

# Volatiles (He, C, N, Ar) in the mantle: assesment of shallow-level assimilation and fractionation, and evaluation of source composition

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It is now well established that the mantle contains significant amounts of volatiles which have isotopic compositions different from those of atmospheric volatiles. Part of these differences are due to radioactive production and accumulation in the different mantle domains, but some of these isotopic "anomalies" cannot result from nuclear reactions within the Earth and reflect heterogeneities in the Earth-Atmosphere system which were established early in the Earth's history, as attested by chronometers based on extinct radioactivities. Thus comparison between the different terrestrial inventories allows to constrain processes which might have contributed volatiles to the surface (atmosphere, hydrosphere, sediments) reservoirs.

In an effort to document the volatile composition of the convective mantle, the abundances and the isotopic ratios of carbon, nitrogen, helium and argon have been analysed in 45 mid-ocean ridge basalts (MORB) from the Mid-Atlantic Ridge between 24°N

and 36°N, the East Pacific Rise at 21°N, 13°N, and 17–19°S, the Red Sea (18–20°N), the Indian Ocean near the Triple Junction, and the central North Fijji basin. Gases were extracted by crushing and splitted for purification and analysis, by static mass spectrometry for N, He and Ar, and by conventional dynamic mass spectrometry for C. The data confirm the occurrence of near-constant He isotope ratios ( $^3\text{He}/^4\text{He} = 8.53 \pm 0.79 \text{ Ra}$ ,  $n = 36$ ) and C isotope ratios ( $\delta^{13}\text{C} = -5.3 \pm 0.8\text{‰}$  vs PDB,  $n = 21$ ), and of a light nitrogen component in the convective mantle ( $\delta^{15}\text{N}$  is in the range of  $-9\text{‰} \sim +4.5\text{‰}$ , with a mean of  $-3.3 \pm 0.8$  vs. ATM, for samples with  $^{40}\text{Ar}/^{36}\text{Ar} > 1000$ ).

## Shallow fractionation versus source composition

The abundance of volatiles varies over three orders of magnitude (Fig. 2). Because vesicles have concentrated magmatic volatiles, the variation of abundances reflect in fact the outgassing state of the magmas, plus the variable addition of atmospheric

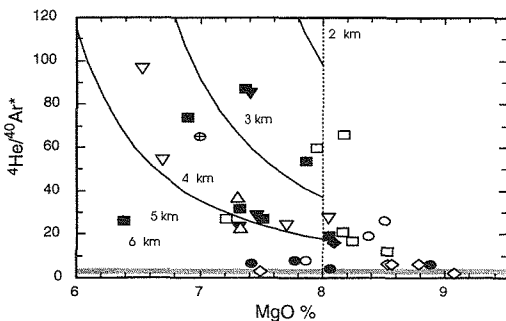


FIG. 1. Example of the effect of AFCD on the  $^4\text{He}/^{40}\text{Ar}^*$  ratio, for an initial  $\text{CO}_2$  content in the magma of  $2.4 \times 10^{-5} \text{ mol CO}_2/\text{g}$  and 8% MgO.

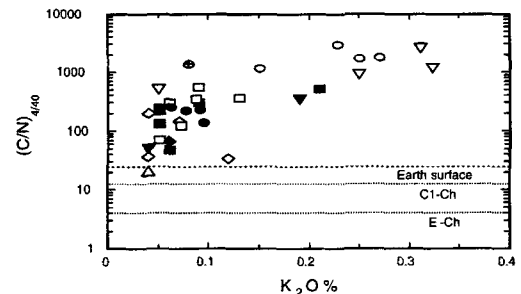


FIG. 2. C/N (corrected for AFCD) versus potassium content in MORB worldwide.

volatiles. Variations of the  $^4\text{He}/^{40}\text{Ar}^*$  ratios (Fig. 1) as well as  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios (not shown) are consistent with fractional crystallisation-assimilation-degassing (AFCD) taking place in the depth range 3–6 km. Thus, investigation of source composition of volatiles necessitates to correct volatile abundances and isotopic ratios for AFCD. This can actually be done using the observed  $^4\text{He}/^{40}\text{Ar}^*$  ratios since the mantle  $^4\text{He}/^{40}\text{Ar}^*$  ratio prior to AFCD can be anticipated from the abundances of the parent elements, U, Th and K. The corrected  $(\text{C}/^3\text{He})_{4/40}$  ratios, where  $^3\text{He}$  is juvenile in the mantle, tend to increase with increasing  $\text{K}_2\text{O}$  %. The enrichment of incompatible elements including potassium in E-MORB cannot be solely explained by local assimilation and calls for the occurrence of recycled material in the mantle source over long periods of time (Le Roex, 1987). Therefore, the correlation between  $(\text{C}/^3\text{He})_{4/40}$  and potassium provides a good evidence that carbon is efficiently recycled into the convective mantle. The case of nitrogen is different in that there is no specific dependency of the  $(\text{N}_2/^3\text{He})_{4/40}$  ratio with  $\text{K}_2\text{O}$ %. Furthermore, the  $(\text{N}_2/^3\text{He})_{4/40}$  ratio varies by less than one order of magnitude, whereas the  $(\text{C}/^3\text{He})_{4/40}$  ratio shows variation over two orders of magnitude. It therefore appears that nitrogen recycling is probably much more limited than that of carbon, qualitatively consistent with the survival of N isotope anomaly in the convective mantle over the age of the Earth (Marty and Humbert, 1997), whereas carbon appears to be homogenised between the mantle and the Earth's surface. The  $(\text{C}/\text{N})_{4/40}$  variation (Fig.2) is consistent with mixing between a mantle end-member showing low C/N (possibly as low as chondritic), and a recycled component enriched in C relative to N. Thus this study supports the view that the exchange rate of carbon between the mantle and the surface of the Earth is characterised by a time constant sufficiently short to allow isotopic homogenisation, whereas that of nitrogen has been probably more restricted and has allowed N isotope heterogeneities to survive.

## Volatile composition of the mantle

Comparison of elemental and isotopic characteristics of volatiles between the atmosphere and the mantle, and shows that the atmosphere is depleted in light elements and isotopes, by 260‰ in the light isotope  $^{20}\text{Ne}$  relative to  $^{22}\text{Ne}$  (e.g. Sarda *et al.*, 1988), by approx. 100‰ in hydrogen compared to deuterium (e.g. Kyser and O'Neil, 1984), and by 5~20‰ in  $^{14}\text{N}$  relative to  $^{15}\text{N}$  (Marty and Humbert, 1997, Cartigny *et al.*, 1997, this study). Likewise, the  $^{20}\text{Ne}/^{36}\text{Ar}$  and  $^{14}\text{N}/^{36}\text{Ar}$  ratios are lower in the atmosphere relative to the mantle by one and two orders of magnitude, respectively, and cannot be due uniquely to differential recycling (this study). Therefore, at some early stage of the Earth's evolution, the atmosphere became depleted in light isotopes and in light elements, whereas volatiles in the mantle kept characteristics more comparable to known extra-terrestrial components (e.g. solar for  $^{20}\text{Ne}/^{22}\text{Ne}$ , chondritic for  $\delta^{15}\text{N}$  and  $^{14}\text{N}/^{36}\text{Ar}$ ) than those in the atmosphere. The open question is to decipher if this fractionation took place before trapping, or within parent bodies of atmospheric volatiles, and are therefore extra-terrestrial in nature, or if it was a consequence of processes having affected the early Earth. A recent study suggests that both processes might have acted, affecting differentially each volatile species (Dauphas, 1998).

## References

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