A determination of the neon isotopic composition of the deep mantle

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Abstract

The neon isotopic composition of the deep mantle, which allows to investigate formation processes of the Earth, is subject to debate. We have analyzed Ne trapped in fluid inclusions from plume-related Devonian rocks from the Kola Peninsula, Russia. The lower limit for pristine neon in the deep mantle is set at $^{20}Ne/^{22}Ne \geq 13.0 \pm 0.2$, close to the solar wind (SW) value. We interpret this similarity as evidence that mantle light noble gases were directly incorporated from the solar nebula rather than derived from implanted meteoritic solar component, possibly through gravitational capture of a proto-atmosphere. This constraint is consistent with geochemical observations of rapid accretion of a major part of the growing Earth within the inferred lifetime of the solar nebula. If depleted mantle neon admits an upper limit of 12.5, then the occurrence of plume type neon with $^{20}Ne/^{22}Ne \geq 13.0 \pm 0.2$ may indicate a primordial Ne heterogeneity in the mantle. The $^{3}He/^{22}Ne$ ratios of terrestrial mantle reservoirs sampled by MORB and plumes vary with the degree of volatile element depletion of the mantle. This correlation was possibly established during magmatic events having led to the chemical characteristics of the depleted mantle reservoir.
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1. Introduction

The isotopic composition of mantle neon is different from that of the atmosphere. In a three-isotope diagram ($^{20}Ne/^{22}Ne$ versus $^{21}Ne/^{22}Ne$, Fig. 1), mantle data define several arrays that can be understood as representing mixing between air-like Ne and several mantle components presenting coupled enrichments in ^{21}Ne and ^{20}Ne. High $^{21}Ne/^{22}Ne$ in the mantle are the result or ^{21}Ne production by the nuclear reaction ^{21}Ne $(^{18}O(\alpha, n)\ ^{21}Ne)$, whereas high $^{20}Ne/^{22}Ne$ ratios can hardly be ascribed to any known nuclear reaction and are interpreted as representing a non-atmospheric [1,2], solar-like [3–5], component in the mantle. The mantle arrays tend towards an end-member that could be characterized by the $^{20}Ne/^{22}Ne$ ratio analyzed in the modern solar wind (SW; $^{20}Ne/^{22}Ne=13.5\pm0.2$, average from compilation in [6]) and possibly representing

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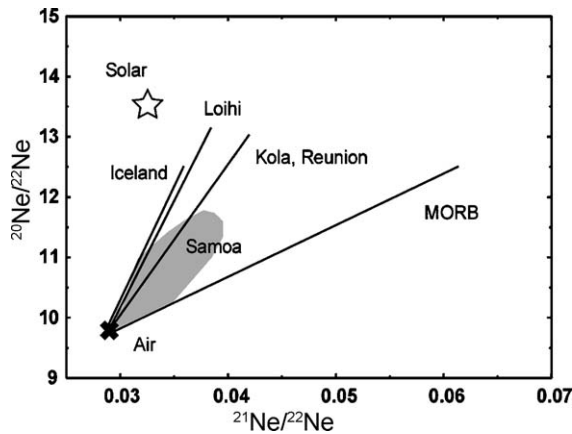*E-mail address:* yokochi@crpg.cnrs-nancy.fr (R. Yokochi).

Fig. 1. Neon three isotope plot for mantle-derived samples. The slopes of the different lines depend on the proportion of primordial neon relative to U and Th, the radioactive parents of nucleogenic neon isotopes. Correlation lines approximate the volcanic provinces: MORB [50], Kola [15], Reunion [8,51], Loihi [7], Iceland [7,34] and shaded area represents Samoa [52].

solar neon. The slopes of the different mantle arrays represent the ratio between trapped, non-atmospheric Ne and nucleogenic Ne in the respective mantle sources, in perfect agreement with He isotope systematics.

There is an active debate on the origin of the mantle excess ^{20}Ne. The precise value of the $^{20}Ne/^{22}Ne$ ratio is not known due to the ubiquitous contribution of air-like neon ($^{20}Ne/^{22}Ne=9.80$) to mantle-derived samples. Trieloff et al. [7,8] proposed that mantle neon sampled in Iceland, Hawaii and Réunion plume provinces is different from solar wind neon in that it admits an upper limit for $^{20}Ne/^{22}Ne$ of 12.5. Harrison et al. [9] found $^{20}Ne/^{22}Ne$ up to 13.75 ± 0.32 in a sub-glacial basalt glass from Iceland, but subsequent analyses of the very sample by Harrison et al. [10] did not confirm this value. $^{20}Ne/^{22}Ne$ ratios higher than 12.5 have been observed occasionally during step-heating experiments [11,12], but it is not clear if such high values represent a primitive component or are due to isotopic fractionation, e.g., during thermal release. According to Trieloff et al. [7], a mantle $^{20}Ne/^{22}Ne$ ratio of 12.5 qualifies a specific component that was defined as an end-member for gas-rich meteorites (Ne–B) in early meteorite studies [13]. This component could represent solar gases trapped onto meteoritic material by irradiation and ion implantation. This controversy has important implication for the

formation of the terrestrial atmosphere and the early evolution of the Earth. Direct trapping of solar gas requires the solar nebula to be present during early stages of the evolution of our planet and specific trapping processes (e.g., dissolution in magma ocean etc.). Contribution from irradiated bodies puts constraints on the time scale for the growth of planetary bodies relative to the lifetime of the solar nebula.

The issue beyond this controversy is largely analytical [14]. Samples having enough neon to permit the analytical precision requested to solve this problem are often contaminated by atmospheric neon, whereas samples which have suffered little air contamination are often extremely depleted in trapped noble gases, preventing high-precision analyses of Ne isotope ratios. In addition, magmatic volatiles are severely lost by degassing during magma residence in shallow magma chambers, and can be contaminated by atmospheric volatiles during assimilation and degassing. Plutonic bodies could be less subject to degassing and shallow contamination due to their crystallization under high pressure.

The Kola carbonatite–ultramafic complex, Eastern Baltic shield, Russia, provides exceptional samples in this context. Rocks and mineral separates from these plutonic bodies contain abundant fluid inclusions having trapped plume-like noble gases with $^{3}He/^{4}He$ ratios up to 24 Ra [15,16]. The neon isotopic ratios define a correlation line clearly less nucleogenic than that of MORBs (Fig. 1). In addition, $^{4}He/^{40}Ar*$ ratios between 1.2 and 13 [15] are much less variable than ratios observed in other mantle-derived samples including MORBs (0.02 to 100: e.g., [17]), and encompass the ratio of 2–5 inferred for production/accumulation in the mantle (e.g., [18]). Thus, Kola noble gases are unlikely to have been largely fractionated by magmatic processes, an important requisite when studying Ne isotopes for which relative mass differences are large. Their plutonic occurrence warranties limited magma degassing and atmospheric contamination compared to volcanic rocks. Because mantle noble gases are concentrated in fluid inclusions in Kola rocks and minerals, vacuum crushing allows to recover a noble gas component well preserved from radiogenic and nucleogenic in-growth after magma emplacement.

In order to precisely document the Ne isotopic signature of the deep mantle, we have undertaken a systematic study of selected Kola samples showing

high $^{20}Ne/^{22}Ne$ and $^{40}Ar/^{36}Ar$ ratios determined in a previous study [15], with the expectation that these samples should represent best the source composition. In this study, we identified the least air-contaminated mineral phases and worked on large sample fractions (several grams) to obtain a high precision on isotopic ratios.

2. Samples and analyses

The Devonian Kola ultramafic–alkaline–carbonatitic complex consists of 36 plutonic massifs. Among the five massifs studied by Tolstikhin et al. [16], four samples were carefully chosen according to their limited atmospheric and nucleogenic contributions. These are: dunite LV1 from Lesnaya Varaka, pyroxenite SB1 and apatite-diopside-phlogopite ore material SB2 and SB3 from Seblyavr. Magnetite was manually separated using a magnet followed by handpicking under a binocular microscope. Samples weighing between 5 and 14 g of bulk rock or mineral separate were washed ultrasonically in acetone. They were then loaded in large crusher tubes (length ≈ 26 cm, diameter ≈ 3.5 cm) which were evacuated and heated at 430–480 K overnight under high vacuum.

Table 1
Isotopic compositions and concentrations of neon and helium in Kola plume-related samples

	Aliquot	Weight (g)	Stroke	^{4}He 10^{-11} (mol/g)	^{20}Ne 10^{-15} (mol/g)	$^{3}He/^{4}He$ (R/Ra)	$^{20}Ne/^{22}Ne$	$^{21}Ne/^{22}Ne$
SB1								
Bulk	1	11.4	10	0.86	0.28	20.2±1.6	11.59±0.24	0.0351±0.0029
		11.4	50	2.2	0.57	20.6±1.2	11.75±0.17	0.0351±0.0019
		11.4	500	23.1	7.7	21.9±1.3	11.80±0.07	0.0359±0.0005
		11.4	500	37.4	13.4	20.8±1.3	11.79±0.04	0.0347±0.0003
SB2								
Bulk	1	14.3	300	3.5	4.1	16.3±1.0	10.96±0.04	0.0331±0.0005
		14.3	400	4.0	3.5	18.0±1.1	11.10±0.04	0.0321±0.0005
		14.3	400	2.8	1.5	15.3±1.5	11.58±0.07	0.0355±0.0006
		14.3	800	4.8	1.8	16.1±1.6	12.23±0.06	0.0364±0.0007
		14.3	800	2.2	0.76	14.1±1.6	11.94±0.13	0.0393±0.0016
Magnetite	2	7.8	500	25.3	10.6	15.9±0.8	12.12±0.07	0.0360±0.0004
SB3								
Bulk	1	7.3	150	13.9	6.0	15.7±1.8	11.06±0.06	0.0329±0.0004
		7.3	300	9.5	3.3	14.4±1.7	11.62±0.06	0.0357±0.0008
		7.3	500	6.0	1.7	11.3±1.3	11.52±0.11	0.0416±0.0013
		7.3	1000	8.9	1.0	6.5±0.7	11.04±0.15	0.0514±0.0022
Magnetite	2*	6.7	100	7.3	8.8	17.1±2.2	10.76±0.03	0.0332±0.0009
		6.7	100	4.7	3.6	18.2±2.0	10.99±0.07	0.0340±0.0012
LV1								
Bulk	1	8.5	200	0.6	0.66	12.6±0.9	11.58±0.16	0.0345±0.0021
		8.5	300	0.6	0.64	11.7±1.1	12.14±0.19	0.0372±0.0022
		8.5	400	0.5	0.47	10.6±0.9	12.91±0.28	0.0409±0.0033
Magnetite	2*	10.2	135	1.0	0.70	13.5±0.8	13.04±0.20	0.0425±0.0040
Magnetite	3*	5.0	400	3.6	1.5	11.9±1.4	12.71±0.20	0.0403±0.0035
		5.0	600	1.7	1.1	11.5±1.1	12.78±0.21	0.0430±0.0049
Magnetite	4*	10.2	600	2.3	1.6	12.3±1.1	12.93±0.12	0.0421±0.0021
Magnetite	5	10.2	500	2.5	1.8	12.7±0.5	12.62±0.11	0.0391±0.0010
Olivine	6*	10.6	500	0.33	0.43	10.9±0.7	12.10±0.22	0.0422±0.0030
Olivine	7	10.7	500	0.40	0.65	13.1±1.8	12.24±0.17	0.0450±0.0041

Blanks are 5.0×10^{-14} mol ^{4}He with an atmospheric He isotopic composition and 8.0×10^{-16} mol ^{20}Ne at $^{20}Ne/^{22}Ne$=9.6, $^{21}Ne/^{22}Ne$=0.027 for the experiments with * along the number of aliquot, and 3.8×10^{-16} mol ^{20}Ne at $^{20}Ne/^{22}Ne$=8.7, $^{21}Ne/^{22}Ne$=0.030 for the others. Errors are 1σ.

All noble gases were analyzed following the procedure described by Marty et al. ([15], electron energy of 60 eV, trap current of 200 µA). Data for Ar, Kr and Xe will be reported elsewhere. Gases were sequentially purified over four titanium sponge getters cycled between 900 K and room temperature. Xe, Kr, Ar were then cryogenically separated using glass and charcoal fingers held at liquid nitrogen temperature. Subsequently, neon was absorbed on a stainless steel grid cooled at 17 K, whereas gaseous helium was introduced in the mass spectrometer for isotope analysis. Neon was then desorbed from the cryogenic trap heated up to 40 K and was admitted in the mass spectrometer source where it was exposed to a stainless steel finger containing activated charcoal at liquid nitrogen temperature for 5 min before starting analysis. This procedure was aimed to minimize mass interferences ($^{40}Ar^{2+}$, $^{44}CO_2^{2+}$). Peak heights and isotopic ratios were extrapolated to the time of measurement start and the reproducibility of the whole procedure was insured by carefully adopting the same time intervals for each procedural step. Blank experiments were done by activation of the solenoid crusher without sample (Table 1). The effect of Ar^{2+} on ^{20}Ne was negligible (less than 0.1%), and the contribution of CO_2^{2+} was corrected as a part of blank, never exceeding 0.5% except for measurements on bulk LV1 (up to 1%). The helium blank was variable around 5×10^{-14} mol and displayed an atmospheric isotopic composition ($\pm 50\%$).

3. Results

3.1. Isotopes

The $^{20}Ne/^{22}Ne$ ratios of single analyses (Table 1, Fig. 2) vary from 10.76 ± 0.03 to 13.04 ± 0.20. Dunite LV1 shows the highest $^{20}Ne/^{22}Ne$ ratios (filled circles in Fig. 2). The $^{20}Ne/^{22}Ne$ ratios lower in SB samples than in LV1 are probably the result of greater atmospheric contamination for the former, a view consistent with microscopic observation (e.g., presence of serpentine and recrystallized calcite in SB series while they are absent in LV1). Ti-magnetite separates from LV1 turned out to be the carrier of the high $^{20}Ne/^{22}Ne$ component (Table 1). Ti-magnetite analyses yielded a statistical mean of 12.80 ± 0.07 ($n=5$). In a
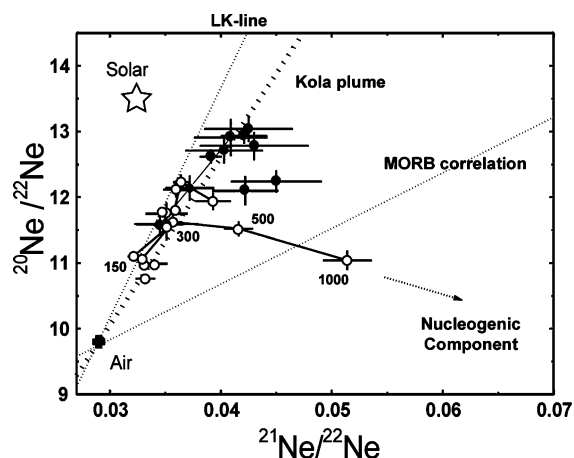

Fig. 2. Neon isotopic data of Kola samples. (●) LV1 (dunite), the sample showing the highest $^{20}Ne/^{22}Ne$ ratios. Tied points represent different steps of crushing on the same aliquot and numbers accompanying the points are the numbers of strokes. LK: Loihi–Kilauea.

three-isotope diagram, isotope data for all four samples show a common correlation close to the Loihi–Kilauea (LK) trend ([19], Fig. 2), consistent with their mantle plume origin inferred in previous works [15,16]. Further crushing of apatite-bearing samples (SB3) showed significant decrease of the $^{20}Ne/^{22}Ne$ ratios due to increasing contribution of nucleogenic neon rich in ^{21}Ne produced within the matrix since the time of magma emplacement. Data away from the correlation line are not used when discussing the elemental $^{3}He/^{22}Ne$ ratio in Section 3.3.

We consider that the highest $^{20}Ne/^{22}Ne$ ratio observed in the Kola samples represents a lower limit for the primordial neon isotopic ratio because:

(i)   atmospheric contamination cannot be discarded,
(ii) nucleogenic ^{22}Ne was also produced in the mantle since terrestrial accretion, and
(iii) such contribution might have occurred since magma cooling.

3.2. Contribution of in situ produced component

Unlike modern oceanic basalts, the Kola samples might have accumulated radiogenic and nucleogenic isotopes produced after magma cooling during the crustal residence time (380 Myr), since the U contents

of Kola rocks are high, up to 1 ppm in dunites [16]. He isotope variations among the four studied samples are likely to result from such effect because He isotopic ratios correlate with bulk U contents [15]. Fig. 3 represents the covariation of ^{4}He extracted from vesicles with radiogenic ^{4}He computed for the bulk samples over 380 Ma, using measured uranium contents, both values normalized to ^{3}He in the vesicles (all data are from [15]). The resulting good correlation indicates that all samples shared a common He isotopic ratio at the time of emplacement, given by the *y*-intercept in Fig. 3. The initial ^{4}He/^{3}He ratio of 33,200±2600 (^{3}He/^{4}He=21.8±1.7 Ra) is fully consistent with the lowest ^{4}He/^{3}He value of $3.0×10^4$ measured by Tolstikhin et al. [16].

The slope of the correlation, $3.6×10^{-4}$ (±10%), is a function of the mean efficiency of radiogenic contribution from U and Th in He in fluid inclusions to the crystalline matrix. Given that the average vesicle size (10 μm or less) is comparable to the alpha track length (10–30 μm), the fraction of in situ produced radiogenic ^{4}He trapped in the vesicles is expected to be proportional to the volume ratio of vesicles to crystalline matrix. Because previous experiments have shown that the major component in the fluid inclusions is H_2O
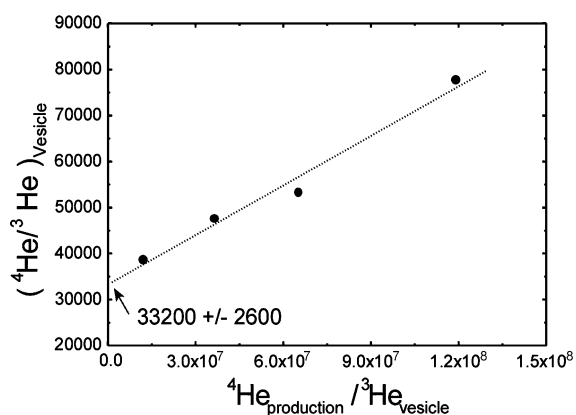

Fig. 3. Comparison between ^{4}He released from vesicles and ^{4}He computed for in situ production, both normalized to ^{3}He from vesicles. The ^{4}He/^{3}He ratio of the vesicle fluid at the time of trapping is given by the *y*-intercept of the correlation and is consistent with the least radiogenic value among [15] and [16]. All data including He isotope and abundance are from [15] because the quantities released in [15] were larger than that released by this study, implying more efficient extraction in the previous study.

[15], the vesicle volume may be approximated by the total amount of water released upon crushing, which averages $3±1×10^{-7}$ mol/g for these four samples (CRPG, unpublished data). Assuming densities of 1.1 and 3.0 g/cm^3 for vesicle fluid (dv) and crystalline matrix (dh), respectively, the computed vesicularity (Vs) is:

$$V_s = Q × m_{H_2O} × \left(\frac{dh}{dv}\right) = 1.5 × 10^{-5} \qquad (1)$$

where Q is the molar quantity of water per gram of rock and m_{H_2O} is the molar mass of water. The vesicularity computed from He mass balance ($3.6×10^{-4}$) and that estimated from water mass balance ($1.5×10^{-5}$) differ by one order of magnitude, therefore implying possible contribution of radiogenic helium by diffusion from the crystalline matrix.

These two possible processes, recoil and diffusion, are less likely to have affected neon. The recoil path length of ^{21}Ne* is only a few micrometers, and the neon diffusion coefficient in minerals is orders of magnitude lower than that of helium [18]. Production of ^{21}Ne* could have taken place directly in fluid inclusions through the $^{18}O(\alpha,n)^{21}$Ne reaction, induced by alpha particles recoiling into fluid inclusions. However, nucleogenic ^{21}Ne* expected from radiogenic ^{4}He constitutes less than 2% in most samples (provided that the ^{4}He/^{21}Ne production ratio in water is similar to that in the matrix). Moreover, isotopic compositions of studied samples do not significantly deviate from the three-isotope correlation line (except for the last steps of apatite-bearing samples, Fig. 2).

3.3. Elemental ratio

Noble gas elemental ratios such as ^{3}He/^{22}Ne allow to investigate the origin and evolution of terrestrial volatiles because they show variable values among potential extraterrestrial precursors and because they have probably been affected by differentiation processes. However, these source ratios are subject to changes due to contribution from the atmosphere or from nuclear reaction products after magma cooling. A method to correct atmospheric contamination was proposed by Honda et al. [19]: measured ^{20}Ne/^{22}Ne values are decon-

voluted into three (atmospheric, solar and mantle) components (Appendix A). Because of its low abundance in air, [3]He does not require correction for atmospheric contamination. Furthermore, in situ produced nucleogenic [3]He is negligible compared to the amount present in mantle-derived samples.

[3]He/[22]Ne$_{cor}$ ratios corrected for atmospheric contribution need further correction for recent elemental fractionation through magmatic processes (e.g., diffusion in minerals and melt, degassing, etc. [20,21]). Among the present samples, there exists a good correlation between [3]He/[22]Ne$_{cor}$ and [4]He/[21]Ne* (Fig. 4) so that the non-fractionated [3]He/[22]Ne ratio is estimated to be 7.9±0.4 for a mantle [4]He/[21]Ne* production ratio of 2.2×10^7 [22].

It must be noted that the [3]He/[22]Ne correction does not depend heavily on the assumed mantle [20]Ne/[22]Ne ratio. For example, adopting a [20]Ne/[22]Ne of 13.0 instead of 13.5 would result in a [3]He/[22]Ne ratio of 6.5±0.6 for the Kola mantle value computed above. Variations in estimated value of the mantle production ratio have some effect on the fractionation-corrected [3]He/[22]Ne. Three recent estimates of [4]He/[21]Ne* [22–24] vary by 27% and lead to [3]He/[22]Ne=10.0 when the highest [4]He/[21]Ne* ratio (2.8×10^7; [23]) is considered. In all cases, these values are significantly different from both solar wind and MORB values.
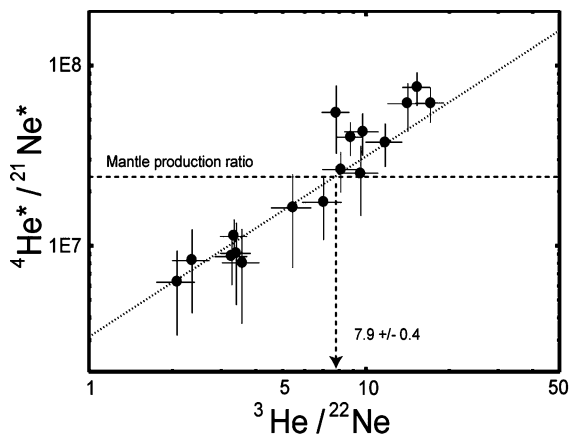

Fig. 4. [3]He/[22]Ne–[4]Ne/[21]Ne* correlation for Kola samples. For computation, the helium isotopic composition of all samples is assumed to be 24 *Ra*. Intersection between the correlation line and [4]He/[21]Ne*=2.2×10^7 (the best estimate for the mantle production ratio) gives [3]He/[22]Ne=7.9±0.4 for the Kola mantle source.

4. Discussion

4.1. Light noble gas implication for solar nebula contribution

Our data show that the mantle source of the Kola plume is characterized by [20]Ne/[22]Ne≥13.0±0.2. Before discussing the significance of this value, it is necessary to precise the solar Ne isotopic composition.

The isotopic composition of solar wind neon has been measured during several Al-foil experiments on the Moon. Neon isotopes may fractionate during solar wind acceleration (Coulomb drag effect), as suggested by a possible correlation between Ne and He isotopic compositions measured in the different Al-foil experiments [6]. This process might explain the [20]Ne/[22]Ne variability observed among lunar soils (see below), and we consider that the average value of all Al-foil experiments [6], 13.5±0.2, gives a first-order estimate for the solar Ne isotopic composition. This value is compatible with that measured in the solar colona by the SOHO spacecraft (13.8±0.7; [25]).

Two solar components have been identified in lunar soils, solar wind (SW: [20]Ne[22]Ne=13.8±0.1 and 13.4±0.1 in lunar ilmenites of different antiquities; [26]) and solar energetic particles (SEPs: [20]Ne[22]Ne= 11.2±0.2; [26]). These two components are also present in solar-gas-rich meteorites (reviewed in [27,28]). Before such an identification, Black [13] proposed an end-member in gas-rich primitive meteorites having [20]Ne[22]Ne=12.52±0.18, labelled Ne–B, which can now be regarded as a mixture of SEP and SW (e.g., [27,28]). Planetary bodies including meteorites and bulk lunar samples presenting [20]Ne/[22]Ne ratios higher than 12.5 are rare, which lead Trieloff et al. [7,8] to propose that an upper limit of 12.5 for the mantle [20]Ne/[22]Ne ratio indicates that primordial mantle neon was carried by irradiated meteoritic material. Our observation of [20]Ne/[22]Ne≥13.0±0.2 does not fit such model and rather suggests the incorporation of mantle neon from the solar nebula gas.

Trieloff et al. [7,8] proposed that the neon isotopic composition of the upper mantle sampled by MORBs admits an upper limit of [20]Ne/[22]Ne=12.5, based for example on uniform Ne isotopic composition for samples little affected by atmospheric contamination.

The present data for plume-derived material suggest that neon sampled by deep mantle plume represents a remnant of a primordial component either stored in the lower mantle or derived from the core, trapped during early stages of terrestrial accretion in a nebular gas-rich environment. A secondary Ne component now seen in the mantle source of MORBs might have been acquired from in-falling bodies or from irradiated dust particles at later stages of Earth's accretion [3]. Thus, neon isotopes may provide the first direct evidence for mixing between nebular and planetary components in Earth.

4.2. Incorporation of solar nebula gas in the mantle

Nebula gas capture by proto-planets and subsequent sequestration in pores upon closure has been advocated in the case of heavy noble gases [29]. This process, however, is expected to fractionate noble gas abundances and isotopic ratios and to drastically deplete light species. Alternatively, noble gases from a gravitationally bound solar-like proto-atmosphere [30] could have been dissolved into a magma ocean [31]. If the proto-atmosphere behaves as an ideal gas in hydrostatic equilibrium, the surface pressure depends on the size of the Earth and on its thermal structure [32,33]. The latter is controlled by the rate of accretion (releasing gravitational energy) and the atmospheric opacity (blanketing the heat). Although detailed modelling is beyond the scope of this study, its feasibility may be evaluated by estimating proto-atmospheric pressure required to account for the Ne content of the deep mantle. The least nucleogenic mantle Ne component had been found in Icelandic basalts [7,34,35]. The $^{21}Ne^*/^{22}Ne$ ratio (where $^{21}Ne^*$ is ^{21}Ne produced in the mantle and ^{22}Ne is mainly primordial, see Appendix A for calculation) is 0.0040 for Icelandic samples (only data with $^{20}Ne/^{22}Ne$ higher than 11 are considered). For a bulk silicate Earth composition, ^{21}Ne produced during 4.55 Gy is 7.5×10^{-17} mol/g, so that the concentration of ^{22}Ne is 1.9×10^{-14} mol/g. Assuming that the $^{4}He/H$, $^{4}He/^{20}Ne$ and $^{20}Ne/^{22}Ne$ ratios of the solar nebula are 0.1, 650, 13.5, respectively [28], the molar fraction of ^{22}Ne in the nebula is 1.3×10^{-5}. Using a Ne solubility (Henry) coefficient of 1.1×10^{-8} mol/g atm [18], only 0.13 atm of proto-solar atmospheric pressure would be required in case of simple melt-gas partitioning. For comparison, Porcelli et al. [36] proposed that a proto-atmosphere pressure of 100 atm would be necessary based on a two-stage mantle evolution model of Xe isotopic composition. Their model took into account the progressive crystallization of the magma ocean, promoting depletion of noble gases in the crystallized mantle [36,37].

Sasaki and Nakazawa [33] modelled the pressure of a proto-atmosphere at a planetary surface as:

$$P(atm) = 7.2 \times 10^{-13} \left(\frac{\mu^4 \bar{\rho}}{\kappa} \right) \tau_{accr} \left(\frac{M}{M_E} \right)^3 \qquad (2)$$

where μ, $\bar{\rho}$ and κ, are the mean molecular weight of gas, planetary mean density and atmospheric opacity assumed to be 2.28 kg/m^3, 5000 kg/m^3 and 0.1 m^2/kg, respectively. M is the mass of the accreting planetary body and τ_{accr} is the accretion time scale for growing 1 M_E, which we assume to be 30 My according to W–Hf systematics of our planet [38,39]. While this model considered that the solar nebula was present through accretion processes because of the short accretion time scale considered by these authors, the lifetime of nebula is estimated to be at most 10 Myr [40]. Assuming that the nebula capture ended at an accreting stage when the nebula dissipated, the surface pressures determined by the accreted masses at the time of dissipation are 0.2, 3.6 and 15 atm at 20%, 50% and 80% accretion, respectively. Accordingly, a pressure of at least an order of magnitude of higher than the one required for melt-gas partition could have been achieved. There are many uncertainties on, for example, opacity, accretion rate, crystallization of the proto-mantle, re-equilibration with escaping atmosphere, that could significantly change these numbers, but the basic message that such a simple approach gives is that incorporation of solar neon during terrestrial accretion is a plausible process rather than an accidental one.

4.3. $^3He/^{22}Ne$ ratio and mantle evolution

Kola mantle noble gases present $^3He/^{22}Ne$ ratios significantly higher than the solar nebula value of 1.5 (Appendix B), requiring a specific fractionation process to enrich helium relative to neon. After the correction for atmospheric contamination and magmatic fractionation [41] (Appendix A) of different

mantle domains, the $^3He/^{22}Ne$ ratios correlate well with the degree of enrichment in nucleogenic ^{21}Ne ($\Delta^{21}Ne$, Appendix A, Fig. 5), implying that a process able to decrease the time-integrated primordial neon component relative to U, Th is also responsible for enhancing the $^3He/^{22}Ne$ ratio.

This correlation is mathematically predictable because both $\Delta^{21}Ne$ and $^3He/^{22}Ne$ are a function of $^{21}Ne*/^{22}Ne$ (Appendix A). Furthermore, the relationship between $^3He/^{22}Ne$ and $\Delta^{21}Ne$ depends on the He isotopic composition (Appendix A, Fig. 5) so that to a given He isotope ratio corresponds a distinct correlation curve in Fig. 5.

4.4. Possible He/Ne fractionation processes

Recent experiments do not support such He/Ne fractionation through melt-mineral partitioning as they tend to show that all noble gases have approximately the same incompatibility [42]. Alternatively, the required fractionation could be linked with magma degassing because (i) helium is more soluble in basaltic melt than neon, and (ii) magma degassing constitutes an obvious way to separate volatile elements from refractory ones. Due to difference in solubility coefficients, dissolution of solar gas in a

Fig. 5. Covariation between $^3He/^{22}Ne$ and $\Delta^{21}Ne$ among various terrestrial mantle sources. Only data with $^{20}Ne/^{22}Ne \geq 11$ obtained by crushing extraction are used. Data having $\geq 50\%$ of total uncertainty are not displayed. Popping Rock (○), Kola (△), Réunion (■), Loihi (▽), Samoa (▲) and Iceland (●). Same data source as in Fig 1.

magma ocean could have fractionated the $^3He/^{22}Ne$ ratio by a factor of 2. This would have raised the $^3He/^{22}Ne$ ratio to about 3, thus accounting for some of the plume-like values. However, further fractionation is required to account for the MORB $^3He/^{22}Ne$ ratio of 10.4.

The $^3He/^{22}Ne$ fractionation could have taken place early in Earth's history during formation of the atmosphere. Models of early atmospheric evolution propose gradual dissipation of the nebula-derived primitive atmosphere either by EUV radiation or by large impacts (e.g., [43–45]). Mantle melts could have exchanged fractionated volatile elements with the progressively fractionated atmosphere. Atmospheric dissipation by hydrodynamic escape favours loss of light species (especially He) relative to heavy ones (in this case, Ne). If this was the case, however, the nucleogenic reservoir (i.e., degassed and depleted in neon) should present a $^3He/^{22}Ne$ ratio lower than initial atmospheric value, contrary to the observation, making this possibility unlikely.

Gas-melt partitioning during magmatic processes may provide enrichment of He relative to Ne in the melt [46]. However, the solubilities of noble gases and of most volatile species prone to develop a gas phase (e.g., CO_2, N_2) are extremely low at low pressure, implying quantitative degassing of mantle-derived magmas and therefore very low retention of residual volatiles. In order to retain a sizeable amount of noble gases in the residual mantle, the gas fraction should have been very low, of the order of 10^{-8} [47], thus requiring specific pressure conditions. Melt segregation in the deep mantle has been suggested as a cause of mantle heterogeneity [48,49]. In these models, the refractory, unmelted, mineral assemblage becomes the depleted mantle source of MORBs and the melt supplies material for the OIB-type source. A plausible consequence of low partial melting rates inferred in these models is volatile oversaturation and development of a fluid phase. Provided that melt-fluid partitioning causes elemental fractionation similar to that resulting from gas-melt partitioning (which is not yet experimentally proven), the observed $^3He/^{22}Ne$ variation could therefore be the result of such mantle melting processes. In case of equilibrium between gas, melt and mineral, helium would be enhanced in the melt. Assuming similar partition coefficient between
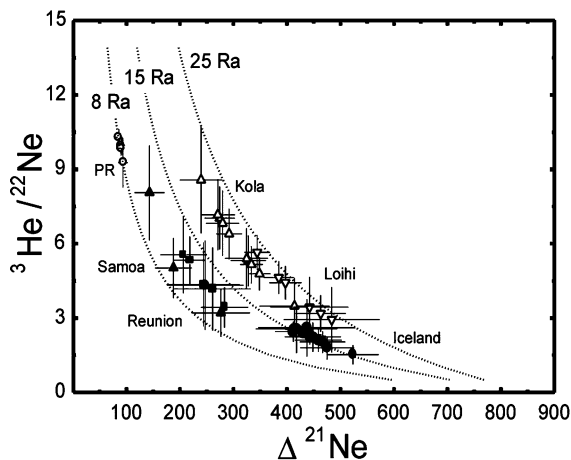
melt and mineral for He and Ne, the refractory mineral assemblage would also be enriched in ^{3}He relative to ^{22}Ne.

The ^{3}He/^{22}Ne fractionation appears linked with the time-integrated depletion of mantle reservoirs. Unfortunately, the behaviour of noble gases during partial melting is still poorly known, precluding any conclusion on involved fractionation processes. Testing this hypothesis will require experimental fluid/melt/mineral partitioning in high P–T conditions.

5. Conclusion

(1) Plume-related minerals host a deep mantle neon component characterized by ^{20}Ne/^{22}Ne$\geq$ 13.0$\pm$0.2. This finding suggests that solar-like light noble gases were incorporated in the terrestrial mantle directly from the solar nebula rather than derived from implanted, meteoritic-like, solar component, thus implying that the Earth grew to a significant size when the proto-solar nebula was still present.

(2) Differences in ^{20}Ne/^{22}Ne between MORB and plume sources, if real, could be a consequence of a transition in the accretion regime of the Earth.

(3) ^{3}He/^{22}Ne ratios of mantle reservoirs sampled by MORBs and by different plumes correlate with the nucleogenic contribution to neon isotopes, the latter reflecting the degree of neon depletion relative to refractory elements U and Th. This correlation is consistent with gas-melt partitioning governing the distribution of volatile elements in the mantle, although it requires a number of specific conditions including partial melting at depth in the mantle. Tests of these possibilities require developing adequate experiments of noble gas partitioning involving a fluid phase under mantle conditions.

Acknowledgements

Appendix A

A.1. Atmospheric contamination

Subscripts a, m, i, obs, correspond to atmospheric, mantle, initial, and observed values, respectively. Let f_a be the atmosphere-derived ^{22}Ne fraction ($f_a+f_m=1$) (^{20}Ne/^{22}Ne)$_{obs}$ is expressed as:

$$\left(\frac{^{20}Ne}{^{22}Ne}\right)_{obs} = f_a\left(\frac{^{20}Ne}{^{22}Ne}\right)_a + f_m\left(\frac{^{20}Ne}{^{22}Ne}\right)_m \qquad (3)$$

Assuming ^{20}Ne/^{22}Ne$_m$=13.5, f_a for each sample may be determined. (^{21}Ne/^{22}Ne)$_m$ is also equal to:

$$\left(\frac{^{21}Ne}{^{22}Ne}\right)_m = \frac{1}{f_m}\left[\left(\frac{^{21}Ne}{^{22}Ne}\right)_{obs} - f_a\left(\frac{^{21}Ne}{^{22}Ne}\right)_a\right] \qquad (4)$$

Provided that nucleogenic ^{22}Ne is negligible, ^{21}Ne*/^{22}Ne is defined as:

$$\left(\frac{^{21}Ne*}{^{22}Ne}\right) = \left(\frac{^{21}Ne}{^{22}Ne}\right)_m - \left(\frac{^{21}Ne}{^{22}Ne}\right)_i \qquad (5)$$

We select a ^{21}Ne/^{22}Ne$_i$ ratio of 0.0333 [6].

Similarly, ^{3}Ne/^{22}Ne corrected for atmospheric contamination is equal to:

$$\left(\frac{^3Ne}{^{22}Ne}\right)_{cor} = \frac{1}{f_a} \times \left(\frac{^3He}{^{22}Ne}\right)_{obs} \qquad (6)$$

because atmospheric ^{3}He can be neglected.

A.2. Elemental fractionation

Honda and McDougall [41] proposed a way to calculate the nonfractionated $^{3}He/^{22}Ne_{cal}$ ratio by using only isotopic data:

$$
\left(\frac{^{3}He}{^{22}Ne}\right)_{cal} = \frac{\left(\frac{^{21}Ne}{^{22}Ne}\right)_{m} - \left(\frac{^{21}Ne}{^{22}Ne}\right)_{i}}{\left(\frac{^{4}He}{^{3}He}\right)_{obs} - \left(\frac{^{4}He}{^{3}He}\right)_{i}} \\ \times \left(\frac{^{4}He}{^{21}Ne}\right)_{pro} \tag{7}
$$

where subscript pro refers to the production in the mantle. We adopt this method for correcting elemental and selected literature data for samples analyzed by crushing and having $^{20}Ne/^{22}Ne > 11$.

It is necessary to note that the Icelandic value of the $^{3}He/^{22}Ne$ ratio is debated between a MORB-like end-member and a ratio even lower than the value characterizing the solar nebula [52]. It has been argued that Icelandic noble gases could have experienced recent mixing between fractionated end-members [34]. In such a case, the correction procedure of the $^{3}Ne/^{22}Ne$ ratio presented in Section 3.3 will not apply. So far, it is not understood if such mixing has occurred, an issue that needs further clarification.

A.3. Correlation

Let $\Delta^{21}Ne$ be the slope of the air-mantle mixing line in the neon three isotope plot:

$$
\Delta^{21}Ne = \frac{\left(\frac{^{20}Ne}{^{22}Ne}\right)_{obs} - \left(\frac{^{20}Ne}{^{22}Ne}\right)_{air}}{\left(\frac{^{21}Ne}{^{22}Ne}\right)_{obs} - \left(\frac{^{21}Ne}{^{22}Ne}\right)_{air}} \tag{8}
$$

which is equivalent to:

$$
\Delta^{21}Ne = \frac{\left(\frac{^{20}Ne}{^{22}Ne}\right)_{m} - \left(\frac{^{20}Ne}{^{22}Ne}\right)_{air}}{\left(\frac{^{21}Ne}{^{22}Ne}\right)_{i} + \left(\frac{^{21}Ne^{*}}{^{22}Ne}\right) - \left(\frac{^{21}Ne}{^{22}Ne}\right)_{air}} \tag{9}
$$

Eq. (7) can be rewritten as:

$$
\left(\frac{^{3}He}{^{22}Ne}\right)_{cal} = \frac{\left(\frac{^{21}Ne^{*}}{^{22}Ne}\right)}{\left(\frac{^{4}He^{*}}{^{3}He}\right)} \times \left(\frac{^{4}He}{^{21}Ne}\right)_{pro} \tag{10}
$$

Eqs. (9) and (10) imply that $\Delta^{21}Ne$ and $^{3}He/^{22}Ne_{cal}$ are inversely correlated. The range of variations is a function of the $^{4}He^{*}/^{3}He$ ratio.

Appendix B

Because ^{3}He was produced in the early sun due to deuterium burning, the present-day solar wind is believed to be enriched in ^{3}He relative to the solar nebula. Therefore, the $^{3}He/^{4}He$ ratio of the Jovian atmosphere (1.66×10^{-4}) may provide a better proxy of the He isotopic composition of the solar nebula, which leads to a $^{3}He/^{22}Ne$ ratio of 1.5 ($^{4}He/^{20}Ne=650$ and $^{20}Ne/^{22}Ne=13.5$ [6,28]). Note that in earlier study [41], a postdeuterium burning value was used and led to a solar $^{3}He/^{22}Ne$ ratio of 3.8.

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