

Noble gases and halogens in the oceanic crust

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Recent studies showed that seawater-derived noble gases and halogens can be recycled into the mantle during the subduction of the oceanic crust [1, 2, 3]. To better understand how this signature is acquired and thus can be preserved, we determined the heavy noble gas (³⁶Ar, ⁸⁴Kr, ¹³⁰Xe) and halogen (Cl, Br, I) concentrations in the pre-subducted material represented by altered MORB (IODP sites 504, 896, 1256 in the Pacific ocean). The measurements were obtained from samples irradiated via neutron activation, by the release of noble gases in vacuo step crushing (N=18) and followed by in vacuo step heating (N=11).

The ¹³⁰Xe/³⁶Ar ratios are on average 2 times higher for the heating data (13 ± 5.10^{-4}) than for the crushing data ($5.0 \pm 4.8.10^{-4}$) for similar ⁸⁴Kr/³⁶Ar (0.05±0.01 and 0.04±0.02 respectively). Thus, the fluid phase is interpreted to be a mixture of air and seawater (± sediments) whereas the solid phases contain an additional altered MORB noble gas component.

An average of ~90% of the halogens are contained in the solid phases and are comparable to the levels present in unaltered MORB glasses. The bulk rock Br/Cl ratio is ~constant ($1.05 \pm 0.45.10^{-3}$) but is 30% lower than in unaltered MORB. In more detail, the Br/Cl ratios of the fluid phases are higher than the seawater's ratio ($1.54.10^{-3}$) and lower than seawater in the solid phases. The I/Cl ratios vary by 4 orders of magnitude for both the fluid and the solid phases (from $5.5.10^{-7}$ to $9.03.10^{-3}$). The halogen ratios of the fluid phases can thus be explained by a mixing of seawater and sediment or marine pore fluid components. In contrast, the lower Br/Cl value of the altered oceanic crust is mainly attributed to the addition of Cl during the alteration process on the seafloor.

For both halogens and heavy noble gases, we observe different partitioning between the fluid phase and the solid phase. While the fluid phases are more likely a mixing between seawater and a sediment/marine pore fluid signature component, the solid phases define an altered MORB signature. Halogens seem to be a powerful tool to trace the seawater and marine pore fluid signature in rocks and the budget of these elements that is potentially available to be delivered to mantle during subduction.

[1] Holland & Ballentine (2006), *Nature* 441, 186-191.

[2] Sumino et al. (2010), *EPSL* 294, 163-172.

[3] Kendrick et al. (2011), *Nature Geosciences* 4, 807-812.

Zircon as a probe of oxygen fugacity: observations and limitations from natural samples

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Ongoing experiments on zircon crystallization confirm the idea that Ce, Eu and Th/U in zircon are sensitive to the oxygen fugacity (fO_2) of the melt from which it crystallizes [1]. At high oxidation states zircons will display a prominent positive Ce anomaly and none or only a weak negative Eu anomaly that are attributed to the predominance of Ce⁴⁺ over Ce³⁺ and Eu³⁺ over Eu²⁺, respectively.

The accurate determination of the Ce anomaly is often problematic due to the low La and Pr concentrations in zircon and possible contamination of the signal during LA-ICP-MS analyses by small LREE-rich mineral inclusions. Alternatively, the Ce⁴⁺/Ce³⁺ ratio can be calculated by using the more enriched REEs, from Nd to Lu, together with Zr, Hf and Th [2]. This ratio can be used to infer the relative oxidation state of magmas if a representative population of zircons for each sample is available. The method is based on the assumption that zircons are in equilibrium with their host rock. If xenocrystic and/or antecrystic zircons are present, the calculated Ce⁴⁺/Ce³⁺ ratio may then be inaccurate. Xenocrysts will alter the trace element budget of the whole rock that had never been available in the magma and then affect the calculated Ce⁴⁺/Ce³⁺ value of the neofomed zircons. Antecrystic zircons (that cannot be differentiated from autocrysts unless high-precision dating can be done) may have crystallized in a magma of different composition from the rock they are found in. Their relative effect was investigated by numerical simulations on a dataset from dated zircons (by LA-ICP-MS) of the Eocene-Oligocene calc-alkaline Corocochuayco magmatic suite in southern Peru, associated with porphyry and skarn copper mineralization.

Results show that the effect of xenocrystic zircons on the calculated Ce⁴⁺/Ce³⁺ is very limited. Values obtained on antecrystic zircons can be inaccurate if the melt from which they crystallized has a significantly more fractionated REE pattern than the rock they are finally found in. The absolute zircon Ce⁴⁺/Ce³⁺ ratio was also found to be very sensitive, by almost one order of magnitude, to the number of REEs used for its calculation. The Ce anomaly does not necessarily correlate with Ce⁴⁺/Ce³⁺. Nevertheless, the interpretations of the Ce⁴⁺/Ce³⁺ ratio calculated using different REEs and of the Ce anomaly are very similar, if a representative number of zircons per sample is available. In our dataset, the zircon Eu anomaly was found to correlate with the bulk rock Eu anomaly and not with the zircon Ce⁴⁺/Ce³⁺, suggesting a first order control by the primary melt composition. The zircon/rock partition coefficient of the Th/U ratio decreases systematically with increasing zircon Ce⁴⁺/Ce³⁺ values (i.e., fO_2). This supports the idea that U can also occur as U⁵⁺ and/or U⁶⁺ in magmas, altering the relative partitioning of Th and U.

[1] Burnham & Berry (2011) *Mineral. Mag.* 75, 600.

[2] Ballard et al. (2002) *Contrib. Mineral. Petrol.* 144, 347-364.