

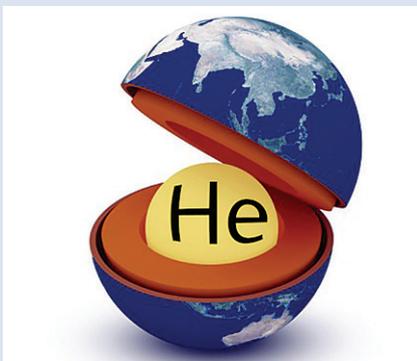
The primordial He budget of the Earth set by percolative core formation in planetesimals

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Abstract



The primordial He budget of the Earth's interior is commonly thought to have been set by full liquid metal-silicate equilibration in a terrestrial magma ocean. However, incomplete metal-silicate equilibration during accretion will have a substantial effect on this budget. Here we present liquid-solid partitioning experiments indicating that He behaves as a moderately siderophile element during percolative core formation in planetesimals. Mass balance considerations show that even minor disequilibrium will allow the Earth's early core to incorporate sufficient primordial He—and possibly other noble gases—to supply the lower mantle throughout Earth's history. We conclude that the high $^3\text{He}/^4\text{He}$ ratios in basalts may well represent primarily the last vestiges of metal-silicate disequilibrium in a terrestrial magma ocean preserved from the time of Earth's formation.

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Introduction

The isotope composition of He in Earth's interior provides key information on the processes of planetary accretion and differentiation. The two isotopes of He, ^3He and ^4He , are both primordial in origin, but ^4He is also produced during Earth's history by the radioactive decay of the lithophile elements U and Th. Basalts from different geological settings (mid-ocean ridges (Graham, 2002) and a number of ocean islands and continental flood basalt provinces (Kurz *et al.*, 1982; Hilton *et al.*, 1999; Stuart *et al.*, 2003; Starkey *et al.*, 2009)) have $^3\text{He}/^4\text{He}$ ratios higher than that in air indicating the presence of an undegassed reservoir in the solid Earth rich in ^3He . The highest $^3\text{He}/^4\text{He}$ ratios are observed in basalts from ocean islands and continental flood basalt provinces implying a deep mantle origin. The Earth's core is an attractive location for such a reservoir (Porcelli and Halliday, 2001; Herzberg *et al.*, 2013). Recent experimental work (Bouhifd *et al.*, 2013) determined He partitioning between liquid silicate and metal, at conditions anticipated in a terrestrial magma ocean. The derived partition coefficients are much smaller than unity, indicating that He prefers to reside in the silicate mantle, rather than the core. Nevertheless, based on estimated concentrations of primordial He, the Earth's early core could still have incorporated sufficient He to supply the lower mantle to the present day (Bouhifd *et al.*, 2013).

The Earth is thought to have largely formed through the accretion of numerous planetesimals and planetary embryos that were already differentiated into a metallic core and silicate mantle (Chambers, 2004). Due to the significantly lower melting temperature of S-bearing Fe-rich alloys than silicates, it is inevitable that core formation on these planetesimals and small planetary embryos will initially involve the percolation of liquid metal through solid silicate (Yoshino *et al.*, 2003; Terasaki *et al.*, 2008; Ghanbarzadeh *et al.*, 2017) prior to the formation of a magma ocean (Greenwood *et al.*, 2005; Elkins-Tanton, 2012) and the loss of volatile elements (Porcelli *et al.*, 2001; Schönbachler *et al.*, 2010; Norris and Wood, 2017; Pringle and Moynier, 2017). Experimental studies (Yoshino *et al.*, 2003; Terasaki *et al.*, 2008) and numerical simulations (Ghanbarzadeh *et al.*, 2017) have shown that during this period liquid metal can form an interconnected network and can percolate and segregate by porous flow towards the planetary bodies' centre. Consequently, He will efficiently partition between liquid metal and solid silicate before isolation of these two phases. Many planetesimals and planetary embryos likely possessed cores that were liquid for several tens of Myr (Chabot and Haack, 2006; Nimmo, 2009; Elkins-Tanton *et al.*, 2011; Hunt *et al.*, 2018). During impacts the liquid cores of the impactors will disperse or sink rapidly through a magma ocean into the Earth's proto core. Models suggest that during descent, erosion and emulsification result in mixing and equilibration

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with Earth's liquid silicate mantle (Dahl and Stevenson, 2010). However, these models also indicate that large cores (>10 km in diameter) will not emulsify entirely, and perhaps only 1–20 % of Earth's core would equilibrate with the silicate mantle during accretion. Likewise, Hf-W and U-Pb isotope systems (Rudge *et al.*, 2010) and recent N-body accretion simulations (Rubie *et al.*, 2015) allow for partial equilibration. Consequently, the He budget of the Earth's core may have been at least partially set in the cores of differentiated planetesimals and planetary embryos that subsequently accreted to form the Earth, rather than later in a terrestrial magma ocean. Here we present new experimental constraints on He partitioning between solid silicate and liquid Fe-rich metal at the conditions expected to prevail during core formation in planetesimals.

Methods

We performed seven high pressure, high temperature experiments at 1 GPa using a conventional solid-media piston-cylinder apparatus. This pressure corresponds to that at the centre of a planetesimal with a radius of about 100 km. Starting materials were 1:5 mass mixtures of submillimetre-size olivine fragments from the Admire pallasite (stony-iron meteorite) and powdered iron sulphide with a composition of $\text{Fe}_{0.705}\text{S}_{0.295}$ (mass fraction; referred to hereafter as [FeS]) corresponding to the eutectic composition at 1 GPa (Fei *et al.*, 1997). Although the chemical composition of our metal is likely different from that of most core-forming liquids, no important influence is expected on the partitioning of the noble gases, which are inert. These materials provide two isotopically distinct noble gas sources: cosmogenic noble gases from the meteoritic olivine ($^3\text{He}/^4\text{He} = 0.1483 \pm 0.0020$, $^{20}\text{Ne}/^{22}\text{Ne} = 0.8557 \pm 0.0022$, and $^{21}\text{Ne}/^{22}\text{Ne} = 1.0419 \pm 0.0018$; 2 sd, Table 1) and atmospheric noble gases (essentially no ^3He , and $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ of about 9.8 and 0.03, respectively) from the air trapped within the sample capsules. The starting materials were loaded into graphite inner capsules and subsequently sealed in welded Pt outer capsules. Five experiments were conducted at 1200 °C and two at 1450 °C. Both temperatures are above the eutectic of [FeS] and below the melting point of olivine so that [FeS] was molten and olivine remained solid. Experimental run

durations ranged from 2 hours to 6 days. After quenching and recovering the samples, olivine and [FeS] aliquots of a few hundred μg were hand-picked using dental tools under a binocular and the noble gases were extracted in vacuum by melting with an infrared laser. Helium and Ne isotopic concentrations were then measured using a magnetic sector field mass spectrometer equipped with a unique high-sensitivity compressor source (Baur, 1999) following the procedure given by Riebe *et al.* (2017). Metal-silicate (*i.e.* liquid-solid) partition coefficients (D_i) were calculated as the ratio of the concentration of a given noble gas isotope i (in cm^3 STP/g) in [FeS] and in olivine.

Results

The observed He and Ne isotopic concentrations in the run products were up to four orders of magnitude lower than in the starting materials (Table 1), indicating that He and Ne were lost by diffusion through the capsule walls. However, the two isotopically distinct noble gas sources in the starting materials provided a proxy for the extent of equilibration between olivine and [FeS]. At equilibrium and assuming no isotopic fractionation, the He and Ne isotopic compositions are expected to be the same in the two phases. As shown in Figure 1a, for each run the $^3\text{He}/^4\text{He}$ ratios in olivine and [FeS] were identical within analytical uncertainties, except for the experiment with the shortest run duration of 2 hours, indicating insufficient time for equilibration. The situation is different for Ne, where isotopic ratios never attain common values (Fig. 1b). While some degree of isotopic equilibration in [FeS] can be inferred from the linear mixing trend observed between the two initial sources, the Ne isotopic composition of olivine does not substantially deviate from the starting cosmogenic composition, probably due to the much lower diffusion coefficient of Ne compared to He (Trull *et al.*, 1991; Gourbet *et al.*, 2012). Nevertheless, our new He data imply that, despite loss of noble gases from the capsules, true equilibrium concentrations between olivine and [FeS] were measured (Fig. 2). Excluding the results from the insufficiently equilibrated experiment (performed for only 2 hours) yielded an average partition coefficient of He between liquid metal and solid silicate (D_{He}) of 11.8 ± 1.8 (2 se)

Table 1 Helium and Ne isotopic concentrations. The noble gas concentrations are in $10^{-10} \text{ cm}^3 \text{ STP/g}$ ($1 \text{ cm}^3 \text{ STP}$ corresponds to 2.6868×10^{19} atoms). The ^4He concentration in the olivine of the two-day experiment was not measured. The uncertainties are 2 sd and include only ion beam measurement uncertainties and sample mass uncertainties.

Sample	Duration	^3He	^4He	^{22}Ne	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$
Olivine start. mat.		10072 ± 133	67914 ± 120	4242.2 ± 6.2	0.8557 ± 0.0022	1.0419 ± 0.0018
1200 °C						
Olivine	2 hours	7.44 ± 0.14	81 ± 12	2026.7 ± 4.2	0.8390 ± 0.0023	0.9712 ± 0.0021
[FeS]		2.607 ± 0.041	55.7 ± 8.5	87.70 ± 0.26	2.262 ± 0.085	0.8413 ± 0.0038
Olivine	1 day	0.412 ± 0.022	7.3 ± 3.1	889.8 ± 1.4	0.8534 ± 0.0016	0.9763 ± 0.0017
[FeS]		4.361 ± 0.097	73.8 ± 8.7	31.68 ± 0.16	1.716 ± 0.018	0.8909 ± 0.0059
Olivine	2 days	0.284 ± 0.017	-	1034.8 ± 2.4	0.8543 ± 0.0030	0.9756 ± 0.0026
[FeS]		4.25 ± 0.14	100 ± 27	17.59 ± 0.57	8.43 ± 0.34	0.1677 ± 0.0093
Olivine	4 days	0.776 ± 0.031	12 ± 10	1407.7 ± 2.0	0.8735 ± 0.0035	0.9775 ± 0.0017
[FeS]		6.033 ± 0.095	180.8 ± 4.9	13.87 ± 0.24	9.19 ± 0.18	0.1067 ± 0.0039
Olivine	6 days	0.465 ± 0.013	7.1 ± 3.2	1086.8 ± 3.3	0.8460 ± 0.0027	0.9781 ± 0.0045
[FeS]		7.18 ± 0.15	88.4 ± 5.3	3.12 ± 0.23	5.95 ± 0.49	0.325 ± 0.042
1450 °C						
Olivine	2 hours	1.25 ± 0.32	19 ± 12	785.5 ± 2.7	0.9629 ± 0.0063	1.0245 ± 0.0042
[FeS]		18.37 ± 0.55	215 ± 11	6.45 ± 0.52	4.11 ± 0.41	0.680 ± 0.057
Olivine	1 day	0.82 ± 0.11	17.4 ± 9.5	58.03 ± 0.45	0.928 ± 0.042	1.0116 ± 0.0088
[FeS]		8.78 ± 0.26	116.2 ± 9.4	6.76 ± 0.38	7.02 ± 0.57	0.413 ± 0.026



for the conditions in our experiments. There was no resolvable difference between the partitioning of ^3He and ^4He (which implies no isotopic fractionation) or between the partitioning values obtained at the different run durations or temperatures.

Any major non-systematic cross-contamination of the olivine-[FeS] pairs is unlikely as the derived partition coefficients for the equilibrated experiments are concordant.

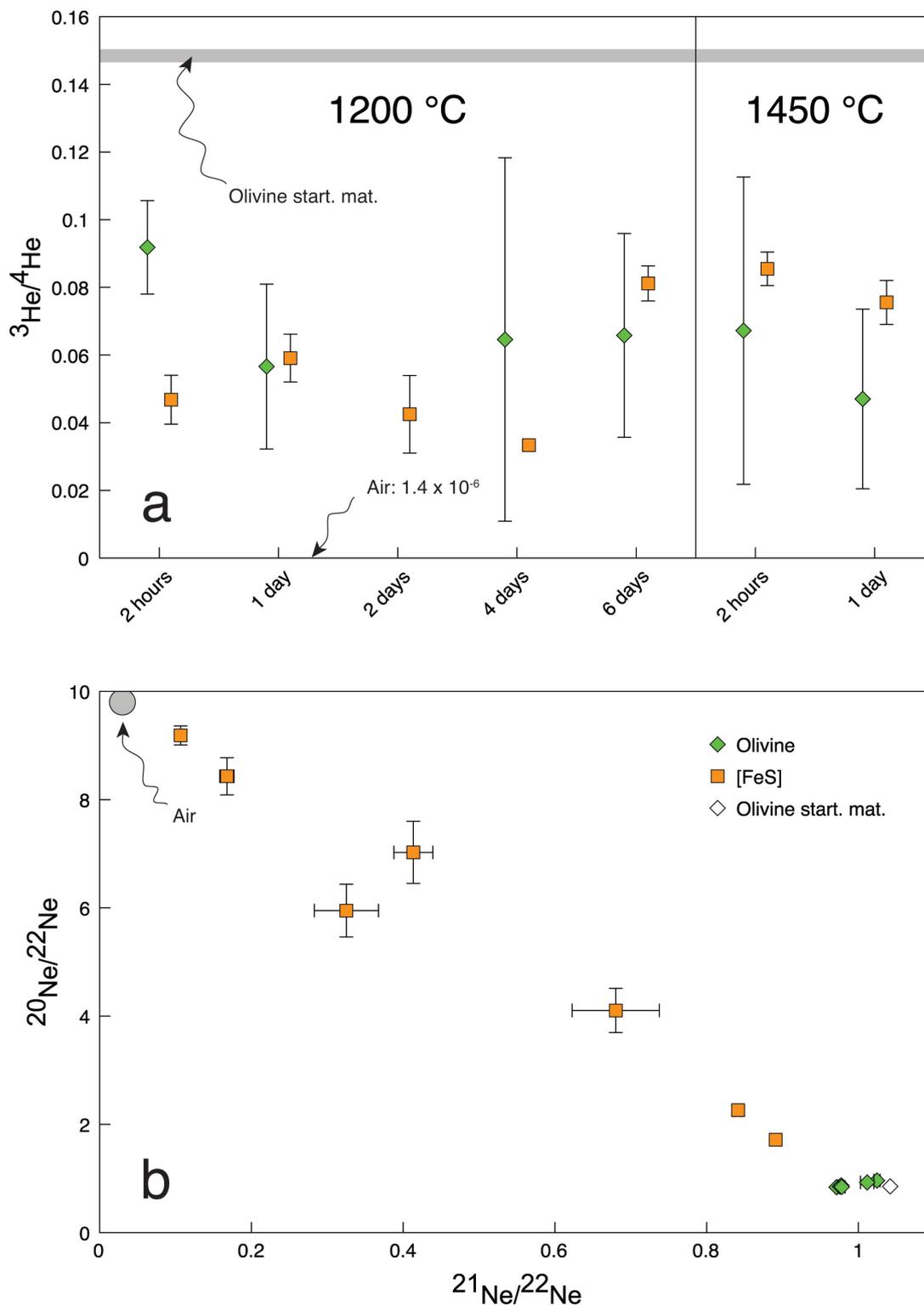


Figure 1 Helium and Ne isotopic compositions in the run products. Materials contain mixtures of atmospheric and cosmogenic noble gases. (a) Olivine-[FeS] pairs have within analytical uncertainties the same $^3\text{He}/^4\text{He}$ ratios except for the experiment conducted at 1200 °C for 2 hours. (b) All olivine-[FeS] pairs have different Ne isotopic compositions. Error bars are 2 sd.

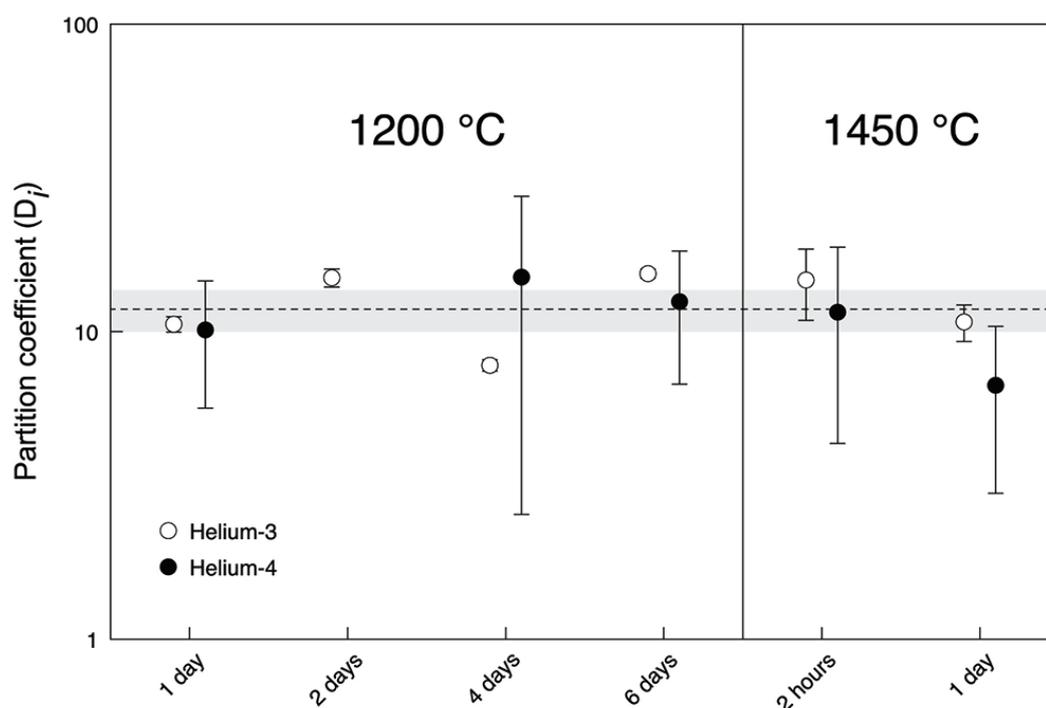


Figure 2 Metal-silicate (liquid-solid) partition coefficients for He. The dashed line shows the average partition coefficient D_{He} value of 11.8 ($n = 11$). The shaded area defines the two standard error of the mean (2 se) of 1.8. Data for the two-hour experiment are excluded and the ^4He partition coefficient for the two-day experiment is missing. Uncertainties include only gas concentration uncertainties. Error bars are 2 sd.

Discussion

Our experimental results (Fig. 2, Table 1) show that He behaves as a moderately siderophile element under conditions similar to percolative core formation in planetesimals, and that He is enriched in core-forming liquids. These data can now be used to explore the consequences for the Earth's primordial He budget assuming that some fraction of the precursor cores contributed to the Earth's core without complete equilibration in a terrestrial magma ocean for the reasons outlined previously (Dahl and Stevenson, 2010; Rudge *et al.*, 2010; Rubie *et al.*, 2015). Mass balance calculations (Fig. 3) (see Supplementary Information) can be used to illustrate the He distribution between the Earth's early core and mantle as a function of the fraction of the precursor cores equilibrating with a magma ocean. At full equilibration, the He concentration in the Earth's core is entirely set by liquid-liquid partitioning (Bouhifd *et al.*, 2013) (where D_{He} ranges from 10^{-2} to 10^{-3} , depending on the average depth of the magma ocean due to pressure dependence of D_{He}). Due to the lithophile behaviour of He under such conditions, the absolute He concentrations in the Earth's core are low (Bouhifd *et al.*, 2013). In contrast, based on the conditions studied here, core-forming liquids from planetesimals and planetary embryos are enriched in He by up to four orders of magnitude relative to Fe-rich metal in equilibrium with a magma ocean. Therefore, even small contributions from those enriched liquids to the Earth's core will have a significant impact on the total He balance. For example, if 90 % of precursor cores equilibrate with the mantle, our model predicts that the He concentration in Earth's core is 18 to 168 times higher than in the case of full metal-silicate (liquid-liquid) equilibrium, depending on the assumed depth of the magma ocean (Bouhifd *et al.*, 2013). This "enrichment factor" rises to about 110 to 1100 when using the lowest limit of equilibration of 36 % constrained by geochemical systems (Rudge *et al.*, 2010). However, even at 99 % equilibration of precursor cores, the enrichment factor is still around 10.

The new metal-silicate (liquid-solid) partition coefficient for He (Fig. 2) obtained here shows that the Earth's

core may have incorporated significantly more primordial He (= ^3He -rich material) than previously considered possible (Bouhifd *et al.*, 2013) due to a fraction of planetesimal cores that fails to equilibrate with magma ocean liquids. The degree of equilibration and the depth of the magma ocean, for which precise constraints are missing, control the He balance; our new estimates for the initial primordial He concentration in the Earth's core vary by three orders of magnitude (Fig. 3). The lowest limit of equilibration of 36 % (Rudge *et al.*, 2010) should be regarded with caution because more recent accretion models for Earth based on N-body simulations (Rubie *et al.*, 2015) are only compatible with substantially higher degrees of equilibration.

Interestingly, all noble gases behave similarly when partitioning between crystal and melt (Heber *et al.*, 2007) or between metal and silicate (liquid-liquid) (Matsuda *et al.*, 1993). Assuming this holds true between metal and silicate (liquid-solid) during percolative core formation, we infer that all noble gases are enriched in core-forming liquids in planetesimals and that the Earth's core incorporated not only primordial He but also Ne, Ar, Kr, and Xe, although elemental fractionation likely altered their relative initial abundances. In this scenario, the Earth's core could be the source of other primordial noble gases found in the lower mantle, such as solar-like Ne (Farley and Poreda, 1993). Because there is no evidence of direct assimilation of core-derived materials into the silicate Earth (Scherstén *et al.*, 2004; Mundl *et al.*, 2017), diffusion must be the mechanism by which the noble gases efficiently migrate from the Earth's outer core to the Earth's lower mantle. Core crystallisation (Hirose *et al.*, 2017) can be a driving force. The noble gases, which most likely prefer to reside in the liquid, are enriched in the liquid outer core, causing a permanent disequilibrium at the core-mantle boundary. We conclude, based on our mass balance considerations, that the high $^3\text{He}/^4\text{He}$ ratios in basalts (Kurz *et al.*, 1982; Hilton *et al.*, 1999; Graham, 2002; Stuart *et al.*, 2003; Starkey *et al.*, 2009) may well represent primarily the last vestiges of metal-silicate disequilibrium in a terrestrial magma ocean during Earth's formation.



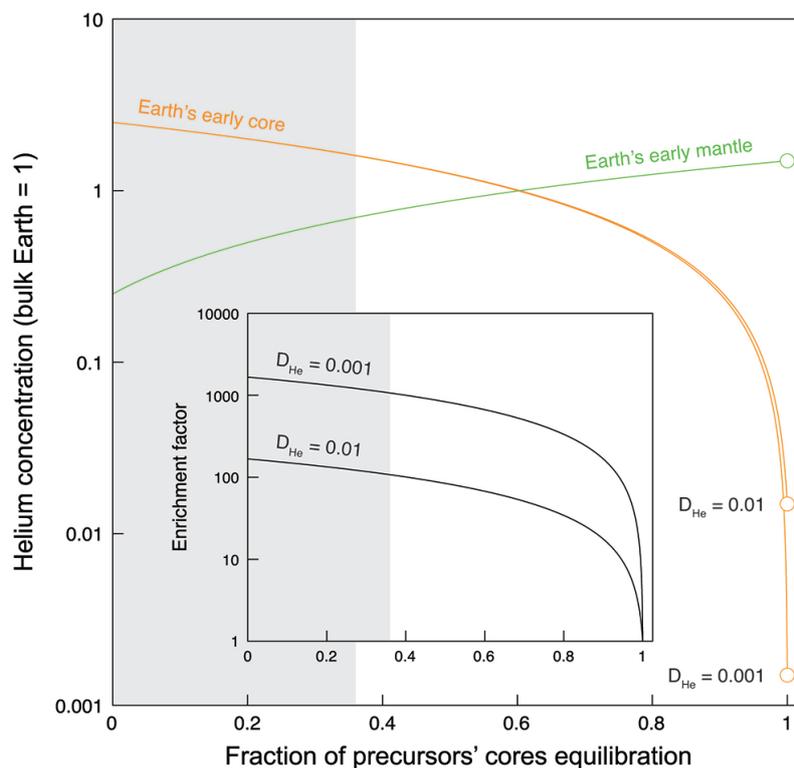


Figure 3 Helium concentration in the Earth's early core and mantle as a function of the fraction of precursors' cores equilibration with a terrestrial magma ocean. Mass balance calculations assume 1/3 metal and 2/3 silicate by mass and a He concentration in the bulk Earth that equals 1 (see Supplementary Information). Two scenarios are evaluated whereby metal and silicate (liquid-liquid) equilibrate in a shallow magma ocean ($D_{\text{He}} = 0.001$) and in a deep magma ocean ($D_{\text{He}} = 0.01$) (Bouhifd *et al.*, 2013). Datasets for the Earth's early mantle overlap on the diagram. The inset shows the enrichment factor, i.e. the He concentration in the Earth's early core at any fraction of equilibration relative to that assuming full (liquid-liquid) equilibrium. The shaded areas represent the range of equilibration from 0 to 36 %, for which geochemical models do not have satisfactory matches between siderophile element abundances and isotopic constraints (Rudge *et al.*, 2010).

Author Contributions

ASGR and HB conceived the idea. ASGR conducted the experiments and analyses with assistance from CL, CM and HB. ASGR, KWB and CL wrote the manuscript. All authors contributed to interpreting the results and commenting the manuscript.

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Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1901>.



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