

Low-temperature melt-fluid miscibility: Experimental evidence for enhanced mass transport in the upper crust by cooling fluids

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Half a century after Tuttle and Bowen's hypothesis [1], we present experimental evidence for extensive fluid-melt miscibility in residual granitic solutions at upper-crustal pressures (P) and temperatures (T) as low as 350° C. We demonstrate that late-stage magmatic-hydrothermal fluids separating from hydrous granitic magmas by boiling can largely increase their solute contents upon cooling, resulting in a fully miscible solution at very low temperatures.

We have characterized the composition of aqueous fluid in equilibrium with quartz, muscovite and K-feldspar at 1.0 GPa and 650 to 700°C and found that high- P granitic fluids are very siliceous and peralkaline, with non-negligible but low aluminum content. Quartz-hosted fluid and melt inclusions were synthesized to investigate the low- T fluid phase relations of such solutions in the quartz-saturated $K_2Si_4O_9$ - SiO_2 - H_2O system. In this system, strongly retrograde solubility behaviour leads to the down- T evolution of low-density aqueous vapors towards high-density melt-like phases.

Lower critical solution phenomena can be explained by a negative excess enthalpy of mixing in K_2O - SiO_2 - H_2O melts at low P and T . Also at low- T , the increasing strength and directional nature of hydrogen bonds and associated silicate polymerization play a vital role in solvent-solute ordering and thus ultimately lead to the onset of supercriticality in peralkaline aqueous-silicate solutions at low- P upon cooling.

Such alkali-silicate aqueous solutions and their phase relations have been underestimated in Earth science literature. Their high solvent power is likely to play an important role in the evolution of many low- PT geological processes, such as the origin of coagulated colloidal silica in geothermal waters and potassic metasomatism associated with granites. Supercriticality is not restricted to the deep Earth, as often thought.

[1] Tuttle & Bowen (1958) *Geol Soc Am Mem* 74.

Effect of humic acid redox status on the sorption of organic pollutants

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Natural organic matter (NOM) is the primary environmental sorbent for many organic pollutants. While their sorption to oxidized NOM has been extensively studied, it is unknown whether NOM-redox status (i.e., quinone/hydroquinone ratio) affects NOM-pollutant interactions. Yet, many contaminated soils, sediments and aquifers contain (partially) reduced NOM. The aim of this work was to test whether NOM-redox status affects organic pollutant sorption. To this end, we studied the sorption of the following test chemicals to oxidized (o-) and reduced (r-) Leonardite Humic Acid (LHA): apolar naphthalene, monopolar acetophenone and quinoline, bipolar β -naphthol, and cationic methyl viologen.

We generated r-LHA from o-LHA by bulk electrolysis with an average of 1040 (± 80) $\mu\text{equiv g}^{-1}$ transferred. None of the tested chemicals showed significant differences in sorption to o-LHA and r-LHA (tested at pH 7 for all non-ionic chemicals and at pH 7, 9, and 11 for methyl viologen). This implied that the organic probe molecules did not experience any differences in the cohesive energies (apolar probe), the H-donor and acceptor properties (mono- and bipolar probes) and numbers of anionic sorption sites (cationic probe) between o-LHA and r-LHA. Yet, when comparing the sorption of all non-ionic compounds relative to a hexadecane reference state in which only van-der-Waals interactions occur, the mono- and bipolar chemicals sorbed more strongly to LHA than apolar naphthalene. This showed that the polar molecules indeed probed for H-donor-acceptor properties of LHA and that these properties were not significantly changed by reduction. Re-oxidation of r-LHA to o-LHA over the course of the experiment could be ruled out as an explanation for the lack of differences as r-LHA reduced the redox-dye dichlorophenol indophenol to the same extent before and after the sorption experiment.

These results indicate that model parameters that describe the sorption of organic pollutants to oxidized NOM may also be applied to reduced NOM.