

## Differentiation of mantle-derived calc-alkaline magmas at mid to lower crustal levels: Experimental and petrologic constraints

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This contribution compares experimentally derived liquid-lines-of-descent on primary, hydrous calc-alkaline magmas ranging from picrobasaltic to basaltic andesite at pressures of 1bar to 15 kbar with geochemical evolutionary trends of contrasting subduction related continental arc systems, namely the Adamello batholith, the Kohistan Arc and the Cascadian Arc system.

Field, petrologic and geochemical data of all three systems are indicative for polybaric crystallization over basically the entire crustal column. This is clearly supported by experimental data that reveal that the majority of basic to intermediate rock compositions are not only close to the liquid line of descent indicating that crystal retention in plutonic systems is not very efficient in basaltic to intermediate magmas, but also that the mean crystallization pressures obtained from oxide-oxide variation diagrams are in the range 5-15 kbar consistent with deep-level (crust-mantle boundary) and intermediate crustal level (15-25 km) magma storage areas where the principal crystallization-driven differentiation took place. In the case of the southern Adamello, subtle differences in the liquid-lines-of-descent are fully consistent with experimental data and trace element geochemistry indicating that different rock suites (plutons) have acquired their major and trace element characteristics at different crustal levels. The principal difference in crystallization-differentiation with increasing depth is the decreasing plagioclase stability leading to delay of the onset of plagioclase crystallization and the enhancement of earlier clinopyroxene, amphibole, and, in the case of the Kohistan arc, garnet, crystallization with increasing depth shifting derivative liquids closer to the metaluminous / peraluminous limit or even within the peraluminous field with increasing pressure, fully consistent with the geochemical evolution of associated granitoid plutonics that partly evolve to peraluminous compositions that cannot be linked to extensive crustal assimilation.

## Nano-scale structure and stability of biogenic Uranium(IV) oxide

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The chemical stability of biogenic U(IV) oxide, a product of environmental bioremediation, is a seminal issue for successful U immobilization. Fundamental differences in particle size and crystal structure with synthetic  $UO_{2+x}$  ( $x \sim 0$ ), such as disorder and hyperstoichiometry ( $0 < x < 0.25$ ), are expected to substantially impact the stability of biogenic  $UO_2$  in groundwater.

Biogenic  $UO_2$  nanoparticles (~3.5 nm diameter) formed by *Shewanella oneidensis* MR-1 both at pH 6.3 and 8.0, were compared to their abiotic analog with respect to local and long-range atomic and nano-scale structures as well as dissolution kinetics under environmentally relevant conditions. Synchrotron-based powder diffraction, X-ray absorption spectroscopy, and transmission electron microscopy provided structural insight. Dissolution rates were quantified by continuous flow-through experiments under anoxic or oxidizing conditions.

The biogenic and synthetic  $UO_2$  exhibited similar equilibrium solubility and the lowest dissolution rates under reducing, near neutral pH conditions. The rates increased logarithmically with decreasing pH. Similar surface area-normalized rates for the two solids suggest similar reactive surface site densities. This finding is consistent with the discovered structural homology of the two solids with the interior of the particles being consistent with an uncompressed fcc lattice, whereas a ~1 nm thick outer zone exhibits local static disorder similar to that in  $UO_{2+x}$ .

The presence of carbonate increased the dissolution rate of biogenic  $UO_2$  almost to the value obtained under oxidizing conditions, and as much greater than that of synthetic  $UO_2$ . Thus, biogenic  $UO_2$  particles are more susceptible to surface oxidation by water and reactive oxidants originating from  $\alpha$ -radiolysis of adjacent water. Even in anoxic aquifers,  $UO_2$  dissolution may be controlled by thermodynamics of surface U(VI) rather than U(IV) phases.