

Influences of variable reactivity of calc-silicates on fluid fluxes in contact-metamorphic aureoles

PETER I. NABELEK

Department of Geological Sciences, University of Missouri, Columbia, MO 65211, USA (nabelekp@missouri.edu)

Simulations of fluid flow and mineral reactions

A consequence of pluton emplacement into the upper crust is the generation of metamorphic aureoles and hydrothermal systems. When fluids have multiple components, the production of minerals and fluid flow are coupled. The primary influences on fluid fluxes are fluid-pressure gradients and permeability. In contact aureoles both vary over time as temperatures change, fractures develop, and rock volume changes with reactions. Numerical simulations were conducted to evaluate how differential reactivity of calc-silicate rocks influences fluid fluxes.

The model aureole had subhorizontal calc-silicates with metamorphic minerals in the KCMASHC system interbedded with limestones with minor dolomite plus quartz and metamorphic minerals in the CMSHC system. The potential reactivity of the calc-silicates was significantly larger than that of the limestones. Seventeen reactions were included in calculations. Equations for the transport of heat and H₂O and CO₂ (assumed to be miscible) were solved iteratively. Pluton exsolved H₂O between reaching saturation during crystallization and the solidus. The grid-spacing was 5×1 m. The 1 m vertical spacing reflects the scale of bedding in many contact aureoles. Transient enhancement of permeability was assumed to occur by fracturing when *P*_{fl} exceeded *P*_{lith} and by increase in porosity with decrease in the volume of mineral assemblages during reactions. The potential porosity was 2.5% for limestones and 14.4% for calc-silicates.

Results

Simulations show that the inner aureole stays over-pressured during early stages of metamorphism as CO₂ is produced by mineral reactions and this CO₂ flows away from the pluton down the pressure gradient. High metamorphic fluid pressures initially force flow of magmatic H₂O upward along the contact through fractures and preclude infiltration of the aureole until cessation of diopside-forming reactions. Higher reaction-enhanced permeability in calc-silicates ultimately results >10-fold higher H₂O fluxes than through marbles. Model high-temperature minerals in calc-silicates include wollastonite and diopside whereas in the marbles they are forsterite, diopside and tremolite. The model assemblages correspond to those seen in analogous contact aureoles.

Enhanced dissolution of cinnabar by dissolved organic matter in anoxic solutions

K.L. NAGY^{1*} AND M. KERR^{1,2}

¹Department of Earth and Environmental Sciences, University of Illinois at Chicago, 845 West Taylor St., Chicago, IL 60607 (*correspondence: klnagy@uic.edu)

²Current address: Environmental Protection Agency, 77 West Jackson Blvd., Chicago, IL 60604-3507

Dissolution of cinnabar in the presence of simple quinones (hydroquinone and benzoquinone), selected as models for redox-active components of dissolved organic matter (DOM), and DOM (Suwannee River fulvic (SRFA) and humic (SRHA) acid from the International Humic Substances Society, and 'walnut tea' provided by D. Macalady) was investigated experimentally under anoxic and initially air-equilibrated (oxic) conditions. Cinnabar was prepared as described previously [1] and released mercury concentrations were determined by CVAFS. Batch experiments under anoxic conditions were carried out in amber glass bottles using deionized water sparged initially with high purity Ar (g) and maintained under an Ar (g) atmosphere after addition of cinnabar and the organic reactant. Total released mercury was the sum of the amount in solution at the end of the experiment plus the cumulative amount released as Hg⁰ (g), which was trapped in a second oxidizing solution and sampled with time. Experiments under oxic conditions were carried out either as in [1] or as in the anoxic experiments, but without sparging, and the concentration of dissolved mercury was measured with time. Benzoquinone increased slightly the amount of released mercury compared to the amount in pure water under oxic conditions; whereas at an equivalent ratio of mol quinone to cinnabar mass, hydroquinone had a much larger effect compared to pure water under anoxic conditions. Dissolution rates in units of mol Hg normalized to cinnabar surface area and mass of C were approximately 10, 20, and 50 times faster under anoxic compared to oxic conditions for SRHA, walnut tea, and SRFA, respectively (with oxic dissolution rates in reasonable agreement with those reported in [1]).

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[1] Waples, Nagy, Aiken & Ryan (2005) *Geochimica et Cosmochimica Acta* **69**, 1575–1588.