Mineral solubilities in aqueous fluids at high pressures and temperatures: New thermodynamic model and implications for mass transfer in the Earth's crust and mantle

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Aqueous fluids are produced by metamorphic devolatilization and magmatic activity in a variety of settings including continental orogens, subduction zones with magmatic arcs as well as oceanic ridges and sea floor. They are responsible for mobility and transport of inorganic and organic solutes as manifested by alteration or veining, distinct element depletion-enrichment patterns or isotopic disturbances. The impact of many fluid-mediated processes is promoted by high time-integrated fluid fluxes, 10^1-10^6 m^3 m^{-2}, inferred for diffuse and focused fluid flow through lithosphere. Previous approaches to aqueous speciation have almost exclusively been based on the Helgeson-Kirkham-Flowers equation of state, which, however, suffers from inaccuracies in the vicinity of critical point of water and cannot be extrapolated to very high temperatures and pressures due to the lack of experimental data on dielectric constant of H_2O.

We propose a new thermodynamic model for dissolution of minerals in aqueous fluids at high temperatures and pressures, which is derived from individual energetic contributions to lattice breakdown, solute hydration and compression of the hydration shell. The thermodynamic properties depend on temperature and H_2O density only and are calculated using three to five model parameters calibrated by experimental data. Our formulation of the density dependence has the advantage of behaving as a smooth function at the critical point of H_2O, it closely corresponds to the generalized Krichevskii parameter, and it linearly correlates with the Born electrostatic energy.

Solubilities of quartz, corundum, rutile, calcite, apatite, fluorite, and portlandite monotonously increase for a given phase by 4-5 orders of magnitude as temperature rises from 200 to 1100 ^{o}C along typical geotherms. At constant pressure, however, mineral solubilities initially increase with rising temperature, but subsequently drop. This effect results from a reversal in isobaric expansivity of the aqueous solvent and it is proportional to the charge of solute species. Oxide minerals such as quartz, corundum and rutile dissolve in pure H_2O as predominantly neutral species. Consequently, their solubility behavior shows little dependence on solvent properties and their retrograde solubilities are limited to pressures below 1.3 kbar. The Ca-bearing phases (calcite, fluorite, apatite and portlandite), by contrast, dissolve to variably charged species, and the electrostriction effects become more significant. The solubilities of these minerals still decrease at medium and high metamorphic grades and over wide range of pressures.

Application of transport theory to our thermodynamic model permits calculation of time-integrated fluid fluxes needed to precipitate mineral veins during metamorphic events. The integrated fluid fluxes along geotherms of 20 and 7 ^{o}C km^{-1} vary from 10^4 to 10^{15} m^3 m^{-2}. Quartz and calcite require the lowest fluid fluxes, and this is in broad agreement with observations of high mobility and veining of these minerals in many metamorphic environments. Conversely, typical integrated fluid fluxes in crustal shear zones predict transfer of quartz and calcite in quantities of several to tens vol. % whereas the mobility of apatite or rutile lies below 1000 ppm. Although less important for the major element metasomatism, such a transfer may substantially affect trace element budget in metasomatized rocks.