## The link between the Kohistan arc granitoids and processes in the lower Kohistan arc crust

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A long-standing debate circles around the relative importance of assimilation vs high-pressure fractional crystallization in the lower crust to form the upper continental crust. The lack of well exposed deep levels of magmatic arc hampers process in the discussion. A notable exception is the Kohistan arc in NW Pakistan, where the whole crustal sequence of a paleo intra oceanic arc from upper mantle to unmetamorphosed sediments is exposed. These exposures allow studying deep crustal processes. We will present field, geochronological and petrological evidence from the Kohistan arc, which elucidate the relative importance of partial melting and fractional crystallization:

The Kohistan arc is dominated by the voluminous Chilas Complex one of the largest mafic intrusion complex exposed, which intruded during intra arc extension in the deeper level of the arc. Accordingly, intrusion of the Chilas Complex could have provided a favorable environment for granitoid formation by partial melting. U-Pb zircon intrusion ages from I-type granitoids sampled along a crustal transect in the vicinity of the Chilas complex are however, generally younger than the Chilas Complex. The new results indicate, in conjunction with literature data, that granitoid formation in the Kohistan arc was a continuous rather than punctuated process and is not related to the emplacement of voluminous mafic units.

Contrary field relations, petrographic observations and major and trace element compositions of the lower crustal Jijal complex, suggest that hydrous, high-pressure fractional crystallization was a dominant crust-forming process in the Kohistan lower crust, even if there is minor evidence for dehydration melting. A fractionation model is presented that incorporates cumulate and partial melt compositions to explain the Kohistan granitoids. Depending on the parental magma composition, assimilation of few percent of melts derived by low degree of amphibole dehydration melting is a crucial process to explain the silica-rich continental upper crust composition. Additionally, the model shows that assimilation in the lower crust tends to reduce initial compositional differences of parental magma compositions. Therefore, we propose that assimilation in a lower crustal "hot zone" acts as an "equalizer" of magma compositions.

## Molecular modeling of Li speciation in aqueous fluid at high P and T and implications for Li-isotope mineral-fluid fractionation

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Speciation of solutes in aqueous fluids is a key parameter for understanding geologically important processes that involve e.g. the dissolution or precipitation of minerals, geochemical transport via diffusion or electrical conduction in fluid containing rocks. It also affects the fractionation of isotopes between minerals and fluids via differences in the coordination environment of the respective species. However, due to experimental difficulties little is known about the *in situ* molecular structure of aqueous fluids at high pressures and high temperatures corresponding to conditions in the Earth's lower crust and upper mantle.

We use *ab initio* molecular dynamics simulations to study the pressure dependence of the Li speciation in aqueous fluids at a constant temperature of 1000 K. The simulation cell contains 64 water molecules and a single Li<sup>+</sup> ion that is charge compensated by either an F<sup>-</sup> or OH<sup>-</sup> anion. Our simulations show a steady increase in Li coordination with pressure from 3.2 at 0.3 GPa to about 5.0 at 6 GPa. Towards low pressures, association takes place and produces increasingly long-lived LiF complexes. Due to the fast dynamics in the fluid at high temperatures we are able to evaluate the average life time of various complexes and the mean residence time of water molecules in the first hydration shell of the cation. Pressure induced structural changes of the solvent also seem to have an effect on the speciation.

Finally, we will discuss the Li-isotope fractionation between minerals and fluids. Although the pressure dependence of the fractionation coefficient is usually expected to be small, there is experimental evidence that the fractionation behavior depends on the difference between cation coordination in the mineral and in the fluid. Significant pressure effects are only expected in the range where both coordinations are similar. The influence of coordination changes in the fluid on the fractionation is indeed observed in high pressure experiments, which is fully consistent with our simulation results.