

Behaviour of noble gases during dehydration processes in the subducting oceanic crust

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Since the early years of terrestrial noble gas geochemistry, the origin of an isotopically atmosphere-like noble gas component found in many mantle-derived samples has been a matter of debate. Recent recognition that there might be a significant input of atmospheric noble gases by subduction of hydrated oceanic crust and its sediment cover is largely based on circumstantial evidences suggested from isotope analysis on natural mantle-derived samples (e.g. [1-4]). However, there are many unresolved issues about the feasibility of air recycling — for example, the presence of a carrier in subducting materials that can relay air-like noble gas into the deeper mantle regions. In order to clarify the possibility of noble gas recycling, we carried out high-pressure dehydration experiments on materials analogous to the subducting crust. Unlike the case of trace element study, choice of starting material is more critical for noble gases due to a possible diffusive input of atmospheric noble gases in a pressure chamber under high pressures and temperatures. To circumvent this problem, we have selected starting materials enriched in radiogenic noble gas isotopes (such as ⁴He, ²¹Ne, ⁴⁰Ar and ^{129, 131-136}Xe) as isotope markers. Then dehydration experiments under upper mantle P/T conditions were carried out by using multi-anvil high-pressure apparatus. Comparison of concentrations of radiogenic noble gas isotopes before and after the dehydration experiments suggests that virtually 100 % of helium is removed from the slab upon dehydration, whereas upto 4 % of argon can survive amphibolite dehydration process. This is consistent with the previously found signatures in natural mantle samples with suspected recycled atmospheric noble gases.

[1] Sarda *et al.* (1999) *Science* **283**, 666-668. [2] Matsumoto *et al.* (2001) *EPSL* **185**, 35-47. [3] Matsumoto *et al.* (2005) *EPSL* **238**, 130-145. [4] Holland & Ballentine (2006) *Nature* **441**, 186-191.

Zn isotopes as tracers of atmospheric emissions from a Pb-Zn smelter

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As atmospheric deposition is a major mechanism for metal input to soils and terrestrial organisms, metallurgical activities are among the major sources of airborne Zn, which needs to be better isotopically characterized.

The present work closely examines the Zn isotope fractionation during pyrometallurgical processes, compared to dry fallouts within a 5-km zone around a Pb-Zn refinery (in France).

Zn isotopic ratios are measured on a Nu Plasma MC-ICP-MS, after a Zn purification performed by a novel chromatographic method on micro-columns.

From the enriched ores (mean $\delta^{66}\text{Zn}$:0.11‰), dusts produced by the successive Zn extraction steps show strong variations in $\delta^{66}\text{Zn}$ values and reveal pronounced Zn isotope fractionation ($\delta^{66}\text{Zn}$:-0.66‰) in the Pb blast furnace, where the highest temperature of the process is reached (up to 1700K). Assuming a Rayleigh fractionation in the volatilized zinc, the Zn isotope fractionation factor $\alpha_{(\text{ore}/\text{vapor})}$ is 1.00083.

Considering the balanced Zn outputs of the main plant chimneystacks and the isotopic/elemental compositions of Zn emissions, a theoretical average $\delta^{66}\text{Zn}$ of the total Zn smelter atmospheric emissions gives -0.13‰. Dry fallouts located from 1720 to 4560m from the smelter show such negative $\delta^{66}\text{Zn}$ values (-0.52 to -0.02‰). In contrast, proximal dry fallouts reflect a main contribution of resuspension of slag heaps and local emissions of sintering units.