

Extreme crystal-scale variability of $\delta^{13}\text{C}$ in hydrothermal calcite from Yucca Mountain, Nevada

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Isotopic properties of calcite crystals from open fractures in the vadose zone of the Miocene rhyolitic tuffs of Yucca Mountain, Nevada were studied by means of the GC-IRMS *in situ* technique (analytical spot size from 90 to 300 μm). Systematic decrease in $\delta^{13}\text{C}$ from +7.4 to -9.6 ‰ PDB was documented across the 1.4 mm-thick calcite (+ minor fluorite and opal) crust. Concurrently, $\delta^{18}\text{O}$ increased from -20.6 ‰ PDB at the base to -14.5 ‰ PDB in outer layers of the crust. Multiple profiles allowed us to construct the isotope maps that have portrayed isotope distributions generally consistent with the crystallography of the crust, and hiatus-free growth.

Similar data were obtained on a number of samples from the 8 km-long exploratory tunnel. At early stages of calcite deposition isotope properties seem to be independent of the calcite crystal morphology: "heavy" $\delta^{13}\text{C}$ values of +4 to +8 ‰ PDB were measured in granular, blocky, platelet and bladed varieties of calcite. This suggests that C-isotope properties were controlled by chemistry of fluids and were unaffected by the kinetics of crystal growth. Paragenetically youngest blocky calcite associated with opal invariably has "light" $\delta^{13}\text{C}$ of -5 to -10 ‰ PDB.

Interpretation. Anomalously "heavy" positive $\delta^{13}\text{C}$ at the crystal bases suggests that the oxidized carbon species in early mineral-forming fluid were substantially equilibrated with reduced species (likely, CH_4) and thus become enriched in ^{13}C . The process requires elevated temperatures and high-Eh (reducing) environment ($\log f\text{O}_2 \leq -35$). The inferred environment suggests the deep-seated origin of fluids. With time, the fluid evolved toward the low-Eh parameters, typical of the meteoric waters. The interpretation is supported by the presence in calcite of the low-density (internal pressure close to atmospheric) gas-filled inclusions containing CH_4 and CO_2 (bulk GC analyses) as well as aromatic/cyclic hydrocarbons (tentatively identified by fluorescence under Raman spectrometry). Paleozoic sedimentary carbonates underlying volcanic tuffs of Yucca Mountain and known to have thermal potential for natural gas may have served as a source of hydrocarbons.

Increasing with time $\delta^{18}\text{O}$ values apparently reflect the overall cooling of fluids. The interpretation is supported by fluid inclusion homogenisation temperatures obtained on a large suite of samples (calcite, fluorite, and quartz). The temperatures decrease from ~75-85 °C in early calcite growth zones to < ~30-50 °C in the outer zones.

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Thermodynamic modelling of lithium-bearing aqueous fluids

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Lithium in geological fluids

Lithium can reach high concentrations in fluids of evaporitic, pegmatitic and some metamorphic environments. An estimate of the composition of paleo-fluids in such environments can be obtained from the study of fluid inclusions, but the interpretation of fluid inclusion data requires a complete knowledge of the thermodynamic properties of lithium-bearing aqueous solutions. We present a thermodynamic analysis of the $\text{LiCl-H}_2\text{O}$ and the $\text{NaCl-LiCl-H}_2\text{O}$ systems to high concentration in a wide temperature range down to the eutectics.

Results and discussion

The $\text{H}_2\text{O-LiCl}$ phase diagram is characterised by the existence of 5 salts (anhydrous LiCl and 4 hydrates including respectively 5, 3, 2 and 1 water molecules), and by the low eutectic temperature (199K). We compiled and critically evaluated literature data (more than 450 experimental points) for the $\text{LiCl-H}_2\text{O}$ and for the $\text{NaCl-LiCl-H}_2\text{O}$ systems (fusion of ice and salt solubilities). The thermodynamic properties of LiCl containing solutions were calculated to very high concentrations (up to 30M) using two different models: Pitzer's ion interaction approach and the Mean Spherical Approximation (MSA). Pitzer's model (as parameterised by Holmes and Mesmer, 1983, for LiCl) appears to be limited to concentrations below 11M. Above this limit we used MSA.

We have been able to calculate the water-ice equilibrium constant down to 199K, as well as the solubility products of the various LiCl hydrates. Entropies and standard enthalpies of formation of the various LiCl salts are shown to be correlated with the number of water molecules in the hydrate structure, as already found for example for MgCl_2 and for Na_2CO_3 .

Results for the $\text{Na-Li-Cl-H}_2\text{O}$ system will also be presented.

Conclusions

This work is a first step toward the inclusion of lithium in thermodynamic models of natural solutions to very high concentrations and to very low temperatures.

References

Holmes H. F. and Mesmer R. E. (1983), *J. Phys. Chem.* **87**, 1242-1255.