

U-Pb and Th-Pb dating of apatite by LA-ICPMS

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Apatite is a common U- and Th-bearing accessory mineral in igneous, sedimentary and metamorphic rocks and ore systems. However, low U, Th and radiogenic Pb concentrations, elevated common Pb and the lack of a U-Th-Pb apatite standard remain significant challenges in dating apatite by LA-ICPMS.

This study has determined U-Pb and Th-Pb ages for seven apatite occurrences (Durango, Emerald Lake, Kovdor, Mineville, Mudtank, Otter Lake and Slyudyanka) by LA-ICPMS [1]. Analytical procedures involved rastering a 10µm spot over a 40x40µm square to a depth of 10µm using a Geolas 193nm ArF excimer laser coupled to a Thermo ElementXR single-collector ICPMS. These raster conditions minimized laser-induced inter-element fractionation which was corrected for using the back-calculated intercept of the time-resolved signal. A Tl-U-Bi-Np tracer solution was aspirated with the sample into the plasma to correct for instrument mass bias. External standards (Plešovice and 91500 zircon, NIST SRM 610 and 612 silicate glasses and STDP5 phosphate glass) along with Kovdor apatite were analysed to monitor U-Pb, Th-Pb and Pb-Pb ratios.

Common Pb correction employed the ²⁰⁷Pb method, and also a ²⁰⁸Pb correction method for samples with low Th/U. The ²⁰⁷Pb and ²⁰⁸Pb corrections employed either the initial Pb isotopic composition where known or the Stacey and Kramers model. No ²⁰⁴Pb correction was undertaken because of ²⁰⁴Pb interference by ²⁰⁴Hg in the argon gas supply.

Age calculations used a weighted average of the common Pb-corrected ages and Tera-Wasserburg Concordia intercept age (both unanchored and anchored through common Pb). The samples yield ages consistent with independent estimates of the U-Pb apatite age, which demonstrates the suitability of the analytical protocol employed. Weighted mean age uncertainties are as low as 1-2% for U- and/or Th-rich Palaeozoic-Neoproterozoic samples [1].

[1] Chew *et al.* (2011) *Chem. Geol.* **280**, 200–216.

Aqueous CO₂ solutions at silica surfaces and confined environments

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The CO₂ capture and sequestration in geological reservoirs have been considered as a potential approach to mitigate its release into the atmosphere and reduce its contribution to the greenhouse effect on climate change. The feasibility and safety of this process for long-term storage of CO₂ depends on the low hydraulic permeability of the caprock and its ability to hold the aqueous fluid in its porous structure, *i.e.*, its interfacial and confinement properties.

Interfacial and confined fluids exhibit microstructural, dynamical, and thermophysical behavior that differ dramatically from their bulk counterparts. The immediate consequence is the inherent inability of current modeling approaches to capture the actual (aqueous-caprock) fluid-solid and fluid-fluid interfacial mechanisms underlying the geological CO₂ sequestration.

Here we present a molecular-based study of the microstructural and dynamical behavior of CO₂-aqueous solutions at silica surfaces and under extreme confinement, to address fundamental issues, including (a) how the degree of surface hydrophobicity affects the interfacial structure, (b) how the overlapping of interfacial structures affects the confined fluid composition (relative solubility), and (c) how to account for the effect of medium polarization on the species solubilities.

Toward those goals we developed (i) a synergistic approach to calibrate the CO₂-H₂O interactions for the accurate and simultaneous prediction of the compositions of the two phases in liquid (water-rich)-liquid (CO₂-rich) equilibrium at realistic well conditions [1]; and (ii) we applied a molecular dynamics protocol that allows the simultaneous study of the behavior of the aqueous system at interfaces and within confinement between silica surfaces, while the fluid remains in equilibrium with its own bulk at isobaric-isothermal conditions.

[1] L. Vlcek, *et al.*, "Optimized Unlike-pair Interactions for Water-Carbon Dioxide Mixtures described by the SPC/E and EPM2 Models" *Journals of Physical Chemistry B*. In press

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