Solubility of carbonate in aqueous fluids at HP-HT: A combined X-ray and Raman spectroscopic study

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The increase of P and T in the subducting oceanic lithosphere leads to devolatilization reactions releasing C-O-H-Si bearing fluids. The composition of natural HP fluid inclusions indicates that H_2O is the main solvent phase. The increase of their CO_2 content as a function of depth is interpreted as a result of the progressive decarbonation of the slab. Consequently, the solubility of carbonate minerals at P-T conditions of subduction is a key for understanding the fate of incoming C in the deep carbon cycle.

We report here *in situ* measurements of the solubility of strontianite $SrCO_3$ as a carbonate model, at P up to 8 GPa and T up to 500 °C. A single crystal of strontianite and milli-Q water were loaded in an externally heated diamond anvil cell, in a sample chamber lined with platinum. The total amount of dissolved Sr was measured *in situ* after the intensity of the Kα X-ray fluorescence line of Sr. Experiments were carried out at the ESRF (ID22 beamline) using a bright monochromatic beam (19 keV, ca. 10^{11}ph/s). The relative amount of dissolved carbonate and bicarbonate was measured by Raman spectroscopy in our lab. with a confocal LabRamHR800 vis Jobin Yvon Horiba. The latter new Raman data show that bicarbonate is the most abundant species in low-pressure fluids whereas carbonate becomes progressively dominant at high pressure. Taking into account activity coefficients, measured concentrations of dissolved Sr and measured carbonate-bicarbonate ratios in the aqueous fluid at equilibrium with a crystal, the solubility constant of $SrCO_3$ could be assessed at pressure conditions relevant to the upper mantle.

Tectonothermal history of the Black Forest (Germany): A triple dating approach on a single apatite sample

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We triple dated possibly the largest (up to ~5 mm long) apatite grains in Central Europe, sampled in a key outcrop of the Black Forest (Germany) using TIMS U-Pb, fission track (FT) and (U-Th)/He dating methods. By adopting the multi-dating approach on a single sample we were able to further constrain thermo-tectonic evolution of the Black Forest from the formation of crystalline basement during the Variscan orogeny (U-Pb age: ~290 Ma) to Cenozoic exhumation related to formation of the Upper Rhine Graben rift (FT age: ~38 Ma; He ages: ~25-65 Ma).

The results emphasize that knowledge of the spatial distribution of parent nuclides within the dated mineral and in its 'neighbourhood' is critically important for understanding and interpreting (U-Th)/He ages [1]. Traditional alpha ejection corrections (e. g, [2], [3]) based on the assumption of homogeneous distribution of parent nuclides, can result in massive overestimation of true He ages. We also demonstrate that the apparent discrepancy between FT and He ages encountered in the dataset may arise merely from a statistical misconception and conventional data treatment. Instead of central FT age, we recommend using the oldest FT single grain age as an upper limit for 'acceptance' of He ages.

[1] Meesters & Dunai (2002) *Chem. Geol.* **186**, 345–363. [2] Farley *et al.* (1996) *GCA* **60**(21), 4223–4229. Farley (2002) *Mineral. Soc. Am. RiMG* **47**, 819–844.