

## Interpretation of weathering profiles from the Paleo-Proterozoic and present using reactive transport modeling

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Despite the important role that chemical weathering plays in regulating the global CO<sub>2</sub> cycle over geologic time (and perhaps the O<sub>2</sub> cycle in the past), the overall controls on the rate of chemical weathering are still not completely understood. This may be due in part to the fact that mechanistic process models for chemical weathering that incorporate the coupled effects of water flow, transport, erosion, and chemical reactions have not been routinely applied to the interpretation of weathering profiles. Such models can potentially provide the basis for quantifying the relative importance of competing time-dependent effects such as mineral dissolution and solute transport. To provide real interpretive value, however, these models must be compared extensively against actual field examples of weathering. Two such examples are considered here.

The first example involves the leaching of iron in the uppermost portions of a number of Paleo-Proterozoic paleosols. The observation of these Fe-depleted zones has led some workers to suggest that atmospheric O<sub>2</sub> levels in the Archean and Paleo-Proterozoic were significantly lower than they are today. Recent evidence, however, suggests that these Fe-leached zones may be overlain in some cases by an Fe-enriched cap. We use reactive transport modeling to estimate the range of atmospheric O<sub>2</sub> and CO<sub>2</sub> values in the Paleo-Proterozoic that could have generated these both the Fe-enriched cap and underlying Fe-depleted zone.

A second example involves the weathering of corestones in a tropical setting in Costa Rica. Multicomponent reaction-diffusion simulations based on age constraints provided by dating of geomorphic surfaces in the area are used to determine the control(s) (diffusion, surface reaction, or both) on the overall rate of chemical weathering of the corestones.

## The hydrolysis of gold(I) and the formation of chlorogold(I) complexes in hydrothermal solutions to 600 °C and 2 kbar

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A knowledge of the stability of aqueous gold(I) complexes in hydrothermal solutions is essential for quantitative interpretation of the transport and deposition mechanisms of gold by hydrothermal fluids in the Earth's crust. The solubility of gold has been measured in aqueous chloride and chloride free solutions at temperatures to 600°C and pressures to 2 kbar in order to determine the stability and stoichiometry of chloride and hydroxy complexes of gold(I) in hydrothermal solutions. The experiments were carried out in a flow-through system, which approach allowed the determination of the concentrations of all critical aqueous species in solutions independently without disturbing the chemical equilibrium, thus permitting the evaluation of the stability and stoichiometry of the gold(I) complexes. The gold solubilities were in the range  $9.9 \cdot 10^{-9}$  to  $3.3 \cdot 10^{-5}$  mol kg<sup>-1</sup> (0.002-6.5 ppm), in solutions of total dissolved chloride between 0.00 and 1.72 mol kg<sup>-1</sup>, and total dissolved hydrogen between  $4.0 \cdot 10^{-6}$  and  $7.9 \cdot 10^{-4}$  mol kg<sup>-1</sup> and pH<sub>T,p</sub> of 0.6 to 13.9. A non-linear least squares treatment of the data demonstrate that gold dissolves in chloride and chloride free solutions to form AuOH(aq) and AuCl<sub>2</sub><sup>-</sup> where AuOH(aq) dominates in neutral and alkaline chloride and chloride free solutions and AuCl<sub>2</sub><sup>-</sup> in acidic chloride solutions. The solubility constants and the cumulative and stepwise formation constants for the respective species have been calculated to 600°C and 2 kbar. The complex formation at 25°C is characterised by an exothermic enthalpy and positive entropy. With increasing temperature and decreasing pressure, the formation reaction to form AuOH(aq) and AuCl<sub>2</sub><sup>-</sup> become endothermic accompanied with large positive entropy indicating much greater electrostatic interaction between Au<sup>+</sup> and OH<sup>-</sup> and Cl<sup>-</sup>, respectively. The reverse is true with increasing pressure and at 2.0 kbar and 600°C the formation reactions are driven by exothermic enthalpy accompanied with small negative entropy. Gold(I) hydroxy and chloride complexes play an important role in transporting gold in dilute aqueous solutions and aqueous acidic chloride solutions above 400°C, respectively.