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## Fluid fluxes from petrological record: links to mineral-fluid thermodynamics and implications for flow patterns

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Fluid flow through the Earth's lithosphere is an inevitable consequence of fluid production during sediment compaction, prograde metamorphic reactions, and magmatic degassing, in settings ranging from subducting zones, continental crust underplating to shallow magma chambers. In addition, high buoyancy and low viscosity of aqueous fluid in a rock environment make flow universally viable and efficient. Fluids are not preserved in their pathways and much of their evidence including chemical composition is often retrieved from mineral mode, chemical, or isotopic variations. Several important links, advantages and artifacts arising from dimensional consistency and from correlations with mineral-fluid thermodynamics are worthy to revisit.

The magnitude of fluid-rock interaction is measured by the fluid-rock ratio  $(m_{fl}^3 \ m_r^{-3})$  or a time-integrated fluid flux  $(m_{fl}^3 \ m_r^{-2})$ . These two measures differ by  $m_r$ , the characteristic distance of alteration or front propagation, parallel to the flow direction. As a consequence, the fluid-rock ratios depend on spatial relationships between flow direction, temperature- and pressure-gradient orientation, and alteration zone or vein geometry. The reservoir ratios, which are required in mass-balance or phase-equilibrium calculations, can still be unambiguously defined when the above variables are scaled to the flow direction. Gradients in mole amounts of reaction progress or mineral precipitated, n, per unit temperature or pressure are directly related to standard reaction enthalpy and volume, respectively. The effects of pressure are commonly assumed to be negligible. Systematic evaluation of mineral solubilities, however, reveals that (i)  $\partial n/\partial T$  is nearly identical for a variety of phases and from subduction to collisional geotherms but minerals dissolving into charged species exhibit higher solubilities, therefore, yield greater reaction progress and lower fluid fluxes along low-dT/dzgeotherms; (ii) during lateral (isobaric) flow,  $\partial n/\partial T$  are strongly pressure-dependent and have variably positive or negative values at upper crustal conditions, e.g. around magmatic intrusions.

In these approaches, fluid flow was assumed to occur in local equilibrium with host rocks, where fluid-mineral interactions are induced by pressure and temperature gradients only. In an opposite case, fluid is considered to be out of equilibrium with rocks at inflow, thus producing an alteration sequence as the integrated fluid flux increases. These two approaches yield the lower and upper limits of the flux, respectively, which differ by several orders of magnitude. Application to fracture-controlled hydrolytic alteration in the Western Krušné hory pluton in central Europe reveals time-integrated fluid fluxes from  $10^2$  to  $10^6$  m $_{fl}^3$  m $_r^{-2}$ , which covers the plausible range observed globally. Separation of gradient- vs. disequilibrium-driven effects is possible by considering that the reaction progress is greater and mass and volume changes are substantially smaller in the latter case. For a volume-conserved replacement to occur, the fluid fluxes are generally smaller,  $10^{2-3}$  m $_{fl}^3$  m $_r^{-2}$  and require influx of disequilibrium fluids. Therefore, vein-producing fluid fluxes may be several orders of magnitude lower than previously thought, and this implies that the fluid flow in the lithosphere is much more pervasive and distributed. The same petrological record will be produced by alternating periods of episodic flow and stagnant fluid-rock interaction. Such discontinuous flow mechanism is consistent with cycles of transient permeability enhancement and subsequent chemical or mechanical sealing.