

The noble gas and halogen composition of the hydrated oceanic crust

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Mantle heavy noble gases have a remarkable similarity to those found in marine pore fluids [1,2]. This implies a significant contribution of these gases into the mantle recycled through subduction zones. In order to better constrain the quantity and character of noble gases available for subduction, we are reassessing the major host phases of noble gases in pre-subducted material.

We have acquired, from different ODP sites, a sample suite that is representative of the altered oceanic crust. Noble gas (He, Ne, Ar, Kr and Xe) isotopes and abundances are being determined using crushing release measured with an upgraded VG5400 mass spectrometer.

Preliminary results from four altered basalts (ODP sites 504B and 1256D in the Southeast Pacific Ocean, respectively 5.9 and 15 Ma) show Ne to Xe isotopically identical to air. ³He/⁴He ratios are uniform at 6.82±0.42 (R/Ra). Heavy noble gas elemental ratios fall within a narrow range, with ¹³⁰Xe/³⁶Ar and ⁸⁴Kr/³⁶Ar ratios varying between seawater values and values enriched in Xe and Kr and indistinguishable from mantle values [1]. The range of ¹³⁰Xe/⁸⁴Kr, varying by up to a factor 2.5, suggests that different trapping or fixation sites could control such compositions.

This is supported by an observed correlation of increase of the ¹³²Xe/³⁶Ar ratio relatively to ⁸⁴Kr/³⁶Ar with crushing step in the same sample, which does not seem related to air contamination. This could be representative of the different phases retaining different amounts of heavy nobles gases.

These measurements will be extended to include halogen determinations which are tracers of marine pore fluids and seawater interaction [2]. Analysing noble gases and halogens in basalts characterized by different alteration patterns and in gabbros and sediments will allow the identification of the noble gas host phases, as well as the controls of the seawater noble gases interaction with the oceanic crust.

[1] Holland & Ballentine (2006), *Nature* **441**, 186-191. [2] Sumino *et al.* (2010), *EPSL* **294**, 163-172.

Experimental constraints on magmatic wolframite

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Wolframite is normally a hydrothermal mineral but at the Yaogangxian tungsten deposit, Hunan, China it also occurs as an apparent magmatic phase disseminated in a medium-grained two-mica granite. The magmatic wolframites are tabular crystals, hundreds of µm long, in planar contact with magmatic K-feldspar and quartz. The major elements of magmatic wolframite are similar to hydrothermal crystals in quartz veins from the main zone of mineralization at the deposit. However, Zr, Nb, Ta and Mo are more abundant in magmatic wolframites compared to hydrothermal varieties.

The solubilities of synthetic hubnerite (MnWO₄) in flux-rich water saturated haplogranitic melts have been determined at 850° to 700°C and 2000 bars in order to test the magmatic hypothesis. The melts contain 1.1, 1.7 and 2.02 wt % of Li₂O, P₂O₅ and B₂O₃, respectively. Up to 6 wt% fluorine was added as AgF; the ASI of the melt is close to 1, but if Li is considered to be an alkali element, the melts are alkaline. Hubnerite solubility is weakly dependent on F. At 800°C the solubility products for hubnerite (*K*_{sp}) range from 38x10⁻⁴ mol²/kg² for a 0 wt% F melt to 69x10⁻⁴ mol²/kg² for a 6 wt% F melt. Hubnerite solubility is strongly temperature dependent. *K*_{sp} for a 6 wt% F melt decreases from 162x10⁻⁴ mol²/kg² at 850°C to 17x10⁻⁴ mol²/kg² at 700°C. Another potential control on hubnerite solubility is *f*_{O₂}. The *K*_{sp} is 38x10⁻⁴ mol²/kg² at an *f*_{O₂} near Ni-NiO, 53x10⁻⁴ mol²/kg² using a Co filler rod and 69x10⁻⁴ mol²/kg² using Ti filler rod (see [1] for approximate *f*_{O₂} values). The weak variation of solubility with *f*_{O₂} implies that the predominant oxidation state of W in the melts is +6, even at reduced conditions.

The above experimental solubilities are too high to support the magmatic wolframite hypothesis, however the melts in these experiments are alkaline and solubilities are lower in subaluminous compositions [2]. Because of the strong temperature dependence, magmatic wolframite may nevertheless occur in nature, but the melts should have crystallized at a low temperature and be subalkaline to peraluminous in composition.

[1] Matthews *et al.* (2003), *Amer. Mineral.* **88**, 701-707.

[2] Linnen and Cuney, (2005), *Geol. Assoc. Can Short Course* Vol. **17**, 45-67.