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## Plate tectonic cycling modulates Earth's <sup>3</sup>He/<sup>22</sup>Ne ratio

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### ABSTRACT

The ratio of  ${}^{3}$ He and  ${}^{22}$ Ne varies throughout the mantle. This observation is surprising because  ${}^{3}$ He and <sup>22</sup>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  ${}^{3}\text{He}/{}^{22}\text{Ne}$  ratios of 7.5  $\pm$  1.2 and 3.5  $\pm$  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  ${}^{3}\text{He}/{}^{22}\text{Ne}$  values; ~1 for chondrites and ~1.5 for the solar nebula. The high  ${}^{3}\text{He}/{}^{22}\text{Ne}$  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  ${}^{3}\text{He}/{}^{22}$ 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 <sup>3</sup>He/<sup>22</sup>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 <sup>3</sup>He/<sup>22</sup>Ne mantle may be best preserved in the lower mantle where relatively high viscosities impede mechanical mixing.

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#### 1. Introduction

<sup>3</sup>He and <sup>22</sup>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 <sup>3</sup>He/<sup>22</sup>Ne variations exist within mantle-derived rocks

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and that by inference; the mantle has a net elevated  ${}^{3}\text{He}/{}^{22}\text{Ne}$  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).  ${}^{3}\text{He}/{}^{22}\text{Ne}$  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  ${}^{3}\text{He}/{}^{22}\text{Ne}$  compared to ocean island basalt (OIB) sources (7.5  $\pm$  1.2 and 3.5  $\pm$  2.4 respectively; see the electronic supplement for a description of our



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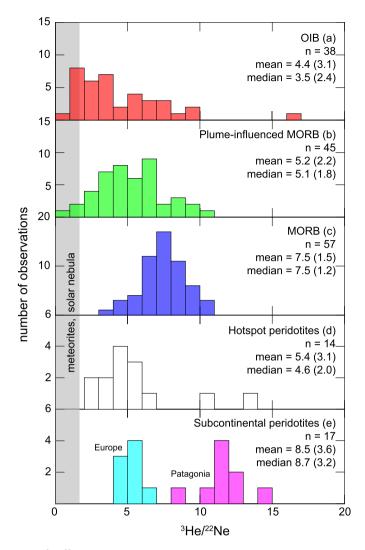


Fig. 1. <sup>3</sup>He/<sup>22</sup>Ne ratios of ocean island basalts (a), plume-influenced MORBs (b), MORBs (c), hotspot sourced mantle xenoliths (d), and subcontinental lithospheric mantle (e). <sup>3</sup>He/<sup>22</sup>Ne for all samples are calculated using methods detailed in the electronic supplement. 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 <sup>3</sup>He/<sup>4</sup>He and radiogenic isotope ratios.

methods). The low  ${}^{3}\text{He}/{}^{22}\text{Ne}$  of OIBs approaches chondritic (~1) and solar nebula values (~1.5), whereas the high  ${}^{3}\text{He}/{}^{22}\text{Ne}$  of the MORB mantle is not similar to solar sources or any known family of meteorites. Such a high  ${}^{3}\text{He}/{}^{22}\text{Ne}$  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  ${}^{3}\text{He}/{}^{22}\text{Ne}$  invokes fractionation from magma ocean degassing (Honda and McDougall, 1998; Tucker and Mukhopadhyay, 2014). He is  $\sim 2 \times$  more soluble than Ne in peridotitic melt (e.g., lacono-Marziano et al., 2010); degassing a magma ocean to form a primitive atmosphere would elevate the  ${}^{3}\text{He}/{}^{22}\text{Ne}$  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  ${}^{3}\text{He}/{}^{22}\text{Ne}$  ratios of ~1.5 (e.g., Harper and Jacobsen, 1996; Mahaffy et al., 1998; Ott, 2002; Trieloff and Kunz, 2005). Thus, accounting for  ${}^{3}\text{He}/{}^{22}\text{Ne}$  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  ${}^{3}\text{He}/{}^{22}\text{Ne}$  ratio in the mantle, rather than the proposed increase.

Here we explore the possibility that elevated  ${}^{3}\text{He}/{}^{22}\text{Ne}$  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; Barfod 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 <sup>3</sup>He/<sup>22</sup>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 <sup>3</sup>He/<sup>22</sup>Ne ratios and indices of depletion, including La/Sm, and the Rb-Sr and Sm-Nd isotope systems. It requires the entire high  ${}^{3}\text{He}/{}^{22}\text{Ne}$  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; Kenvon, 1990, 1993; Spiegelman and Kenvon, 1992). The extent of diffusive interaction between the dunitehosted basaltic melt and adjacent wallrock depends on the effective diffusion rate of the element in the wallrock.

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