

Novel insights into the ion sorption properties of calcite in aqueous solutions using cavity ring-down spectroscopy

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Despite significant advances on the elucidation of the structure of the calcite-water interface, much controversy still surrounds some of its most fundamental physical-chemical properties [e.g. the pH of the isoelectric point, the point of zero net surface charge, the proton and lattice-derived ion sorption properties]. This is largely due to the lack of suitable experimental approaches allowing a rigorous characterization of calcite surface equilibria over expanded compositional ranges. Electrokinetic techniques do not allow direct probing of surface reactions whereas conventional wet-chemical approaches (batch and titration) fail to control or monitor CO_{2(g)} exchange across the air-water interface which leads to large uncertainties in the computed (ad)sorption data. Recently, a novel titration protocol that addresses this difficulty was developed and tested over a relatively wide range of chemical conditions [1]. The new data was interpreted in terms of the following 2H⁺/Ca²⁺ ion exchange equilibrium:



If true, this mechanism may impact the aqueous speciation of carbonate-rock systems with restricted CO_{2(g)} ventilation via the buffering of pH and calcite dissolution. It follows that a careful verification of this reaction is warranted. To this end, and to gain further insight into the ion sorption properties of CaCO_{3(s)} in aqueous solutions, we are conducting new titrations of high-purity, additive-free, synthetic calcite and aragonite powders over a broader range of conditions using a novel titration approach that allows, for the first time, a reliable monitoring of the chemistry of the CaCO_{3(s)}-H₂O_(l)-CO_{2(g)} system. Accurate *p*CO₂ measurements are obtained via a gas-recirculation device and a last-generation cavity ring-down laser spectrometer which avoids interferences from water vapor with negligible sample perturbation, a notable advantage over IR spectrometer-based strategies. Our approach yields very high-quality data suitable for the calibration of ion sorption models for CaCO_{3(s)} surfaces.

[1] *Phys. Chem. Chem. Phys.* (2009) **11**, 8895–8912.

Molybdenum isotopes in the altered oceanic crust, a novel proxy for recycling?

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During movement of the oceanic crust away from mid-ocean ridges, hydrothermal alteration of the oceanic crust results in a distinct elemental and isotopic signal. The change in isotopic composition compared to unaltered MORB is an important tracer for the involvement of fluids released from the altered oceanic crust at the base of arc volcanoes during subduction. Any isotopic system not fractionated during dehydration reaction and inert to diffusion is therefore a valuable tracer to shallow or deep recycling of subducted material. Recent studies showed that Mo isotopes could be such a novel proxy [1, 2, 3] as measured Mo isotope values in arc and ocean island basalts differ significantly from mantle values (estimated to be similar to continental crust 0‰ δ^{97/95}Mo). This study investigates the change in Mo isotopes through the altered oceanic crust to better constrain the input into the subduction zone.

Samples of the altered oceanic crust across the Pacific Ocean have been measured for Mo isotopes and Mo concentrations (ODP Sites 1179, 1301, 1256). Combined the studied samples show a decreasing down-hole trend varying over 1‰ δ^{97/95}Mo. The heavier isotope ratio in the upper part of the crust might be the source region for the heavy isotope ratio seen in the Mariana arc [2] and the lighter isotope ratio further down-hole might be the source for the light isotope ratio seen in ocean islands basalts [1, 3]. To further constrain this down-hole trend over a complete section of the altered oceanic crust (through pillow basalts, sheeted dyke complex, and gabbros), additional Mo isotope and concentration measurements on the deepest ODP hole (Site 1256) are currently in process.

[1] Willbold *et al.* (2009) *GCA* **73 suppl.** A1444.

[2] Freymouth *et al.* (2011) this volume. [3] Lai *et al.* (2011) this volume.