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Surface noble gas recycling to the terrestrial mantle

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Abstract

In a recent paper, Ballentine and Barfod [Earth Planet Sci. Lett. 180 (2000) 39–48] emphasize the general existence of an atmospheric noble gas component closely resembling modern air in glass samples of Mid-Ocean Ridge Basalt (MORB) and Ocean Island Basalt (OIB). They show that this atmospheric component cannot be due to interaction of melt with seawater. They propose that air is added after sample recovery, perhaps in the laboratory, and trapped in microfractures that affect glass in response to cooling, where these microfractures should reseal after air trapping. In this paper, I show that this air component could also be of deep, mantle origin via recycling. This alternative concept explains virtually all of the puzzling observations and paradoxes related to the atmospheric component, and helps understanding noble gas systematics as generally seen in MORB and OIB samples. In particular, it explains why the air component is mainly borne by the largest vesicles. If this model is correct, popping rocks have in their vesicles a full volatile record of the melting process that affected the two-component or marble-cake upper mantle.
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1. Introduction

An atmospheric noble gas component is widely seen, together with mantle rare gases, in submarine basalt glass samples of Mid-Ocean Ridge Basalt (MORB) or Ocean Island Basalt (OIB), as pointed out in a recent work by Ballentine and Barfod [1]. This atmospheric component is generally attributed to addition of atmosphere-derived rare gases to magmas on the ocean floor at eruption, or shortly before in the last stages of ascent, such as, e.g., during stay in a magma chamber or through digestion of altered rocks. This is based on the enormously larger noble gas concentrations in sea water compared to basalts (except for helium).

Along many years, researchers have been more interested by mantle rare gases as is understandable (e.g., [2–5]). However, as shown in [1], noble gases

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often represent binary mixtures, and invariably one of the end members appears to be air, both in its isotopic and, more surprising, elemental ratios [5–8]. This atmospheric component was mentioned in some previous papers, such as Staudacher et al. [9] (their Figs. 2 and 3) and, more recently, Burnard et al. [10] and Trieloff et al. [5], but, to my knowledge, has never been extensively discussed until [1]. The crushing analyses on 2ΠD43 popping rocks by Moreira et al. [8] very clearly show a binary mixture of degassed mantle and atmospheric noble gases.

However, the intimate mechanism of this air addition, usually called contamination, was never completely understood, and none of the hypotheses above were ever validated. Ballentine and Barfod [1] rigorously show that they don't even work at all, and they conclude the atmospheric component is modern air trapped in cooling-related [11] microfractures after sample recovery, perhaps in the laboratory.

In this paper, I would like to present some remarks inspired by the Ballentine and Barfod [1] contribution. I focus on popping rocks and stress that these particular MORBs are doubly paradoxical. First, at a centimeter scale, they contain two strong noble gas components, degassed mantle and atmospheric. Second, their noble gas signatures make them considered as one of the best representative of the degassed mantle [5,7,8,12], while nonvolatile, isotopic tracers such as Pb, Sr or Nd point to a recycled mantle source [13,14]. I propose a different view of these paradoxes, leading to the idea that part of the air component is of mantle origin via recycling.

2. Some observations about vesicles and the atmospheric component in MORB and OIB glasses

2.1. About vesicles

2.1.1. Vesicles are heterogeneous

Ballentine and Barfod [1] provide a careful study of published data leading them to conclude that most samples actually display a heterogeneity in their vesicles at the scale of a hand specimen (typically 1 cm; typical vesicle size: 1 mm or less). Some vesicles bear mainly the atmospheric component, some others the mantle component, others

have a mixture of both. The same conclusion is reached by Trieloff et al. [5]. I believe it is obvious to any noble gas scientist who performed crushing or heating analyses that such a vesicle heterogeneity occurs in many MORB and OIB glass samples.

I strongly support Ballentine and Barfod [1] when they state that these observations rule out air addition to occur in the magma chamber, because it is not reasonable to assume that air might be added to some vesicles only, not to some others, at the scale of a hand specimen.

2.1.2. Vesicles are overpressured in MORBs

Popping rocks show the clearest evidence for having a pressure higher than 1 bar in their vesicles. Massive blocks of popping rocks were banging spontaneously on the deck of the R/V Akademik Boris Petrov, on which I was, when dredge 2ΠD43 was recovered. This noise made us realize that these might be popping rocks similar to the 1972 dredge [15,16]. Vesicles were bursting out in response to pressure drop from 350 to 1 bar. The high pressure was also measured, almost directly, by Burnard [17].

In the laboratory, 2ΠD43 is the only MORB sample for which I saw the vacuum gauge turn off due to off-scale excursion when a sample was placed in the crusher and pumped out. This happened typically two or three times in the 10^{-4} to 10^{-7} Torr range during about half an hour of pumping. Overpressured vesicles were bursting out in response to the lowering external pressure on the sample (see also [18]). Other MORBs also must have pressurized vesicles when they are not opened, but as they are much less numerous, the rocks do not explode spontaneously.

That vesicles contain atmospheric rare gases under pressure was stressed by Ballentine and Barfod [1], who write that "it is very hard to envision direct air contamination of vesicles at greater than 1 bar pressure".

2.2. About the sitting of the air component

2.2.1. Air is in the largest vesicles

Another simple observation, also discussed by Ballentine and Barfod [1], is that the air component generally appears in the first steps of crushing analyses. This is clearly shown in [8] and [5] for 2ΠD43 popping rocks, which have a complete vesicle

diameter distribution from about 0.1 to 1.5 mm [19], and it is obvious from my own experience for various samples (e.g., [7]). Ballentine and Barfod [1] write "The sitting" of the air component "is related to sites that are more easily ruptured than the sites containing the magmatic gas".

I believe this observation means that the air component is mainly borne by the largest vesicles. The most isotopically anomalous gas tends to appear in the final steps of crushing, hence to come from the smallest vesicles (see, e.g., Fig. 3 in [5]). In detail, the release scheme may be more complex than this, as seen for 2ΠD43 popping rocks [8] and discussed in Section 6.1.2.

2.2.2. That volatiles are mostly in vesicles explains the variability of noble gas data

In step-heating analyses of MORB, a very large amount of air is sometimes released in the lowest temperature step [7,20]. This was emphasized by Ballentine [21] and by Ballentine and Barfod [1] for one of my analyses of 2ΠD43 [22].

For this experiment, I decided not to bake the sample before analysis, because large amounts of gas might be lost if the bursts observed in the crushing analyzes (2.1.2) were due to large vesicle opening. This is certainly the reason to the fact that my step-heating analysis of 2ΠD43 gave more than an order of magnitude more gas than crushing ones. The first, 700 °C, temperature step in this experiment represents 99% of all the neon released, and this neon is isotopically atmospheric [22]. Uncontrolled vesicle bursting, in nature, then on recovery and during sample preparation and analyses, induces variations in the number of closed vesicles that explain the "large difference in observed noble gas concentrations of the 2ΠD43 sample" [1] together with the variable composition of its volatiles among various analyses.

2.2.3. Popping rocks have an enormous amount of air in their largest vesicles

The above observations are consistent with this very abundant atmospheric neon to reside in the largest vesicles in 2ΠD43. Argon data from the same experiment is not published since, at that time, the mass-spectrometer ARESIBO II had problems with Ar measurement [22], but I can say that, in the 700°C step, the $^{40}Ar/^{36}Ar$ ratio was low, around 860, and ^{36}Ar

was about 98% of the total. Xenon was atmospheric at 700 °C and showed very large anomalies at higher temperatures (Fig. 1a, Table 1). The first, 700 °C step has 89% of the ^{130}Xe in this experiment (Fig. 1b). I remark that the first step also contains a vast amount of ^{3}He representing 77% of the total.

The crushing experiments made later by Moreira et al. [8] give a better picture of this air component
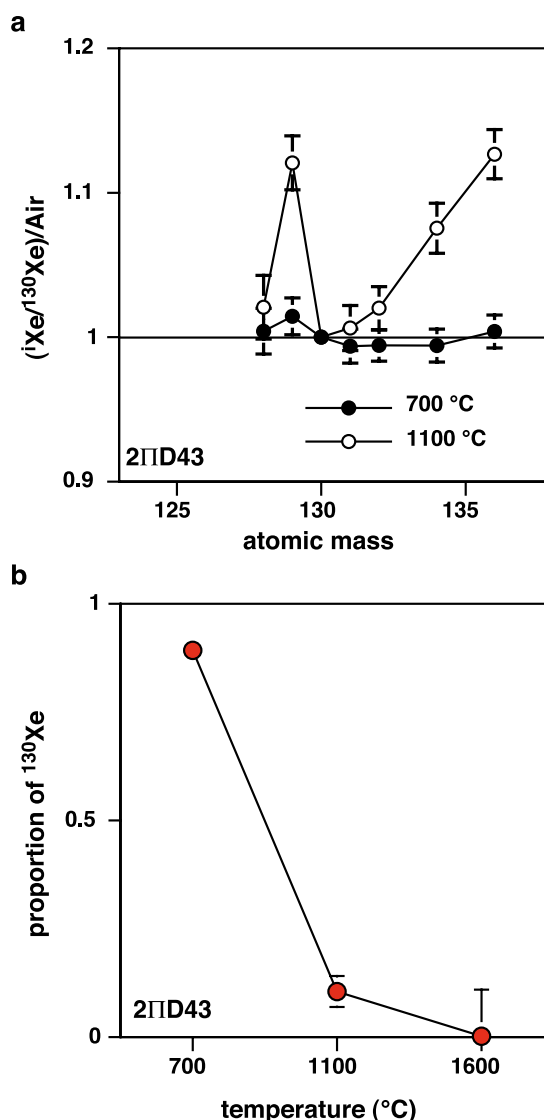
Fig. 1. Xenon results for the 2ΠD43 popping-rock sample reported in Sarda et al. [22] for He and Ne. (a) Isotope pattern for the 700 and 1100 °C temperature steps. (b) ^{130}Xe abundances in the 700, 1100 and 1600 °C steps. Data in Table 1.

Table 1
Xenon data for the same step-heating analysis of the 2ΠD43 popping rock as reported in [22] for helium and neon

T (°C)	^{130}Xe (cm^3 STP/g)	$^{128}Xe/^{130}Xe$	$^{129}Xe/^{130}Xe$	$^{131}Xe/^{130}Xe$	$^{132}Xe/^{130}Xe$	$^{134}Xe/^{130}Xe$	$^{136}Xe/^{130}Xe$
700	$1.016\pm0.016\ 10^{-11}$	0.472 ± 0.07	6.574 ± 0.083	5.159 ± 0.061	6.553 ± 0.072	2.544 ± 0.029	2.183 ± 0.025
1100	$1.198\pm0.039\ 10^{-12}$	0.480 ± 0.010	7.263 ± 0.121	5.224 ± 0.081	6.723 ± 0.099	2.752 ± 0.044	2.449 ± 0.037
1600	$2.52\pm0.27\ 10^{-14}$	0.495 ± 0.053	6.41 ± 0.59	4.74 ± 0.45	6.33 ± 0.60	2.39 ± 0.23	2.06 ± 0.19

because they made more steps. I plotted the noble gas concentrations obtained in their experiments 1 and 2 vs. number of strokes. On Figs. 2 and 3, I show such diagrams for ^{4}He and ^{36}Ar respectively. For experiment 2, the amount of ^{36}Ar released in the first crushing step is overwhelmingly larger than for the next steps, to the point that it is difficult to represent all the data on the same diagram (Fig. 3 a and b). A similar pattern is seen for Ne, Kr or Xe (not shown), but not for helium (Fig. 2). Experiment 1 uses a smaller sample of 0.94 g while the sample weights 1.40 g in experiment 2. Thus, more of the larger vesicles must have been lost in experiment 1, which explains why the first step is not as gas-rich as in experiment 2. These results illustrate well that large vesicles of popping rocks, if not cracked open, contain gas at high pressure with an extraordinarily large burden of atmospheric noble gases, except for He, which is not atmospheric.
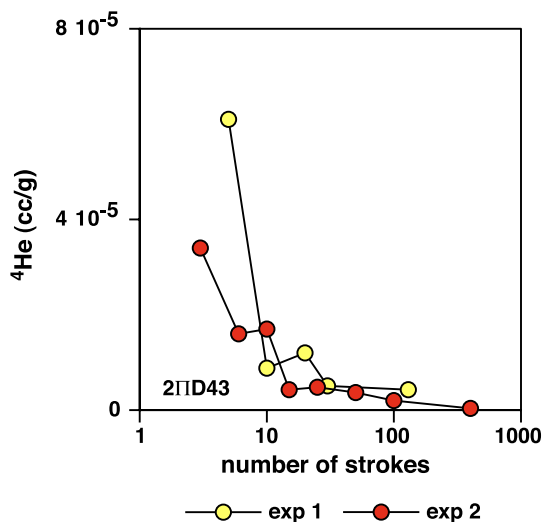
In usual MORBs, the air component is also very variable [7]. It is impossible to predict its magnitude for a given sample, despite remarkable
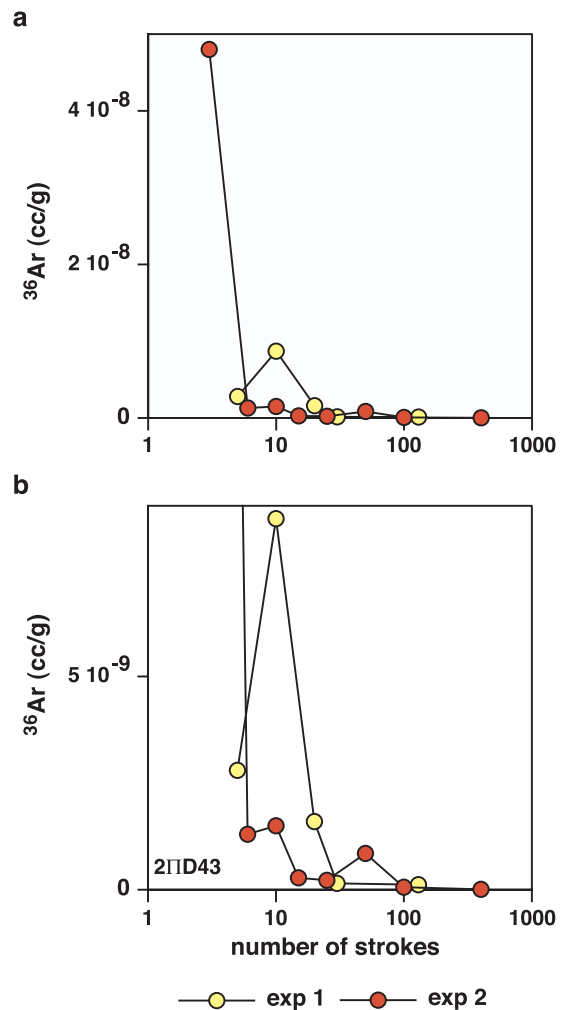

Fig. 3. ^{36}Ar concentrations measured in the step-crushing experiments 1 and 2 reported in Moreira et al. [8] for the 2ΠD43 popping rock. (a) All the data. (b) Same plot where the first step of experiment 2 (three strokes), which has an overwhelming amount of argon, was hidden to show the variations in the other steps.

Fig. 2. Plotted are the ^{4}He concentrations measured in the step crushing experiments 1 and 2 of Moreira et al. [8] for the 2ΠD43 popping rock.

efforts aimed at relating structural features of samples to the importance of atmospheric contamination [23,24]. If the air component is borne by the largest vesicles, the reasoning above may apply to all MORBs and OIB and explain its variability.

3. The popping-rock paradoxes

3.1. Popping rocks have both the mantle and air components in neighboring vesicles

The observations above make the 2ΠD43 popping rocks rather paradoxical, since they bear a large atmospheric noble gas component, and also have typical degassed mantle He, Ne, Ar and Xe [5,8,12]. The key is that these two components are borne by vesicles with different sizes, which coexist at a cm scale.

3.2. Popping rocks are "enriched" but have degassed-mantle noble gases

Another important paradox about popping rocks lies in the contradiction that seems to exist in the literature between noble gas isotopic signatures and those of non-volatile tracers. Based on Sr, Nd and Pb isotope systematics, the topographic elevation of the Mid-Atlantic Ridge at 14°N was considered related to a small plume with an enriched character related to the EMI and HIMU mantle end members [13,14,25]. However, the 2ΠD43 popping rocks are often considered as among the best ridge samples representative of the degassed mantle, with the highest isotopic noble gas anomalies (e.g., [7,8,12]). The record of volatile and that of non-volatile tracers appear contradictory.

3.3. Are popping rocks enriched in volatiles?

Intricated in the above isotopic point of view is the question of why are popping rocks so volatile rich. Several works have shown that popping rocks must represent exceptionally undegassed or poorly degassed samples (e.g., [19,26,27]). However, some authors relate their high volatile concentrations to their enriched character (e.g., [28]), as is also proposed for the Azores [29], where the high volatile content would then be a feature of the mantle source. Both explanations may be valid together.

4. All the air component is perhaps not contamination

4.1. Part of the air component is strongly bound to samples

While air can be released in low-temperature steps (500–700 °C) of step-heating experiments, it is also frequent to get an important air component at higher temperature. This contradicts the hypothesis that air contamination, in such samples, is due to weakly bounded atmospheric noble gases, e.g., adsorbed on surfaces. Given the precautions taken by analysts to remove air adsorbed on surfaces by baking and stepwise heating, Ballentine and Barfod [1] remark that part of the air component must be tightly bound to samples, an opinion certainly shared by many noble gas analysts.

4.2. The relationship between vesicle abundance and volatile concentration

As recalled above, the air component is likely borne by the largest vesicles, which explains data variability (2.2). Ballentine and Barfod [1] showed that the air component is correlated to vesicularity, a slightly different view where the more numerous and/or the larger the vesicles the stronger the air component. To appreciate this view, one should examine how noble gas abundances and vesicles are related.

Published values for vesicularity in MORB tholeiites are relatively rare but show a wide range, from very low values of typically 0.1% and less, up to 17–18% in popping rocks [19,30]. Vesicle sizes are variable but, in many cases, large vesicles with a diameter of 1–2 mm coexist with small vesicles with a diameter of 0.1 mm or less. Only in the case of popping rocks has the vesicle size distribution been measured [19] because of the exceptional abundance of vesicles, and it was found regular, with an exponential decrease of vesicle abundance with increasing size from ~0.1 to ~1.5 mm.

Experimentalists know that, in MORB or OIB glass samples, the rare gases are mostly in vesicles, provided they are closed. The more the vesicles the highest the total concentration as exemplified by 2ΠD43 [19]; however, this trend is less strong for helium, a larger fraction of which resides in melt (e.g., [26]). However, this logic can be reversed if vesicles are large, because large vesicles more easily open up [2].

The correlation between gas concentrations and vesicularity in MORB samples is explained by the simple model where degassing of magmas occurs through vesiculation followed by variable vesicle loss [19,26]. This model is supported by noble gas elemental fractionation [26]. Popping rocks may represent a typical melt with no or minimum vesicle loss, while usual samples would have suffered loss of vesicles [19]. This process, combined with the fact that large enough vesicles open up more easily, likely explains the variety of vesicularity and gas concentration observations. Time between eruption and sampling must play a role, as older glass has more opened vesicles due to cracks developing in it. For example, it is not rare to recover ridge samples with relatively high vesicularities of ~5%, the vesicles of which are visibly not overpressured because they opened on ageing (e.g., [20]). However, time constraints lack on this subject.

The above considerations likely hold for both MORB and OIB [26,31].

4.3. The significance of the air–vesicularity relationship

The simplest interpretation of crushing and getting air is that vesicles are filled with air. The vesicle loss systematics (4.2), and the fact that air often appears strongly bound to glass (4.1), indicate that the air component appears to follow the abundance–vesicularity relationship expected for a magmatic component. The observations above thus raise the question of whether this air could not be a magmatic component that would have been transferred to vesicles and would be more or less abundant according to the volcanic history of each individual melt, i.e., the number of vesicles lost before quenching at eruption.

Ballentine and Barfod [1] looked at Loihi data generated by myself [22], where noble gas isotopic ratios indicate an important air component, which, as they show, is correlated to vesicularity. I examined this Loihi data again. For vesicularities between 1% and 6%, there is a linear correlation in a plot of ^{22}Ne concentration vs. vesicularity (Fig. 4). One sample, KK15-4, has a vesicularity of 18%, and does not plot on the trend because of a low ^{22}Ne concentration. This may be due to large vesicles having opened up. Based on the linear trend, I predict the ^{22}Ne concentration was 1.4×10^{-9} cc STP ^{22}Ne/g for KK15-4 before vesicle opening (Fig. 4). There is a factor of 3 in vesicularities between KK15-4 and the sample with 6% vesicularity, and a factor of 4 between the KK15-4 reconstructed ^{22}Ne concentration and the same 6% vesicularity sample. These similar factors strengthen the view that vesicle loss may explain the linear relationship between vesicularity and concentration. The discrepancy may be related to the density lowering induced by the presence of vesicles (discussed in [32]). The same systematics exist for ^{36}Ar, with again a factor of 4 in concentrations (not shown).

Therefore, a number of arguments may be taken as indicating that the atmospheric component, or part of it, in these Loihi samples and probably other OIBs
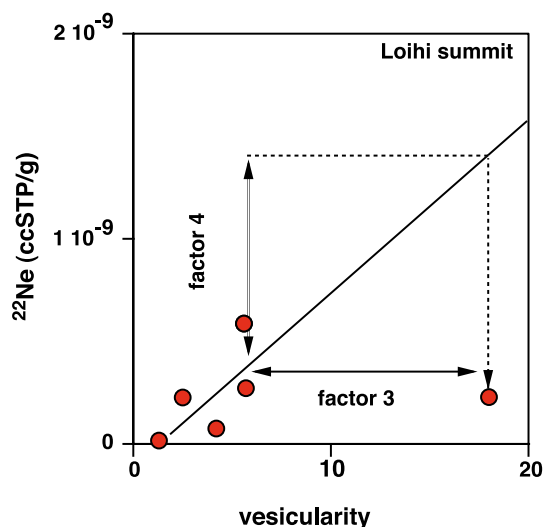

Fig. 4. Plotted are vesicularity and ^{22}Ne concentration for the Loihi summit samples analyzed in [22]. Both quantities are correlated except for a sample with 18% vesicularity. The latter sample must have lost gas by vesicle opening Section 4.3).

and MORBs, is magmatic: this atmospheric gas was possibly dissolved in magma before entering vesicles, and was not added from outside the melt. In this case, it is not meaningful to use the ^{22}Ne concentration [1], or any other noble gas concentration, as a proxy for air contamination.

5. Alternative interpretations of the air component

5.1. The modern air hypothesis

Ballentine and Barfod [1] rigorously show that the air component cannot be due to vaporized seawater dissolving into magma at eruption. They conclude that the only possible explanation is addition of modern air after recovery. Following Mungall et al. [11], they argue that microfractures appear in glass in response to the decrease of the water partial pressure in gas, due to cooling at constant volume. This would induce a tendency of water to exsolve from glass, triggering the development of microcracks in the walls of vesicles, open to their inner side. These cracks should trap air, then reseal and keep this air relatively well protected from subsequent baking in the furnaces of laboratories. They would be a reservoir of atmospheric gas, related to vesicles but residing in the glass matrix close to them, showing up when vesicles are ruptured.

This model is possible. In Mungall et al. [11], the microcracks are open to the inner side of the vesicle walls (their Fig. 1). They should therefore propagate in the glass up to open air before resealing, a likely possibility [11]. However, it is difficult to understand why the trapped air would then be associated to the largest vesicles. In addition, I find difficult to accept that that these cracks, having propagated across the whole glass matrix, should reseal after air trapping, all the more so because this must not affect the high-pressured vesicles.

5.2. The recycled air hypothesis

Ballentine and Barfod [1] provide a rigorous reasoning leading them to the modern air hypothesis. I agree with their reasoning, but I observe that their conclusion is dependent on the unstated assumption, implicit for everyone, that air can only have been

added to samples at the surface or close to the surface of the Earth.

If part of the air component is magmatic (4.3), it must have a mantle origin through recycling from the surface. This hypothesis had not many supporters, but is recently becoming increasingly studied and corroborated by noble gas, carbon and nitrogen isotope tracing (e.g., [33–39]).

The recycled air hypothesis explains simply the intriguing facts discussed above and by Ballentine and Barfod [1]. In particular, it may help explaining the surprising characters of the 2ΠD43 popping rocks (Section 3), as the air component may be the counterpart of the recycled trace element signature.

If the largest vesicles contain atmospheric rare gases of mantle origin, this allows understanding why the air component appears in the first crushing steps. The recycled air hypothesis is also consistent with the air–vesicularity relationship (4.2–3). In a population of exponentially distributed vesicles such as found in popping rocks [19], the largest vesicles dominate vesicularity (Fig. 1 in [32]). As the air component is more abundant than the degassed mantle one (helium aside) [5,8,22] and located in the largest vesicles, the positive correlation between concentration and vesicularity resulting from vesicle loss for one single component [19,26] should still occur with two components.

Burnard et al. [12] found no vesicle filled with air during his laser shot analyses of popping rocks. This is understandable if only large vesicles have the air component. The largest vesicles were lost, as an unavoidable result of rock section preparation. However, Burnard's vesicle data indeed shows a mixture of degassed mantle gas, with $CO_2/^{36}Ar$ around 10^9, and another component isotopically close to air, with $CO_2/^{36}Ar$ possibly as low as the atmospheric value of 0.03 (Fig. 1 in [12]) This is consistent with $^{40}Ar/^{36}Ar$ values ranging from 3600 to 40,000. The ^{36}Ar quantity is on the same order of magnitude for a laser shot on an individual vesicle and on glass because the rare gas quantity of a single vesicle is very small since vesicles are very small. Glass has very little ^{36}Ar because ^{36}Ar was transferred to vesicles, but one single vesicle has a very little fraction of vesicle ^{36}Ar.

In another paper, Burnard [17] laser shot even smaller vesicles for samples of melts that must have lost a large part of their original vesicle population: the air

component is therefore absent. If vesicle loss during magma ascent [19,26] has operated on the majority of melts, it is not surprising that the atmospheric component is sometimes elusive because it is borne by the largest vesicles that are first to be lost.

Conversely, the crushing results of Javoy and Pineau [18] for 2ΠD43 popping rocks exhibit low $^{40}Ar/^{36}Ar$ ratios of 5000–6000, because these authors used large samples of 10 vs. 1 g for standard rare gas analysis. In the same logic, Trieloff et al. [5] used small samples prepared by crushing. One sample weights 0.2 g and was step-heated; the other weights 0.08 g and was step-crushed. The larger sample yields a $^{40}Ar/^{36}Ar$ ratio of 846 in the first, 320 °C step, and a large amount of ^{36}Ar representing 66% of the total. The smaller sample gives, in the first crushing step, a $^{40}Ar/^{36}Ar$ ratio of 10,700 and a small ^{36}Ar amount representing only 0.2% of the total. The smallest sample must have lost open larger vesicles, thus loosing the big atmospheric component seen in the larger sample.

These examples show that different reasoning should apply to rare gas analysis compared to "solid" element analysis, a reasoning that must take into account the main gas carrier in such samples, the vesicles. If there is an atmospheric noble gas compo-nent in the largest vesicles, the size of analyzed samples is of particular importance to the result.

But, just why should the largest vesicles bear the mantle-derived air component?

6. A recycling model

6.1. Generation of air-bearing vesicles by mantle melting

6.1.1. Recycling atmospheric rare gases to the mantle

We know that oceanic lithosphere, with or with-out sediments, is recycled to the mantle. Recycling is the basis of those models that envision the upper mantle as a multicomponent reservoir, sometimes called marble-cake (e.g., [40,41]). Recycled matter may also feed some types of plumes, which may be recorded by noble gases (e.g., [20,42]). Whatever one or the other, or both of the above processes occur, melting is likely to involve two components, normal-lherzolitic and recycled.

In a two-component mantle, melting involves two steps. More fertile recycled matter melts first, at greater depths, and more extensively than lherzolite. Such mantle melting models thus describe a mixture of two liquids coming from these two materials [40,43]. In addition, melting is continuous, starting at the depth where the solidus is crossed along rising [44].

Recycling likely introduces air noble gases into the mantle [45], even if most of them return to the atmosphere at the rare gas subduction barrier [46]. For the Mid-Atlantic Ridge Ar–Pb isotopic correlation [35] to be understandable, the recycled oceanic crust should loose about 90% of its ^{36}Ar at subduction [47]. The remaining 10% are nevertheless an atmospheric component that may be carried down to the mantle, but, because of this strong reduction, does not overwhelm degassed mantle rare gas signatures.

In the following, I will present a two-component mantle melting model that could either apply to marble cake or to recycled plumes rising in the upper mantle. In the melting column, fertile recycled matter would generate a first melt with air rare gases. The major gas for this component is likely CO_2, although this is not demonstrated. On decompression, vesiculation would occur by exsolution of the major gas, generating vesicles with the air rare gases, and a degassed melt. As higher and higher levels are reached, lherzolite would start generating melt that would mix with previous melt. New vesicles would appear, containing the degassed mantle noble gas component mixed with the remaining air component. If, during ascent, vesicles are generated continuously, noble gases will be trans-ferred to them soon after melting, preventing to some extent the two noble gas components from mixing together. Eventually, there must be more of the air component in the largest vesicles and more of degassed mantle noble gases in the smallest ones, simply because the first vesicles have had more time to grow. The whole process must be continuous, so there must be a continuous range of vesicle compositions. In this model, volatiles are physically separated from melt. The vesicles must thus bear a record of this two-stage, melting and mixing continuous process.

6.1.2. The popping-rock data in detail

Step-crushing experiments on the popping-rock 2ΠD43 have shown the coexistence of the mantle

and atmospheric rare gas components. However, plotting the data of [8] vs. number of strokes shows that their mixing ratio is not simply related to vesicle size. We show such a plot in Fig. 6a for $^{40}Ar/^{36}Ar$. The isotopic ratios goes up, then down, then up again to a typical degassed mantle value of ~25,000 for more than 30 strokes in experiment 1 and 100 strokes in experiment 2. The release pattern is otherwise similar in both experiments.

An important difference is that experiment 1 starts with an $^{40}Ar/^{36}Ar$ ratio of 13,800, while experiment 2 starts with a much lower value of 800. This is probably related to the smaller sample size in experiment 1, 0.94 vs. 1.40 g, which must have contributed to open the largest vesicles. The effect on Fig. 6a is to displace the pattern of experiment 1 to the left (the strokes necessary to open the large vesicles lack).

Another important observation is that there are high $^{40}Ar/^{36}Ar$ values of ~10,000 at relatively low number of strokes. The ratio then goes down to low values of about 1000–4000 before going up again to 25,000. The crushing data of Trieloff et al. [5] for 2ΠD43 exhibit an even more pronounced up-and-down pattern in the first four crushing steps (their Fig. 4). This behavior is surprising and should be taken into account in any interpretation. Of course, the problem may partly lie in the details of the crushing process where larger vesicles may survive when smaller are broken, an effect largely uncontrolled. However, the swinging pattern probably also reflects a real phenomenon.

6.1.3. A two-component mantle melting model

I use a simple marble-cake melting model, following Prinzhofer et al. [43], where concentration of a noble gas (i) in melt is given by classical equations for trace elements (e.g., [48,49]). The two melt sources, degassed-depleted mantle and fertile-recycled mantle, are denoted by subscripts d and f respectively. There are two melt fractions, F_d and F_f, two partition coefficients, D_d and D_f, and two melts are generated that mix together. Concentrations in the two melts are

$$C_f^i = \frac{C_{f,0}^i}{D_f^i + F_f(1 - D_f^i)} \quad (1)$$

and

$$C_d^i = \frac{C_{d,0}^i}{D_d^i + F_d(1 - D_d^i)} \quad (2)$$

If X is the mass proportion of fertile solid material before melting, the total melt fraction is given by

$$F = XF_f + (1 - X)F_d \quad (3)$$

and the concentration in the final melt is

$$C^i = X \frac{F_f}{F} C_f^i + (1 - X) \frac{F_d}{F} C_d^i \quad (4)$$

I explored this model numerically for argon, aiming at reproducing the $^{40}Ar/^{36}Ar$ up-and-down pattern (Fig. 6a). Taking experiment 2 of Moreira et al. [8], the intermediate maximum $^{40}Ar/^{36}Ar$ ratio is $14,000 \pm 300$ and the intermediate minimum is 3600 ± 30 (Fig. 6a).

I used identical ^{36}Ar concentrations in both starting materials of 5×10^{-10} cc/g [7,8] (similar concentrations are necessary if one component is not to swamp the other) and $^{40}Ar/^{36}Ar$ isotopic ratios of 296 and 40,000 for recycled and degassed material, respectively.

The two melt fraction curves are chosen similar but with a significant offset, and with reasonable, maximum values of 15 wt.% for F_f and 10 wt.% for F_d. The values of F_f and F_d, and their relative evolution at the beginning of melting, turn out to be critical for reproducing the $^{40}Ar/^{36}Ar$ values and their up-and-down pattern.

In addition, critical are the proportion X of recycled matter and partition coefficients. Noble gas partition coefficients are extremely difficult to measure and therefore not well known. Many authors consider noble gases as incompatible elements, consistent with olivine-melt measurements on natural samples {$D(Ar)=3 \times 10^{-3}$ [50]}, or with laboratory experiments on clinopyroxene–melt partitioning {$D(Ar) \sim 10^{-4}$ [51,52]}. However, higher values also exist including recent data for olivine and clinopyroxene [53].

Therefore, I used two probably extreme values for D_d: 2×10^{-4} and 1×10^{-2}. With the above numbers, I find that D_f must be 100 and 10 times higher than D_d, respectively, for the swinging $^{40}Ar/^{36}Ar$ pattern to be reproduced. At the same time, X must be 15% and

1.5%, respectively. When D_d is low, more degassed mantle Ar goes to melt; thus, more recycled material is necessary to reduce the $^{40}Ar/^{36}Ar$ ratio to the intermediate minimum ($X=15\%$), but not too much recycled Ar should be released to melt for the intermediate maximum to be reached ($D_f=100D_d$). The total melt fraction curve is clearly different from F_f and F_d when $X=15\%$ (Fig. 5), while it is close to F_d when $X=1.5\%$ (Fig. 5), but it always reaches a maximum of about 10%.

As fertile material melts first while the peridotitic matrix does not, the resulting $^{40}Ar/^{36}Ar$ ratio is atmospheric at low melting (F_f values of less than 0.2%), and concentration in melt decreases when F_f increases. At $F_f=0.3\%$, F_d then starts to increase slowly, taking very small values of about $4\times10^{-4}\%$, the Ar concentration in the resulting melt is high and its ^{40}Ar concentration is especially high because of the high $^{40}Ar/^{36}Ar$. The result is a sudden increase in the $^{40}Ar/^{36}Ar$ ratio of the mixture, up to ~14,000 (Fig. 6a). As long as F_d remains that weak, the ratio then decreases to ~3700 because the fertile component

Fig. 6. (a) $^{40}Ar/^{36}Ar$ isotopic ratio vs. number of strokes for crushing experiments 1 and 2 reported in [8]. (b) Result of the marble-cake mantle melting model described in Section 6.1 plotted as $^{40}Ar/^{36}Ar$ vs. number of model steps. X is the proportion of recycled matter in solid before melting (see Fig. 5 and Section 6.1.3).
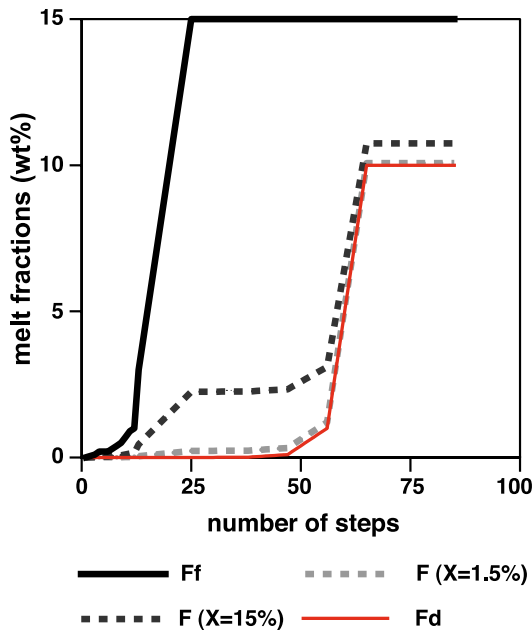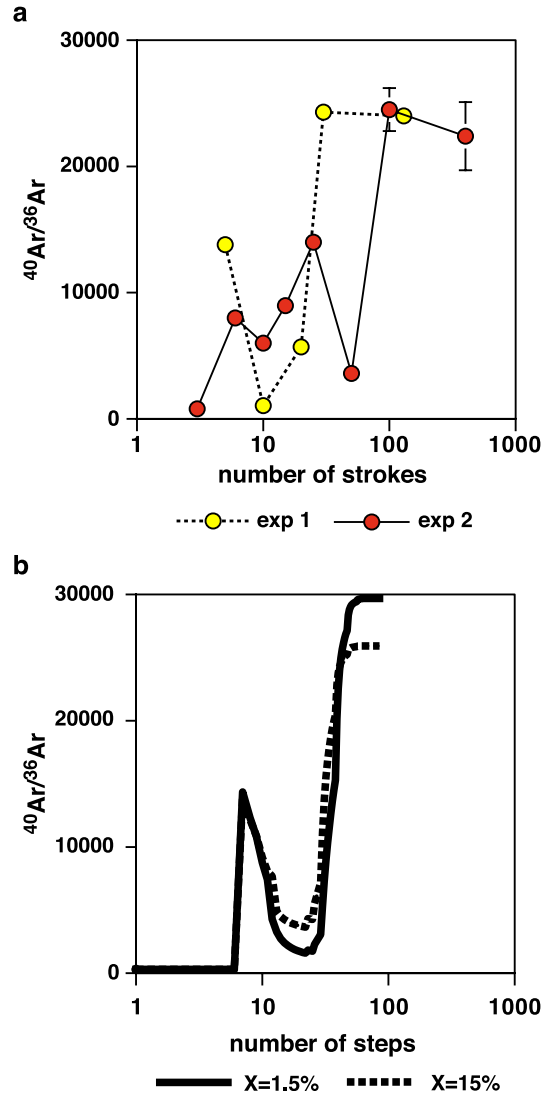
Fig. 5. Evolution of melt fractions used in the marble-cake mantle melting model of Section 6.1, shown vs. number of calculation steps. Melting rate is noted F_f for the fertile recycled mantle component, F_d for the degassed-depleted mantle component, and F is the global melting rate. Proportion of recycled matter in the solid is $X=15\%$ when degassed mantle partition coefficient is 2×10^{-4} and 1.5% when it is 1×10^{-2}.

keeps on melting, which dilutes the other melt. Eventually, the $^{40}Ar/^{36}Ar$ ratio increases again when the degassed component melts more and dominates. In Fig. 6b, the model $^{40}Ar/^{36}Ar$ ratio is plotted vs. model step number.

Now, if vesicles nucleate and grow continuously, any argon arriving in melt is immediately transferred

to the new vesicles, a key point of this model. The two noble gas components may thus be prevented from mixing and be eventually protected in vesicles.

This model may give simple clues for understanding the data, especially the swinging pattern of $^{40}Ar/^{36}Ar$ vs. number of strokes observed in the popping-rock crushing data [5,8] (Fig. 6). It is still speculative and remains to be investigated. The driving mechanism to vesiculation is the continuous decrease of volatile solubilities due to pressure drop during ascent. The regular vesicle size distribution observed in popping rocks [19] indicates that continuous vesiculation is likely. The separation of volatile from non-volatile species then likely explains the popping-rock paradox (3.2.) where the two volatile components survive encapsulated in vesicles, while trace elements mix together and, at the sample scale, display a single signature with recycling imprint. The relatively high proportion of recycled matter (15 wt.%) would be consistent with the concept of a small plume rising under the ridge [14]. The high value of D_f is difficult to assess given that the minerals involved are unknown.

6.2. Critical assessment of the model

The model described above is only an end member one, and Nature is certainly more complex. The model parameters may vary from place to place on Earth and for various events of melting. For example, if vesiculation is retarded, the two noble gas components will have time to mix in melt, giving a more uniform, more air-like isotopic composition, which indeed is observed in some samples.

6.2.1. Duration and scale of chemical heterogeneities in the convective mantle

A first question is how recycled matter maintains its noble gas isotopic and elemental integrity during geological periods of time. Considering the marble-cake upper mantle, durations on the order of the age of oceanic plates, i.e., 200 Ma, or longer, are necessary. Diffusion may be expected to homogenize those compositions during such long times, especially for volatile species. However, based on his helium diffusion experiments in olivine, Hart [54] showed that, for helium, isotopic heterogeneities of 100 m scale, or larger, would not be affected by diffusion after

2 billion years, and thus could persist for much of the geologic time. This applies a fortiori for heavier rare gases as argon.

6.2.2. Helium isotopes

A next question is that the helium isotopic composition is typical of ridges ($^3He/^4He$ ~8Ra) for any of the crushing or heating steps in popping-rock analysis. One answer is that virtually no atmospheric helium is recycled with altered basalts or sediments because air helium is so low.

Upper oceanic crust and sediments are uranium-enriched [55]; therefore helium in such material is mostly radiogenic. Considering gabbros of the lower oceanic crust, the $^3He/^4He$ ratio becomes significantly radiogenic, i.e. lower than MORB, after less than 100 Ma (e.g., [45]). Therefore, one would expect recycled matter to show excess radiogenic helium. There is a hint for this in the popping-rock data. However, stepwise heating induces an isotopic fractionation that enhances the light isotope ^3He in the first temperature step, an effect seen in the popping-rock heating data reported in [22]. In step-crushing analyses, the $^4He/^3He$ ratio is only marginally higher in early steps. In the popping-rock crushing data reported in [7,22] the variations are smaller than the error bars. In the crushing data of Moreira et al. [8], for experiment 2, the average of the first four crushing steps is 87,000 vs. 85,000 for the average of the last four steps. In any case, the effects appear small and their occurrence depends entirely on the preservation of the largest vesicles.

Altogether, no atmospheric helium is recycled, and the helium found in the large vesicles derives from another source with MORB-like helium. One possibility is the recycled lithospheric mantle, which should maintain a MORB-type helium isotopic signature for long periods of time [56]. This source could also be the lherzolite matrix, where helium may leave crystals by diffusion (e.g., [57,58]).

6.2.3. Elemental fractionation at subduction

A problem is that the noble gas elemental ratios of the recycled component are not fractionated relative to air (helium aside). Loss of water and volatiles at subduction should have fractionated the rare gases left in the material eventually returned to the mantle. However, the noble gas elemental ratios of subducted

rocks are probably closer to seawater noble gases than to air, where heavier noble gases are enriched in the order Xe>Kr>Ar>Ne. This is confirmed by analyses of oceanic sediments and altered basalts [46].

We also know that the elemental noble gas ratios found in the vesicles of popping rocks are unfractionated, or almost so, compared to melt before vesiculation. If melt rising under ridges carries an elementally atmospheric noble gas component (except for helium) [1], then, from solid/melt partition coefficients, one could derive the noble gas elemental pattern in the rocks that generated this melt, assuming a melt fraction value. However, the partition coefficients are unknown (only few values for Ar and He seem reliable; e.g., [50–52]).

If the noble gas solid/melt partition coefficients were controlled by solubilities in melt rather than in solids, a solid material having a seawater noble gas elemental pattern could generate a melt with a close-to-atmospheric pattern at the beginning of melting. This is because melt would accept less Xe than Kr, less Kr than Ar, and so on, thereby reversing the fractionation due to solubilisation in water. An analogous reversal of elemental pattern is obtained when calculating the solution of seawater into basalt (e.g., [59,60]). However, this is very speculative in the absence of solid/melt partition coefficients for all the noble gases.

6.2.4. Variations of the recycled component proportion

In the marble-cake framework, the upper mantle should be seen as containing two reservoirs, one with noble gases residual from degassing with the very strong isotopic anomalies, the other with atmospheric noble gases and probably, depending on recycling age, some radiogenic component. This would be consistent with the geochemistry of non-volatile isotopic tracers and trace elements.

The proportion of recycled matter in the mantle source is certainly variable along the ridge axis, and among OIB melts as well. For example, the Lau basin samples analyzed by Bach and Niedermann [61] show an important atmospheric component related to the nearby subduction zone. Conversely, some parts of the mantle may have no recycled matter. Therefore, the magnitude of the noble gas upper mantle signature may vary as well. This was probably seen through the

Ar–Pb isotopic correlation evidenced on the Mid-Atlantic Ridge [35].

6.2.5. Noble gas recycling mechanism

The recycling mechanism for noble gases remains unclear. If the proposed model is correct, there must be some way for a small part of the air noble gases carried by the subducting slab (about 10% [47]) to be stabilized and entrained into mantle circulation. Perhaps a metamorphic mineral forms that traps volatiles, then resists subduction [62]. Phengites appear to be able to do this job for nitrogen in the case of cold subduction [39]. It is work for the future to identify how surface noble gases could survive subduction.

7. Conclusion

The occurrence of an atmospheric noble gas component in submarine basalts is clear [1]. This component shows almost exactly atmospheric elemental ratios for all noble gases except helium. It is associated to the largest vesicles, and can be extremely abundant and overpressured in some samples such as popping rocks.

This atmospheric component has generated a series of questions and problems that have plagued noble gas mantle research for decades, because the mechanism by which air was added to melts has always been unclear.

Ballentine and Barfod [1] proposed that this air component is modern air trapped by glass in microfractures. I criticize this model as failing to explain the association of the air component under high pressure to the largest vesicles and advocating the existence of microfractures in glass, that could trap air while high pressure is maintained in vesicles.

I propose an alternative model, recycling of air volatiles to the mantle through subduction of altered oceanic crust and sediments, followed by differential melting of recycled and degassed mantle. Vesicles must then appear continuously as soon as new melt forms, thus physically isolating noble gases from melt and preventing complete mixing of the two noble gas components, then preserved in vesicles.

I show that this concept helps understanding practically all of the puzzling questions related to the air component in submarine basaltic glass

samples, and accounts for the variability of their noble gas isotopic anomalies and concentrations. Vesicle heterogeneity is then the rule in submarine basalts, where various vesicles contain various mixtures of recycled and mantle-derived noble gases. In particular, this model provides a better interpretation of popping rocks that show both recycled trace element signatures and very pure upper mantle noble gases. The model does not exclude contamination, i.e., addition of air noble gases after eruption.

This recycling model is accepted for non-volatiles elements, and some volatiles such as carbon and nitrogen. It is only beginning to be seriously studied for noble gases (e.g., [35,37,38]) and still has to be validated through more analytical studies. Knowledge of vesicle heterogeneity in submarine magmas should help progressing in this direction.

Acknowledgments

References

[1] C.J. Ballentine, D.N. Barfod, The origin of air-like noble gases in MORB and OIB, Earth Planet. Sci. Lett. 180 (2000) 39–48.

[2] M.D. Kurz, W.J. Jenkins, J.-G. Schilling, S.R. Hart, Helium isotopic variation in the mantle beneath the central North Atlantic Ocean, Earth Planet. Sci. Lett. 58 (1982) 1–14.

[3] I. Kaneoka, N. Takaoka, Noble-gas state in the Earth's interior. Some constraints on the present state, Chem. Geol. 52 (1985) 75–95.

[4] S. Niedermann, W. Bach, Anomalously nucleogenic neon in North Chile Ridge basalt glasses suggesting a previously degassed mantle source, Earth Planet. Sci. Lett. 160 (1998) 447–462.

[5] M. Trieloff, M. Falter, E.K. Jessberger, The distribution of mantle and atmospheric argon in oceanic basalt glasses, Geochim. Cosmochim. Acta 67 (2003) 1229–1245.

[6] P. Sarda, T. Staudacher, C.J. Allègre, ^{40}Ar/^{36}Ar in MORB glasses: constraints on atmosphere and mantle evolution, Earth Planet. Sci. Lett. 72 (1985) 357–375.

[7] T. Staudacher, P. Sarda, S.H. Richardson, C.J. Allègre, I. Sagna, L.V. Dmitriev, Noble gases in basalt glasses from a Mid-Atlantic ridge topographic high at 14°N: geodynamic consequences, Earth Planet. Sci. Lett. 96 (1989) 119–133.

[8] M. Moreira, J. Kunz, C.J. Allègre, Rare gas systematics in popping rock: isotopic and elemental compositions in the upper mantle, Science 279 (1998) 1178–1181.

[9] T. Staudacher, M.D. Kurz, C.J. Allègre, New noble-gas data on glass samples from Loihi seamount and Hualalai and on dunite samples from Loihi and Reunion Island, Chem. Geol. 56 (1986) 193–205.

[10] P.G. Burnard, F.M. Stuart, G. Turner, N. Oskarsson, Air contamination of basaltic magmas: implications for high ^{3}He/^{4}He mantle Ar isotopic composition, J. Geophys. Res. 99 (B9) (1994) 17,709–17,715.

[11] J.E. Mungall, N.S. Bagdassarov, C. Romano, D.B. Dingwell, Numerical modeling of stress generation and microfracturing of vesicle walls in glassy rocks, J. Volcanol. Geotherm. Res. 73 (1996) 33–46.

[12] P. Burnard, D. Graham, G. Turner, Vesicle-specific noble gas analyses of "popping rock": implications for primordial noble gases in the Earth, Science 276 (1997) 568–571.

[13] H. Bougault, L. Dmitriev, J.-G. Schilling, A. Sobolev, J.-L. Joron, H.D. Needham, Mantle heterogeneity from trace elements: MAR triple junction near 14°N, Earth Planet. Sci. Lett. 88 (1988) 27–36.

[14] L. Dosso, B.B. Hanan, H. Bougault, J.-G. Schilling, J.-L. Joron, Sr–Nd–Pb geochemical morphology between 10° and 17°N on the Mid-Atlantic Ridge: a new MORB isotope signature, Earth Planet. Sci. Lett. 106 (1991) 29–43.

[15] R. Hekinian, M. Chaigneau, J.-L. Cheminée, Popping rocks and lava tubes from the Mid-Atlantic Ridge rift valley at 36°N, Nature 245 (1973) 371–373.

[16] F. Pineau, M. Javoy, Y. Bottinga, ^{13}C/^{12}C ratios of rocks and inclusions in popping rocks of the mid Atlantic ridge and their bearing on the problem of isotopic composition of deep-seated carbon, Earth Planet. Sci. Lett. 29 (1976) 413–421.

[17] P. Burnard, The bubble-by-bubble volatile evolution of two mid-ocean ridge basalts, Earth Planet. Sci. Lett. 174 (1999) 199–211.

[18] M. Javoy, F. Pineau, The volatiles record of a "popping" rock from the Mid-Atlantic Ridge at 14°N: chemical and isotopic composition of gas trapped in the vesicles, Earth Planet. Sci. Lett. 107 (1991) 598–611.

[19] P. Sarda, D.W. Graham, Mid-ocean ridge popping rocks: implications for degassing at ridge crests, Earth Planet. Sci. Lett. 97 (1990) 268–289.

[20] P. Sarda, M. Moreira, T. Staudacher, J.-G. Schilling, C.J. Allègre, Rare gas systematics on the southernmost Mid-Atlantic Ridge: constraints on the lower mantle and the Dupal source, J. Geophys. Res. 105 (B3) (2000) 5973–5996.

[21] C.J. Ballentine, Resolving the mantle He/Ne and crustal ^{21}Ne/^{22}Ne in well gases, Earth Planet. Sci. Lett. 152 (1997) 233–249.

[22] P. Sarda, T. Staudacher, C.J. Allègre, Neon isotopes in submarine basalts, Earth Planet. Sci. Lett. 91 (1988) 73–88.

[23] H. Kumagai, I. Kaneoka, Variations of noble gas abundances and isotope ratios in a single MORB pillow, Geophys. Res. Lett. 25 (1998) 3891–3894.

[24] H. Kumagai, I. Kaneoka, Relationship between submarine MORB glass textures and atmospheric component of MORBs, Chem. Geol. 200 (2003) 1–24.

[25] L. Dosso, H. Bougault, J.-L. Joron, Geochemical morphology of the North Mid-Atlantic Ridge, $10°–24°N$: trace element–isotope complementarity, Earth Planet. Sci. Lett. 120 (1993) 443–462.

[26] P. Sarda, M. Moreira, Vesiculation and vesicle loss in mid-ocean ridge basalt glasses: He, Ne, Ar elemental fractionation and pressure influence, Geochim. Cosmochim. Acta 66 (2002) 1149–1458.

[27] D.W. Graham, Noble gas isotope geochemistry of Mid-Ocean Ridge and Ocean Island Basalts: characterization of mantle source reservoirs, in: C.J. Ballantine, D. Porcelli, R. Wieler (Eds.), Noble Gases in Geochemistry and Cosmochemistry, Reviews in Mineralogy and Geochemistry, vol. 47, The Mineralogical Society of America, The Geochemical Society, Washington DC, 2002, pp. 247–317.

[28] A.E. Saal, E.H. Hauri, C.H. Langmuir, M.R. Perfit, Vapour undersaturation in primitive mid-ocean ridge basalt and the volatile content of Earth's upper mantle, Nature 419 (2002) 451–455.

[29] R.H. Kingsley, J.-G. Schilling, Carbon in Mid-Atlantic Ridge basalt glasses from $28°N$ to $63°N$: evidence for a carbon-enriched Azores mantle plume, Earth Planet. Sci. Lett. 129 (1995) 31–53.

[30] M.D. Kurz, W.J. Jenkins, The distribution of helium in oceanic basalt glasses, Earth Planet. Sci. Lett. 53 (1981) 41–54.

[31] M. Moreira, P. Sarda, Noble gas constraints on degassing processes, Earth Planet. Sci. Lett. 176 (2000) 375–386.

[32] D. Graham, P. Sarda, Reply to comment by T.M. Gerlach on "Mid-ocean ridge popping rocks: implications for degassing at ridge crests", Earth Planet. Sci. Lett. 105 (1991) 568–573.

[33] Y. Sano, N. Takahata, Y. Nishio, B. Marty, Nitrogen recycling in subduction zones, Geophys. Res. Lett. 25 (1998) 2289–2292.

[34] Y. Nishio, S. Sasaki, T. Gamo, H. Hiyagon, Y. Sano, Carbon and helium isotope systematics of North Fiji Basin basalt glasses: carbon geochemical cycle in the subduction zone, Earth Planet. Sci. Lett. 154 (1998) 127–138.

[35] P. Sarda, M. Moreira, T. Staudacher, Argon–lead isotopic correlation in mid-Atlantic ridge basalts, Science 283 (1999) 666–668.

[36] R.K. Mohapatra, S.V.S. Murty, Origin of air-like noble gases in oceanic basalts, Geophys. Res. Lett. 27 (2000) 1583–1586.

[37] T. Matsumoto, Y. Chen, J.-I. Matsuda, Concomitant occurrence of primordial and recycled noble gases in the Earth's mantle, Earth Planet. Sci. Lett. 185 (2001) 35–47.

[38] T. Matsumoto, D.L. Pinti, J.-I. Matsuda, S. Umino, Recycled noble gas and nitrogen in the subcontinental lithospheric mantle: implications from N–He–Ar in fluid inclusions of SE Australian xenoliths, Geochem. J. 36 (2002) 209–217.

[39] V. Busigny, P. Cartigny, P. Philippot, M. Ader, M. Javoy, Massive recycling of nitrogen and other fluid-mobile elements (K, Rb, Cs, H) in a cold slab environment: evidence from HP to UHP oceanic metasediments of the Schistes Lustrés nappe (Western Alps Europe), Earth Planet. Sci. Lett. 215 (2003) 27–42.

[40] C.J. Allègre, D. Turcotte, Implications of a two-component marble-cake mantle, Nature 323 (1986) 123–127.

[41] C.C. Lundstrom, J. Gill, Q. Williams, A geochemically consistent hypothesis for MORB generation, Chem. Geol. 162 (2000) 105–126.

[42] D.W. Graham, W.J. Jenkins, J.G. Schilling, G. Thompson, M.D. Kurz, S. Humphris, Helium isotope geochemistry of mid-ocean ridge basalts from the South Atlantic, Earth Planet. Sci. Lett. 110 (1992) 133–147.

[43] A. Prinzhofer, E. Lewin, C.J. Allègre, Stochastic melting of the marble cake mantle: evidence from local study of the East Pacific Rise at $12°50'$ N, Earth Planet. Sci. Lett. 92 (1989) 189–206.

[44] E.M. Klein, C.H. Langmuir, Global correlations of ocean ridge basalt chemistry with axial depth and crustal thickness, J. Geophys. Res. 92 (B8) (1987) 8089–8115.

[45] M. Moreira, J. Blusztajn, J. Curtice, S. Hart, H. Dick, M. Kurz, He and Ne isotopes in oceanic crust: implications for noble gas recycling in the mantle, Earth Planet. Sci. Lett. 216 (2003) 635–643.

[46] T. Staudacher, C.J. Allègre, Recycling of oceanic crust and sediments: the noble gas subduction barrier, Earth Planet. Sci. Lett. 89 (1988) 173–183.

[47] P. Sarda, M. Moreira, T. Staudacher, Origin of argon–lead isotopic correlation in basalts, reply to Burnard, Science 286 (1999) 871a.

[48] D.M. Shaw, Trace element fractionation during anatexis, Geochim. Cosmochim. Acta 34 (1970) 237–243.

[49] C.J. Allègre, J.-F. Minster, Quantitative models of trace element behavior in magmatic processes, Earth Planet. Sci. Lett. 38 (1978) 1–25.

[50] B. Marty, P. Lussiez, Constraints on rare gas partition coefficients from analysis of olivine-glass from a picritic mid-ocean ridge basalt, Chem. Geol. 106 (1993) 1–7.

[51] E.M. Chamorro, R.A. Brooker, J.-A. Wartho, B.J. Wood, S.P. Kelley, J.D. Blundy, Ar and K partitioning between clinopyroxene and silicate melt to 8 Gpa, Geochim. Cosmochim. Acta 66 (2002) 507–519.

[52] R.A. Brooker, Z. Du, J.D. Blundy, S.P. Kelley, N.L. Allan, B.J. Wood, E.M. Chamorro, J.-A. Wartho, J.A. Purton, The 'zerocharge' partitioning behaviour of noble gases during mantle melting, Nature 423 (2003) 738–741.

[53] R.A. Brooker, J.-A. Wartho, M.R. Carroll, S.P. Kelley, D.S. Draper, Preliminary UVLAMP determinations of argon partition coefficients for olivine and clinopyroxene grown from silicate melts, Chem. Geol. 147 (1998) 185–200.

[54] S.R. Hart, He diffusion in olivine, Earth Planet. Sci. Lett. 70 (1984) 297–302.

[55] S.R. Taylor, S.M. McLennan, The geochemical evolution of the continental crust, Rev. Geophys. 33 (1995) 241–265.

[56] M. Moreira, M.D. Kurz, Subducted oceanic lithosphere and the origin of the 'high μ' basalt helium isotopic signature, Earth Planet. Sci. lett. 189 (2001) 49–57.

[57] D.W. Graham, A. Zindler, M.D. Kurz, W.J. Jenkins, R. Batiza, H. Staudigel, He, Pb, Sr and Nd isotope constraints on magma genesis and mantle heterogeneity beneath young Pacific seamounts, Contrib. Mineral. Petrol. 99 (1988) 446–463.

[58] P. Burnard, Diffusive fractionation of noble gases and helium isotopes during mantle melting, Earth Planet. Sci. Lett. 220 (2004) 287–295.

[59] D.B. Patterson, M. Honda, I. McDougall, Atmospheric contamination: a possible source for heavy noble gases in basalts from Loihi Seamount, Hawaii, Geophys. Res. Lett. 17 (1990) 705–708.

[60] T. Staudacher, P. Sarda, C.J. Allègre, Comment on "Atmospheric contamination: a possible source for heavy noble gases in basalts from Loihi seamount Hawaii", Geophys. Res. Lett. 18 (1991) 745–748.

[61] W. Bach, S. Niedermann, Atmospheric noble gases in volcanic glasses from the southern Lau basin: origin from subducting slab? Earth Planet. Sci. Lett. 160 (1998) 297–309.

[62] G.E. Bebout, The impact of subduction-zone metamorphism on mantle-ocean chemical cycling, Chem. Geol. 126 (1995) 191–218.