Origin of Argon-Lead Isotopic Correlation in Basalts

Sarda *et al.* (*1*) show that there is a correlation between $^{206}Pb/^{204}Pb$ and maximum $^{40}Ar/^{36}Ar$ values in Atlantic basalts. The authors argue that this correlation is due to mixing between a degassed-depleted upper mantle ($^{40}Ar/^{36}Ar > 40,000$ and $^{206}Pb/^{204}Pb \approx 17.8$) and a recycled component in the mantle (HIMU) that has unradiogenic Ar resulting from recycling of atmospheric Ar ($^{40}Ar/^{36}Ar = 300$). However, devolatilization of subducting material is well documented in arc environments and it seems extraordinary that Ar, a highly volatile element, can be recycled in significant amounts. I aim to show that the Ar content required of the recycled slab is implausibly high and that most of the variation in Ar isotopic composition could be the result of shallow-level atmospheric contamination.

From the curvature of the hyperbola in $^{40}Ar/^{36}Ar$–$^{206}Pb/^{204}Pb$ space, Sarda *et al.* (*1*) suggest a $^{40}K/^{36}Ar$ ratio of 3000 to 6000 in the recycled endmember. The K content of the HIMU endmember is difficult to constrain, but is unlikely to be less than 0.1 wt % K_2O (*2*), implying a minimum ^{36}Ar content of 20×10^{-9} cm³ STP g⁻¹ in the HIMU endmember. This is similar to the highest values measured in basalts ($\approx 2 - 20 \times 10^{-9}$ cm³ STP g⁻¹) (*3*), and implies that oceanic crust is subducted without ^{36}Ar loss. If average basalt was subducted ($\approx 6 \times 10^{-9}$ cm³ STP g⁻¹) without volatile loss, the *r* coefficient in $^{206}Pb/^{204}Pb$–$^{40}Ar/^{36}Ar$ space would be ≈ 1 (a straight line). It is reasonable to expect that gas loss during subduction would result in *r* values $\gg 1$ (the opposite curvature to that observed). It is difficult to envisage a scenario where subducted Ar can result in an *r* correlation of 0.15 as reported by Sarda *et al.* (*1*); it is therefore necessary to examine an alternative mechanism for the observed correlations.

There is a broad anti-correlation between $^{40}Ar/^{36}Ar$ and eruption depth (Fig. 1) in the data presented by Sarda *et al.* (*1*). This can reasonably be attributed to more extensive magmatic degassing at shallow levels, producing basalts more susceptible to atmospheric contamination. Basalts with elevated $^{206}Pb/^{204}Pb$ ratios in the Atlantic are commonly associated with topographic highs. Yet the correlation between $^{40}Ar/^{36}Ar$ and $^{206}Pb/^{204}Pb$, rather than the consequence of recycled Ar in the HIMU source, may equally be the result of preferential atmospheric contamination of the more shallow erupted HIMU basalts.

This argument does not eliminate the pos-sibility of Ar recycling to the mantle; the correlation between $^{40}Ar/^{36}Ar$ and depth may result from a ^{36}Ar–rich HIMU component which then produces topographic highs on the seafloor. However, given the problems associated with recycling atmospheric Ar in the quantities required, and the viable alternative explanation to the correlation between Ar and Pb isotopes, subduction of atmospheric Ar is not yet proven.

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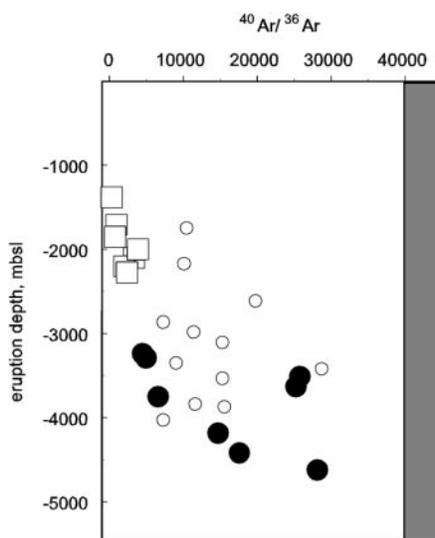3. M. Ozima and S. Zashu, *Earth Planet. Sci. Lett.* **62**, 24 (1983).

Fig. 1. $^{40}Ar/^{36}Ar$ versus depth of eruption for all data in Sarda *et al.* (*1*); squares, Azores; filled circles, north Atlantic; open circles, south Atlantic. Shaded area indicates probable mantle composition. In general, the deepest samples have the highest $^{40}Ar/^{36}Ar$ ratios. The considerable scatter in the correlation is likely due to variable atmospheric contamination.

Response: Burnard states that Ar cannot be recycled in significant amounts. Our data show that argon and lead do correlate at the scale of the whole Atlantic Ocean (and with a data dispersion that is of the same magnitude as for the Pb-Pb correlation); therefore, Ar may be recycled in concentrations high enough in the recycled material to be seen in MORB melts. This does not necessarily contradict the fact that important devolatilization occurs at subduction, and does not necessarily imply that argon is recycled with such high concentrations that the degassed-mantle $^{40}Ar/^{36}Ar$ isotopic anomalies should be erased (they are not).

That this correlation holds at the scale of the Atlantic Ocean is difficult to understand if the correlation is produced by contamination. Here, we suggest that contamination is an erratic process and produces scattered values. See, for example, the rare gas concentration patterns for samples with $^{40}Ar/^{36}Ar < 10,000$ shown in Staudacher *et al.* (*1*, p. 124, figure 4a).

Another point is that just as there is a vague correlation between argon and depth, so is there a rough correlation between lead and depth. No one attributes this to any kind of surface-related process, but rather to plume-ridge interaction. Moreover, as shown in our report, the osmium isotopic data have recently been shown to also correlate with lead, so that there is necessarily a vague correlation between osmium and depth as well. The same kind of reasoning that Burnard is making should thus also apply to osmium. Yet I have not found this suggested in the literature.

Finally, let us turn to simple quantification. Following Burnard, we attempted an order-of-magnitude calculation of the consequences for K of our Ar-Pb correlation. We started from the model used by Chauvel *et al.* (*2*) for the recycling of oceanic crust that explains the HIMU component. These authors assumed a melting rate of 0.5% for both the depleted upper mantle and the recycled oceanic crust and used a simple batch melting equation with the appropriate mineralogical compositions and partition coefficients.

With a beginning ^{36}Ar concentration of 2×10^{-10} cm³/g in the degassed mantle from Allègre *et al.* (1986) (*3*), the resulting concentration in *undegassed* MORB melt is 4×10^{-8} cm³/g, a value similar to concentrations found in popping rocks. We assume that we have two melts that mix together, one from the degassed-depleted mantle, the other from the HIMU recycled matter. For our Ar-Pb correlation to be visible, the Ar concentration in the HIMU melt should be on the same order of magnitude. Let us first assume it is the same, that is, 4×10^{-8} cm³ ^{36}Ar/g melt. With the above melting rate, this is 2×10^{-10} cm³ of ^{36}Ar per gram of HIMU rock (unmelted). With a $^{40}K/^{36}Ar$ ratio of 3000 for the HIMU melt [see our report (*4*)], we have 0.2 wt % of K_2O in this melt, and, assuming the same partition coefficients for K and U, 6.5×10^{-3} wt % of K_2O in the HIMU rock.

If one uses the same geochemical parameters as Chauvel *et al.* (*2*)—a mixture of 75% depleted mantle derived melt and 25% recycled matter derived melt—the yield is a total K_2O concentration of 0.87 wt %. This is consistent with the K_2O concentrations of 0.5–1.5 wt % measured in HIMU-type melts from Tubuaii, as reported in Chauvel *et al.* (*2*). Thus, this calculation supports the idea that atmospheric argon is recycled with oceanic crust at a ^{36}Ar concentration of about 2 $\times$ 10^{-10} cm^3/g. Compared to the data of Staudacher and Allègre (*5*) for altered oceanic crust, this represents a loss of argon by a factor of 16, in agreement with the idea of devolatilization at subduction. Of interest is that if we compare the K concentration obtained above for the HIMU rock to the value given by Staudigel *et al.* (*6*) for altered oceanic crust of 0.1 wt % (used by Burnard), the loss factor for K is 18, the same as that for Ar.

If we want to reproduce a "subduction barrier factor" of 59, as in Staudacher and Allègre (*5*), we need to have a 3.7 lower ^{36}Ar concentration in the HIMU melt than in the degassed mantle derived melt. The K loss factor then becomes 66, and the K_2O changes to 0.06 wt % in the HIMU melt and 0.84 wt % in the final mixed melt. Using a value of 6000 for the $^{40}K/^{36}Ar$ ratio of the HIMU melt, the loss factor for K would be 1.7 times lower than that for Ar.

The calculations above are only first order, but they show that the Ar-Pb correlation that we found are not inconsistent with the model used by Chauvel *et al.* (*2*) for the HIMU source. Our value of 0.2 wt % K_2O is compatible with the one used by Burnard, but applies to HIMU melt in the calculation above instead of to the altered oceanic crust in the work of Staudigel *et al.* (*6*) as cited by Burnard. This implies that K is also lost to some extent at subduction, as seen in studies of island arc volcanic rocks [See (*7*)].

For this model to work, Ar should not be too mobile to remain stored in the subducted matter until it melts. This is not impossible. Hart (*8*) showed that helium moves relatively slowly in mantle silicates. Argon must be even slower.

We thus conclude that, given present knowledge and the uncertainties about the different parameters involved, argon can possibly be recycled at a rather low concentration, that is, of the same order of magnitude as the degassed part of the mantle, due to devolatilization at subduction. This is nevertheless consistent with measured concentrations of both Ar and K in HIMU related lavas, and with the Ar-Pb isotopic correlation evidenced for the mid-Atlantic Ridge glass samples.

As a final note, Pb isotope data by L. Dosso *et al.*, cited as "unpublished data" (*35*) in our report, has now been published (*9*).

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