according to
Xe isotope systematics
2
3
4
5
6
7
8
9
0.5
1
1.5
2
2.5
3
3.5
τ
characteristic mixing
timescale (Gyr)


(a)
(La/Nd)$_N$
1
0.8
0.6
0.4
(b)
^{204}Pb/^{206}Pb
19
18.5
18
17.5
(c)
^{144}Nd/^{143}Nd
0.5132
0.5130
0.5128
0.5126
(d)
^{86}Sr/^{87}Sr
0.7036
0.7032
0.7028
0.7024
0.7020
4
6
8
10
12
^{3}He/^{22}Ne

Electronic Supplement to:

Plate tectonic cycling modulates Earth's $^{3}He/^{22}Ne$ ratio

Nick Dygert[1,2], Colin R.M. Jackson[3,4], Marc A. Hesse[1], Marissa M. Tremblay[5,6,7], David L. Shuster[5,6], Jesse T. Gu[1]

[1]Department of Geological Sciences, Jackson School of Geosciences, University of Texas at Austin, Austin TX 78712

[2]Planetary Geosciences Institute, Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, Knoxville TN 37996

[3]Geophysical Laboratory, Carnegie Institution for Science, Washington DC 20015

[4]National Museum of Natural History, Smithsonian Institution, Washington DC 20560

[5]Department of Earth and Planetary Science, University of California, Berkeley, Berkeley CA 94720

[6]Berkeley Geochronology Center, Berkeley, CA 94709

[7]Now at the Scottish Universities Environmental Research Centre, East Kilbride, Scotland G75 0QF

Table of Contents

Methods for calculating $^3He/^{22}Ne$ ratios

A useful expression used to calculate $^3He/^{22}Ne$ from measured $^3He/^4He$ and $^{21}Ne/^{22}Ne$ ratios in mantle-derived rocks (Honda and McDougall, 1998) is as follows:

$$^{3}He/^{22}Ne = \frac{^{21}Ne/^{22}Ne_E - ^{21}Ne/^{22}Ne_i}{^{4}He/\,^{3}He_{measured} - \,^{4}He/\,^{3}He_i} \times \left(\,^{4}He/^{21}Ne\right)_{production} \quad (1),$$

where $^4He/^3He_{measured}$ is the measured He isotope ratio in the sample, $^{21}Ne/^{22}Ne_E$ is the measured ratio extrapolated to its source value in a $^{20}Ne/^{22}Ne$ vs. $^{21}Ne/^{22}Ne$ plot in order to correct for atmospheric contamination (we assume a mantle source $^{20}Ne/^{22}Ne$ of 12.5 for all samples presented in this study, Tucker et al., 2012), $^4He/^{21}Ne_{production}$ is ratio of radiogenic ^4He to nucleogenic ^{21}Ne production in the mantle (4.5×10^{-8}; Yatsevich and Honda 1997), and $^{21}Ne/^{22}Ne_i$ and $^4He/^3He_i$ are the assumed initial values of Earth’s mantle (0.03129 and 6024, respectively, Trieloff and Kunz, 2005; Mahaffy et al., 1998) This method mitigates uncertainties in $^3He/^{22}Ne$ related to atmospheric contamination and degassing (e.g., Gonnermann and Mukhopadhyay, 2007; Tucker et al., 2014; Weston et al., 2015; Yamamoto and Burnard, 2005).

Post-eruptive ^3He, ^4He, ^{21}Ne and ^{22}Ne nuclides are produced by nuclear reactions with cosmic ray particles (e.g., Kurz, 1986; Niedermann et al., 1993). These reactions will disturb $^3He/^{22}Ne$ ratios calculated using Eq. 1. Because cosmic ray particles are strongly attenuated by seawater at depths relevant to ocean basins (e.g., Higashi et al., 1966), samples collected from submarine environments are much less susceptible to cosmogenic disturbance than samples collected subaerially; therefore we assume no cosmogenic He or Ne production in subaqueous samples. Cosmogenic nuclide production predominantly occurs in crystal lattices where parent isotopes are preferentially hosted (e.g., Craig and Poreda, 1986; Kurz, 1986). Noble gases trapped in fluid inclusions, which can be measured in crush extractions, may be more faithful recorders of source compositions than gases released by step heating, which includes lattice-sited cosmogenic, radiogenic (and nucleogenic) components as well. Data from subaerially sampled basalts and xenoliths discussed here are exclusively from crush extractions; we present data from heating and crush extractions for samples collected in submarine environments.

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Noble gas diffusion experiment methods

To quantify the kinetics of He and Ne diffusion in olivine we conducted step-degassing experiments on a proton-irradiated fragment of San Carlos olivine, a compositionally homogenous sample commonly utilized as an electron microprobe analysis standard (Fo92; Frey and Prinz, 1976; Blard et al., 2008). Proton irradiation generates uniform concentrations of both He and Ne in olivine that are high enough to conduct step-degassing experiments on single crystal fragments (Shuster et al., 2004; Gourbet et al., 2012). ^{21}Ne and ^{22}Ne are most likely produced from nuclear reactions on Si and Mg, while ^{3}He is produced from nuclear reactions on essentially all target nuclei (Leya et al., 1998; Shuster et al., 2004).

We co-irradiated many fragments of San Carlos olivine with a ~220 MeV proton beam for 5 hours with a total fluence of 4.9×10^{15} pm/cm^2 at the Francis H. Burr Proton Therapy Center at the Massachusetts General Hospital in 2007. For a detailed description of the irradiation setup, see Tremblay et al. (2017). We selected a single fragment with no visible fractures, fluid inclusions, or mineral inclusions and measured the dimensions of this fragment using a calibrated petrographic microscope (Fig. S1). We packaged the selected fragment into a Pt-Ir envelope affixed to a K-type thermocouple and placed it under vacuum. We heated the Pt-Ir envelope and sample using a 70W diode laser defocused over the Pt-Ir envelope. We regulated and measured the sample temperature to within ~2°C (in most cases, see below) via a PID-controlled feedback loop between the thermocouple and laser. We then measured the He and Ne released in each heating step separately with an MAP 215-50 sector field mass spectrometer in the Berkeley Geochronology Center Noble Gas Thermochronometry Lab. Details of the gas purification and mass spectrometer analytical procedures can be found in Tremblay et al. (2014). Blank-corrected ^{3}He and ^{21}Ne measurements from each experimental heating step are reported in Table S1. We used the measured release fraction and duration of each heating step to calculate diffusion coefficients using the equations of Fechtig and Kalbitzer (1966), assuming that the olivine diffusion domain is represented by the whole crystal fragment and is spherical, a justified assumption for fragments with modest aspect ratios like the one used here (e.g., Meesters and Dunai, 2002; Huber et al., 2011).

We were unable to fully degas Ne from the olivine fragment using the thermocouple setup. In a few cases at temperatures around ~1000 ºC, drooping of the thermocouple, on which the Pt-Ir envelope and sample are suspended, caused misalignment between the laser beam and

Pt-Ir envelope and as a consequence poor temperature control. To achieve full degassing, we transferred the Pt-Ir envelope to a laser chamber with pyrometer-controlled temperature. Heating steps with pyrometer temperature control, as well as the poorly controlled temperature steps on the thermocouple, are utilized to calculate the cumulative gas fraction released during the step-degassing experiment, but the diffusion coefficients calculated for these steps are not plotted in Fig. 4, and these diffusion coefficients are not used to calculate the activation energy and pre-exponential factor.

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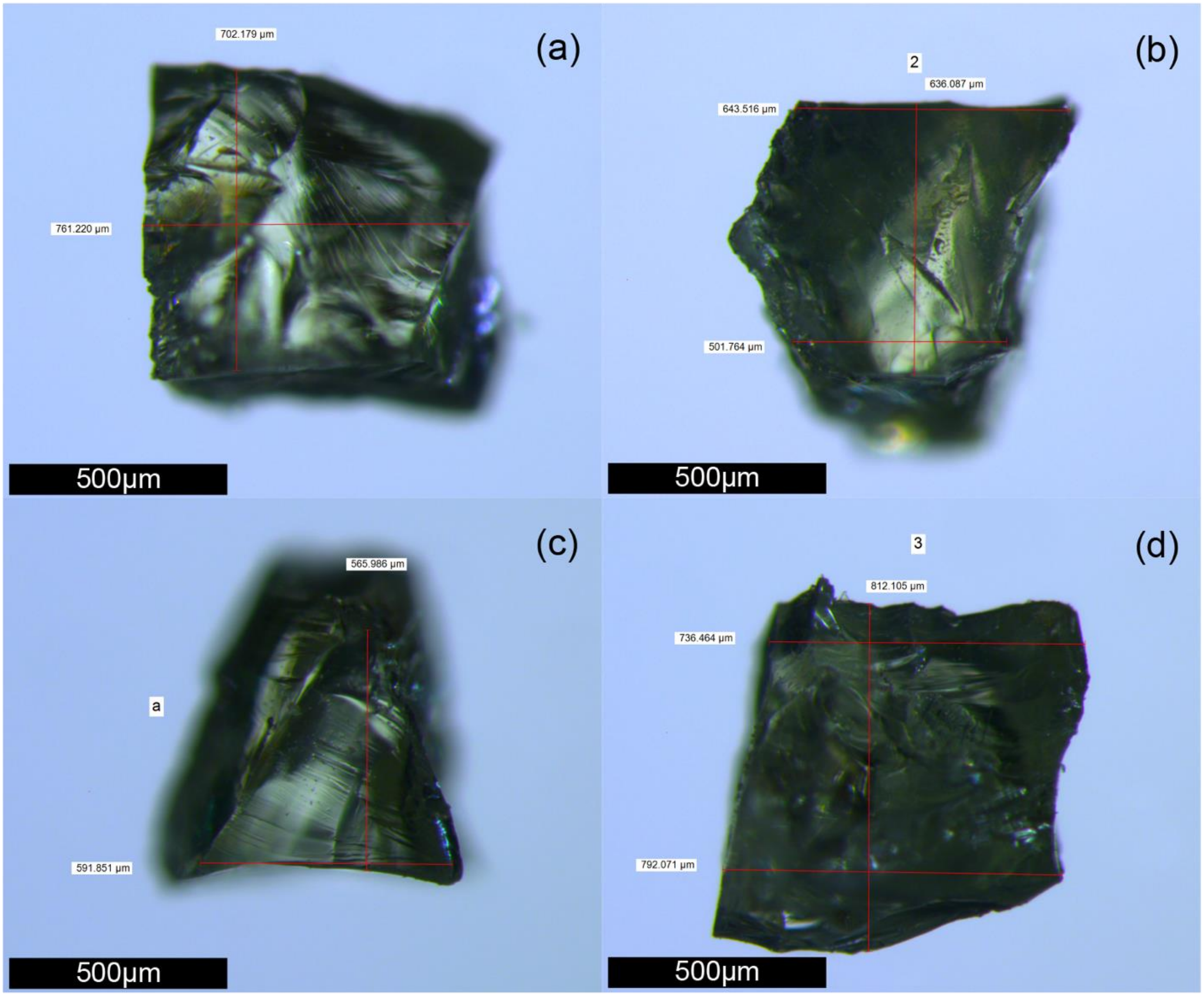

Figure S1. The olivine fragment (SCOL-h) investigated in our degassing experiment. We estimate the effective spherical radius to be 330µm.

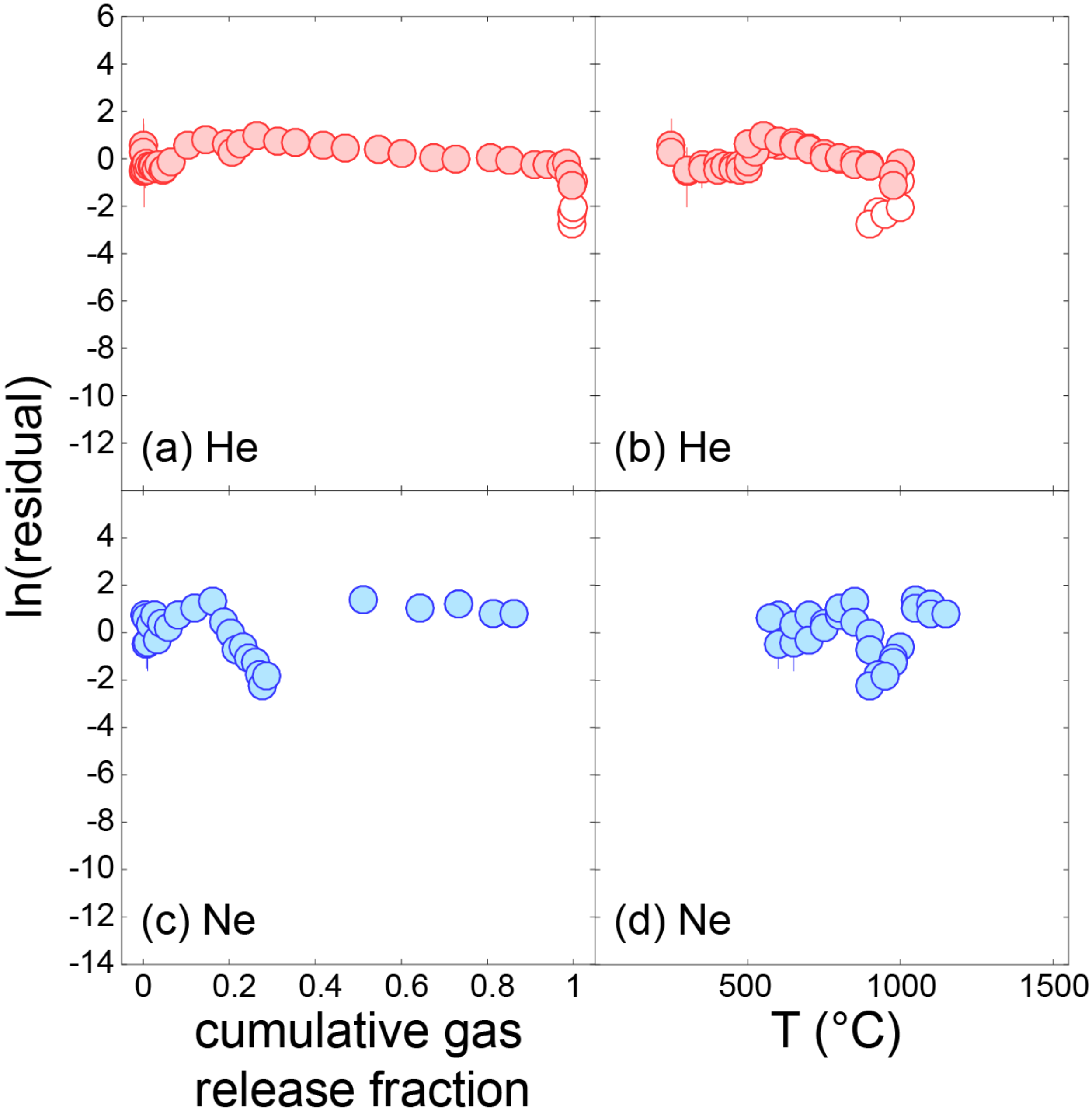

Figure S2. Residuals to Arrhenius fits for He and Ne plotted as a function of cumulative total gas released (a,c) and experimental temperature (b,d). Unfilled red circles in (a) and (b) show data that were excluded from the Arrhenius parameterization.

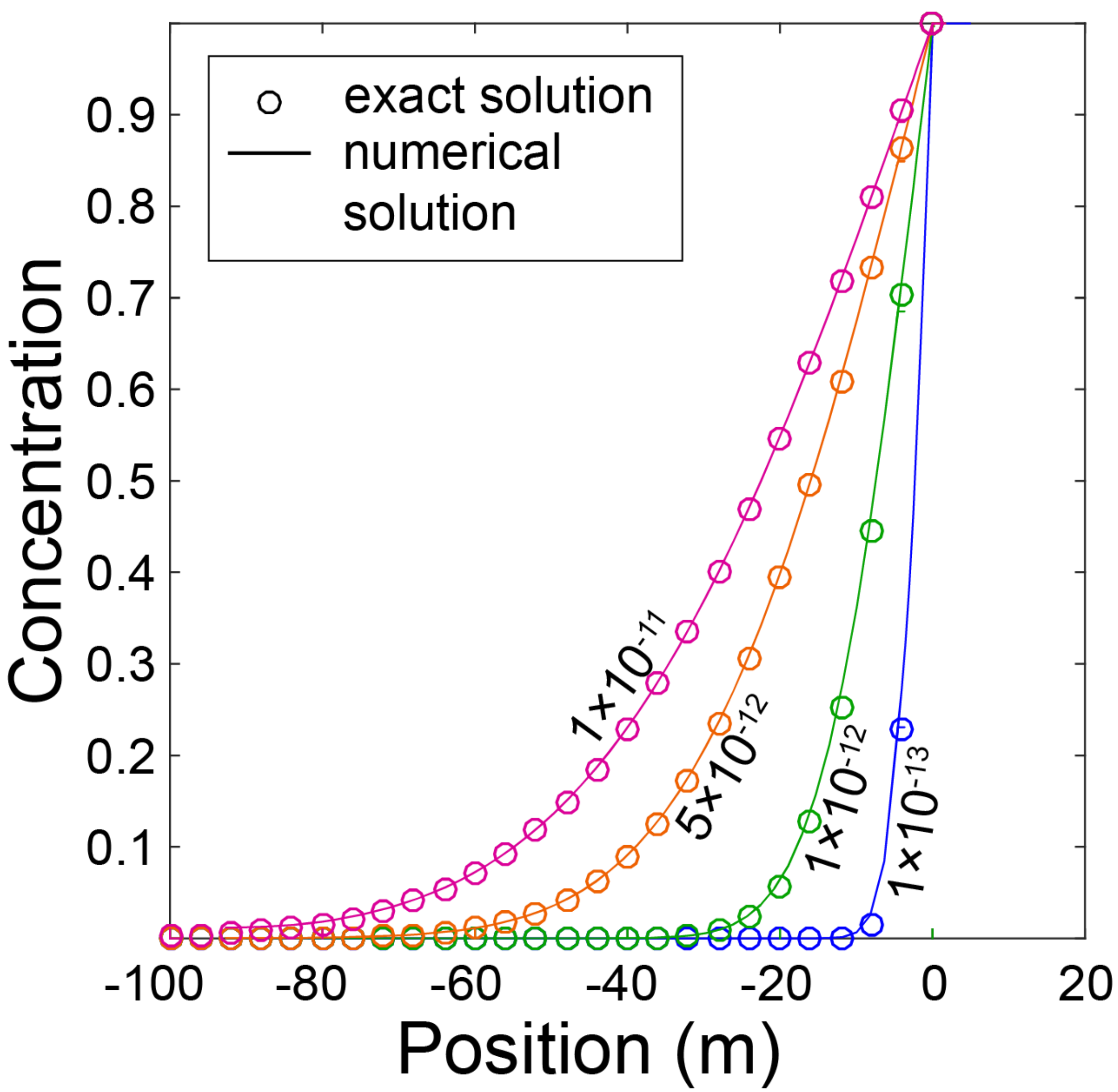

Figure S3. Comparison of numerical solutions (solid lines) to exact solutions (circles) for constant surface diffusion into a semi-infinite halfspace assuming different diffusivities and 1.75 Myr of diffusion. In general the exact and numerical solutions are in excellent agreement. The 1×10^{-11} numerical simulation diverges slightly from the exact solution because the numerical diffusion domain has a finite width (95m).

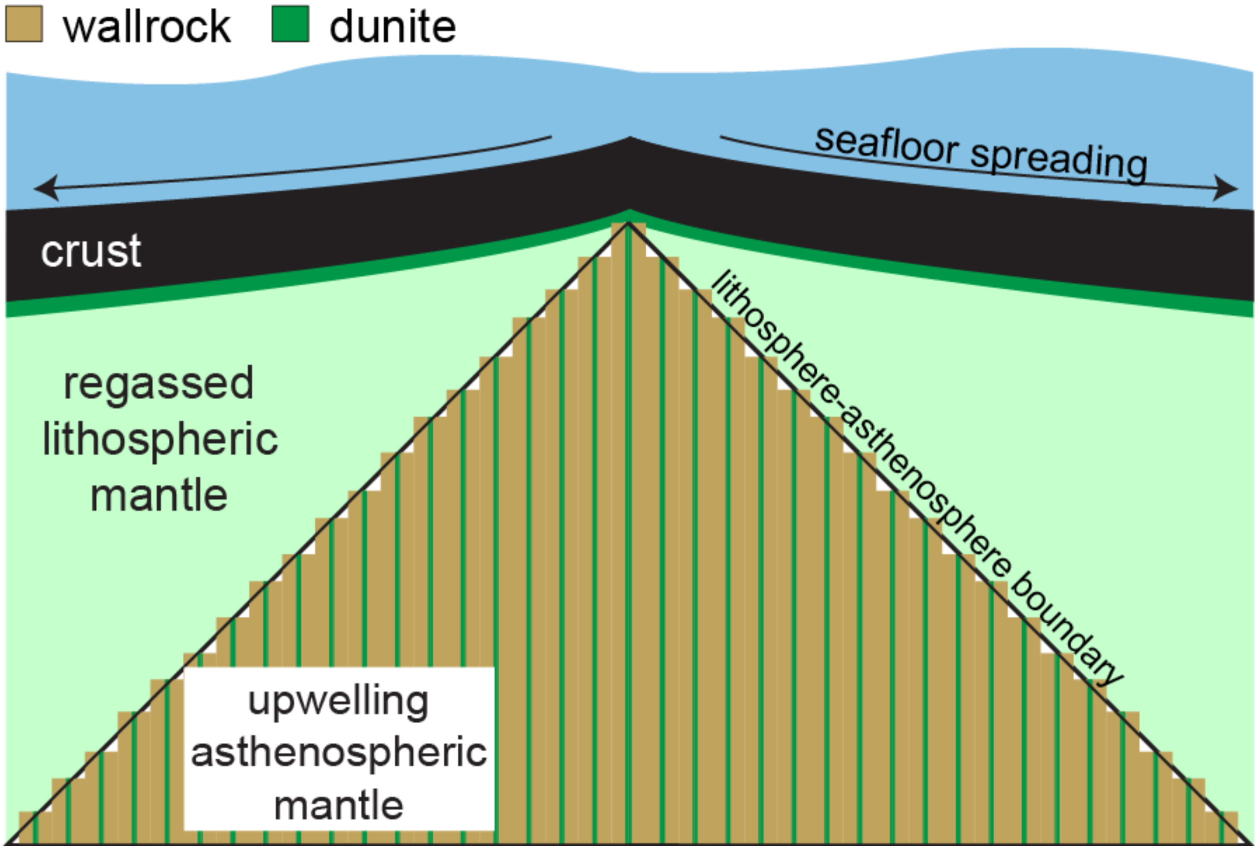

Figure S4. Schematic illustrating the geometry of our lithosphere formation model. The melt triangle is composed of a repeating pattern of dunite channel-wallrock units. Vertically upwelling asthenospheric mantle in the triangle cools sufficiently to become a part of the thickening lithospheric keel (light green), then it advects laterally away from the ridge axis in the direction of seafloor spreading. It ultimately passes through a subduction zone and is mixed back into the convecting mantle.

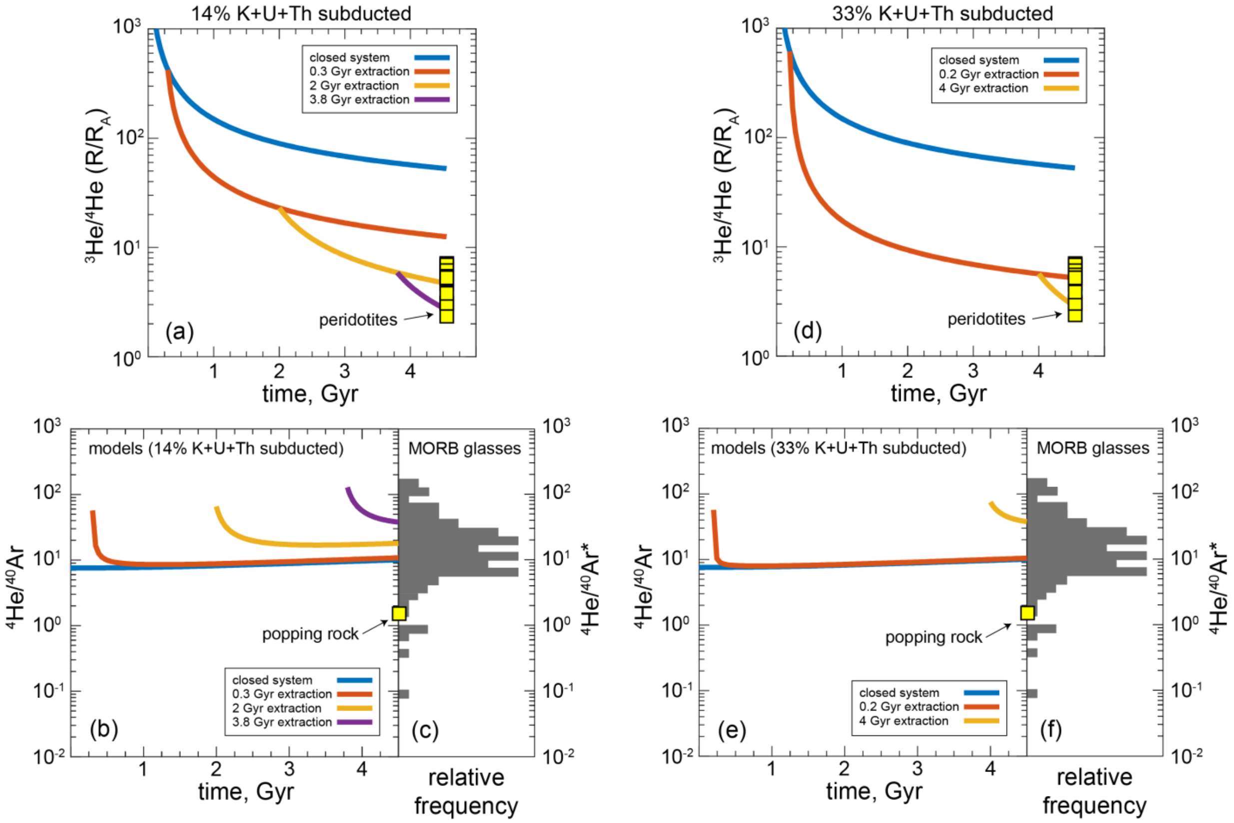

Figure S5. Models for radiogenic ingrowth of ^{4}He and ^{40}Ar in the mantle after kinetic fractionation events for scenarios where (1) 14% of U+Th+K in newly formed crust is recycled back into the MORB mantle reservoir (Figs. a,b,c) and (2) 33% of U+Th+K is recycled back into the MORB mantle reservoir (Figs. d,e,f). These models assume that after each extraction event, kinetic fractionation retains 3% of He in the source and 0.4% of Ar in the source (c.f. Fig. 7), U+Th+K are perfectly incompatible during mantle melting, and that the subducted U+Th+K is instantaneously mixed back into in the MORB reservoir. Assumptions for initial U, Th, ^{4}He, and ^{3}He abundances are as in Harper and Jacobsen (1996). Initial ^{40}K is calculated assuming a present-day bulk Earth U/K of 12,700 (Allègre et al., 1996). (a,d) Predicted mantle ^{3}He/^{4}He compared to measured values in subcontinental peridotites (Day et al., 2005). (b,e) predicted mantle ^{4}He/^{40}Ar compared to (c,f) air contamination-corrected measured values (^{4}He/^{40}Ar*) in MORB glasses (Honda and Patterson, 1999) and popping rock (Moreira et al., 1998). Evolution of an undegassed primitive mantle (the closed system model) is shown as blue lines. Other lines show the evolution of a MORB reservoir after subsequent extraction (partial melting/kinetic fractionation) event(s). Model extensions after an extraction event show how the reservoir would have evolved had an extraction event not occurred. The model results are non-unique; the amount of recycled U+Th+K and the timing and number of extraction events strongly affect the resultant MORB reservoir composition and it is trivial to produce higher or lower ^{3}He/^{4}He and higher ^{4}He/^{40}Ar. Full investigation of variations among these and other parameters are beyond the scope of this study. Nonetheless, these models demonstrate that within the context of our kinetic fractionation model the expected MORB reservoir compositions are in agreement with ^{3}He/^{4}He and ^{4}He/^{40}Ar* observations. We note that popping rock has a lower ^{4}He/^{40}Ar* than our closed system predictions (b,e), suggesting the bulk Earth may have a higher K/U and/or lower Th/U than our assumed values (c.f. Honda and Patterson, 1999); alternatively popping rock may have experienced disequilibrium degassing preferentially retaining Ar relative to He (e.g. Gonnermann and Mukhopadhyay, 2007; Weston et al., 2015), as suggested by its low ^{4}He/^{21}Ne$_{\text{nucleogenic}}$ component (e.g., Fig. 4, Honda and Patterson, 1999). We note that recycling 33% of the oceanic crust subduction flux into the MORB source is consistent with estimates of the amount of subducted oceanic crust in the MORB source (4%, Sobolev et al., 2007) assuming a 50km thick mantle lithosphere and 6km thick crust. If some U+Th+K in the subducting oceanic crust is lost to partial melting or another process, lower U+Th+K recycling values (e.g. 14%) may be expected.

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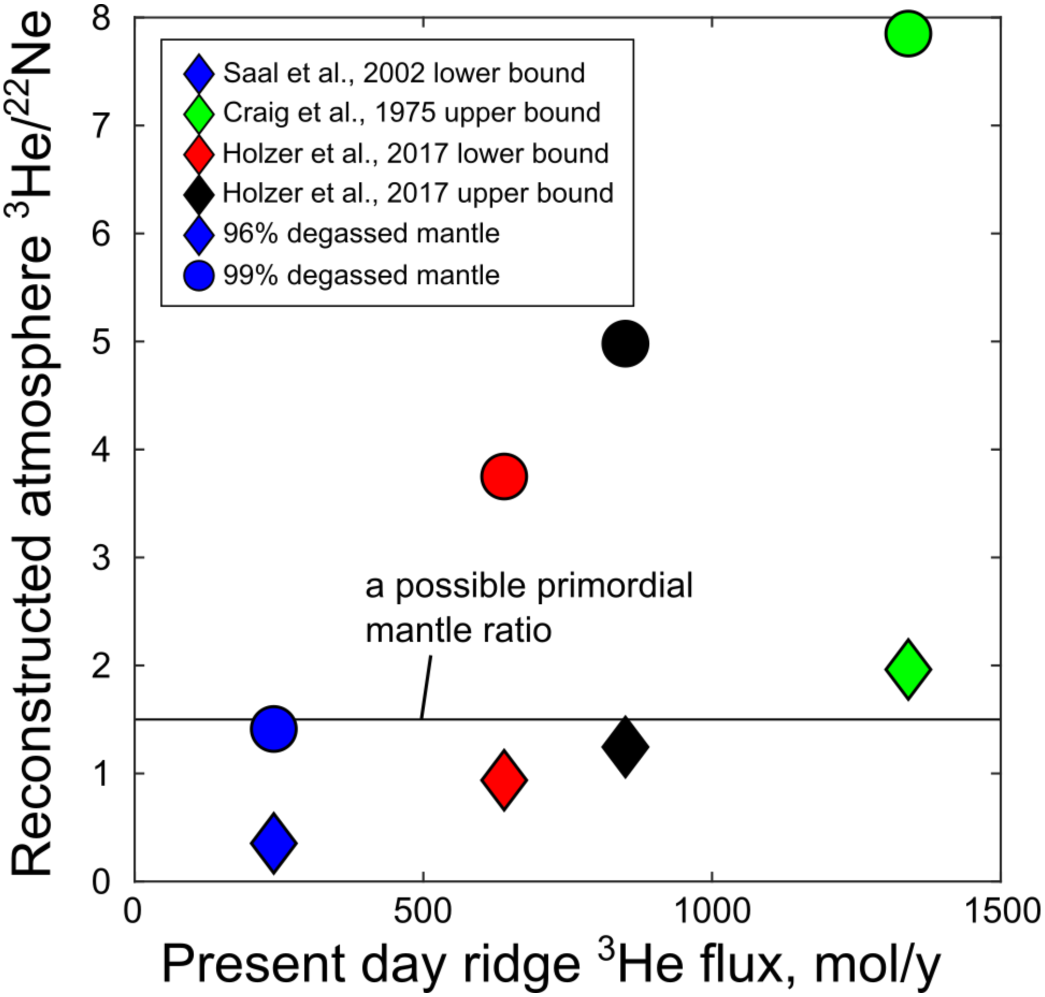

Figure S6. ^{3}He/^{22}Ne ratio of a reconstructed atmosphere produced by mantle outgassing. Our model demonstrates that plate tectonic cycling can generate a mantle with elevated ^{3}He/^{22}Ne ratios. Implicit in the generation of a high ^{3}He/^{22}Ne mantle is the outgassing of a complementary low ^{3}He/^{22}Ne component to the atmosphere. Mantle outgassing, as considered here, is nearly complete such that the ^{3}He/^{22}Ne ratio of the low component is essentially equal to the initial ^{3}He/^{22}Ne ratio of the mantle. Identifying this low ^{3}He/^{22}Ne component in the atmosphere is complicated by the continuous loss of He to space and the uncertain initial composition of noble gases in the primordial atmosphere.

Here we evaluate whether the composition of the modern atmosphere is consistent with the incorporation of the low ^{3}He/^{22}Ne component. We first establish the maximum mantle contribution of ^{22}Ne to the atmosphere. We take the ^{20}Ne/^{22}Ne ratio of the MORB mantle to be 12.5, following modern measurements (Ballentine & Holland, 2008). We also take the ^{20}Ne/^{22}Ne ratio of the primordial atmosphere to be 8.2 (Ne-A, Black, 1972). The modern atmosphere ^{20}Ne/^{22}Ne ratio is

9.8, and this implies a mixture of 37% mantle contribution or 5×10^{13} moles of ^{22}Ne outgassed from the mantle. Total atmospheric ^{22}Ne abundance is from Marty (2012).

The total moles of ^{3}He outgassed to the atmosphere can only be indirectly ascertained because He is lost continuously from the atmosphere to space. The present ^{3}He concentration of the mantle is constrained by the flux of ^{3}He from mid-ocean ridges and the corresponding mass of mantle melted beneath ridges. This calculation assumes perfect incompatibility and complete extraction. Estimates for the global ^{3}He flux range from 241 to 1340 mol/y (Saal et al., 2002, Craig et al., 1975), with a recent estimate giving a range of 640 to 850 mol/y (Holzer et al., 2017). The volume of mantle that melts to support the flux is calculated as the product of the global half-spreading rate (2.5 cm/y, Conrad & Lithgow-Bertelloni, 2007), the length of the global mid-oceanic ridge system (8×10^{9} cm), an assumed height of the melting triangle beneath mid-ocean ridges of 1×10^{7} cm (Kelemen et al., 1997) and a width calculated assuming a 45-45-90 geometry, equating to a volume flux of 4×10^{17} cm^{3}/y or a mass flux of 1.4×10^{18} g/y (for a bulk mantle density of 3.4 g/cm^{3}). Dividing the ^{3}He fluxes by the mass flux yields a potential ^{3}He concentration range of $1.78\text{-}9.9\times10^{-16}$ mol/g or a total ^{3}He abundance range of $7.1\text{-}93.4\times10^{11}$ mol in the modern mantle. The abundance calculation assumes that MORB mantle is the mass of the entire mantle (4×10^{27} g). To convert the modern ^{3}He abundance of the mantle to an integrated outgassing flux we consider both 96 and 99% outgassing.

With the estimates derived above for the integrated abundances of ^{3}He and ^{22}Ne outgassing from the mantle, we now quantify the ^{3}He/^{22}Ne ratio fluxed from the mantle over geologic time as a function of potential ^{3}He flux (Figure S6). A successful model results in a ^{3}He/^{22}Ne ratio outgassed from the mantle lower than the assumed initial value (1.5). The lowest ^{3}He flux estimate yields a ^{3}He/^{22}Ne ratio that is consistent with either 96 or 99% outgassing, whereas the highest ^{3}He flux estimate yields ^{3}He/^{22}Ne ratios above the assumed initial ^{3}He/^{22}Ne. The most recent estimate of ^{3}He flux is consistent with outgassing close to the 96% threshold. We conclude that the reconstructed atmosphere can host the complementary low ^{3}He/^{22}Ne component outgassed from the mantle provided ^{3}He flux is at the low end of reported estimates or the extent of mantle outgassing is ~96%. However, considerations articulated below may relax this constraint.

This is a simplified analysis meant to check if the outgassing of low ^{3}He/^{22}Ne component to the atmosphere violates mass balance. If the atmosphere or mantle had initially higher ^{20}Ne/^{22}Ne ratios, this would raise the ^{3}He/^{22}Ne ratio fluxed to the atmosphere. We stress that (1) the primordial mantle ^{3}He/^{22}Ne ratio may have been higher than 1.5, perhaps due to nebular ingassing of a primordial magma ocean, or solubility-controlled degassing of a magma ocean (Tucker & Mukhopadhyay, 2014) and (2) that the melting triangle may extract ^{3}He from significantly larger volumes of mantle than assumed here (Forsyth et al., 1998). Accounting for these effects would allow for successful models with higher ^{3}He fluxes and higher extents of outgassing.

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