Solubility of K-feldspar, muscovite and quartz at 0.5-2.5 GPa, 600-700°C with implications for mass transport in the crust

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Aqueous fluids transport and precipitate dissolved silicate components in natural hydrothermal processes throughout the earth's crust. To understand the solubility of significant mineral assemblages over large ranges of P-T, we have employed the diamond-trap technique to investigate aqueous fluids in equilibrium with K-feldspar, muscovite and quartz (KMQ) from 0.5-2.5 GPa and 600-700 °C. Fluids were found to be highly peralkaline (K_2O/Al_2O_3 up to 9, by weight) despite relatively high concentrations of dissolved aluminum (>0.04 mAl at 1 GPa, 700°C) in these fluids, compared to corundum ± kyanite solubility in the absence of alkalis [1].

Over the P-conditions investigated, measured fluid compositions have K:Si=1:3, which is higher than HKF* aqueous speciation calculations predict (extrapolated to the investigated *PT*-conditions, following [2]). Our KMQ solubility data indicate K-Si species are significantly more abundant than aluminous 'feldspar-like' complexes [3].

Further experiments, involving synthesis of quartz-hosted fluid inclusions, were conducted to investigate fluid/melt immiscibility and bracket the wet melting reaction quartz + muscovite + K-feldspar + V = L. Inclusion petrography and microthermometry indicate that the occurrence of (supercritical) melt-fluid miscibility in simplified granitic systems is sensitive to the compositional evolution of the fluid and might actually be encountered upon cooling (and not heating) of the system.

Our experimental results reveal retrograde solubility patterns governing the evolution of residual granitic solutions that may be linked to the possible occurrence of continuous solubility between fluid and melt in peralkaline granitic systems, as Bowen postulated 80 years ago [4]. Moreover, the results indicate paths leading to enhanced mass mobilization in natural fluids at low-temperatures.

[1] Manning (2007) *Geofluids* **7**, 258-269. [2] Manning (1998) *Schweiz. Mineral. Petrogr. Mitt.* **78**, 225-242. [3] Anderson and Burnham (1983) *Am. J. Sci.* **283A**, 283-297. [4] Bowen (1928) *Evolution of Igneous Rocks*.
* HKF, Tanger & Helgeson (1988) *Am. J. Sci.* **288**, 19-98.

'Clumped isotopes' in speleothem carbonate and atmospheric CO_2 – Is there a kinetic isotope effect?

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'Clumped isotopes' data (Δ_{47}) are based on abundance of ^{13}C-^{18}O bonds in the carbonate lattice or CO_2 molecules and reflects the temperature dependent thermodynamic preference of two heavy isotopes to create a chemical bond with each other.

The temperature dependency of Δ_{47} values reflects a thermodynamic equilibrium isotope effect. However, kinetic isotope effect that can disturb this equilibrium has been recognized in the process of CO_2 degassing from aqueous solutions. This presentation will discuss examples of deviation from thermodynamic equilibrium in speleothem carbonates and in atmospheric CO_2.

A modern speleothem from Soreq cave (Israel) showed a deviation of -0.036‰ from that expected at modern-day cave temperature, equivalent to an offset of 8°C. Combined with an observed $\delta^{18}O$ offset from equilibrium with drip water, it is consistent with the kinetic effect that would be expected at the current cave temperature of 18°C. Using this offset to calibrate the observed values in last glacial and Holocene samples gave temperatures that were very close to other, independent, temperature estimates in the region.

In atmospheric CO_2, Δ_{47} seasonal variations were observed to have a larger magnitude and an opposite phase than those expected at equilibrium. Diurnal variations suggested that Δ_{47} associated with ecosystem respiration is significantly different from the equilibrium values, so that seasonal variations reflect a balance between photosynthesis and respiration and Δ_{47} can potentially be used to partition these fluxes.