

THERMODYNAMIC PREDICTIONS VS MEASURED FLUID CHEMISTRY: LESSONS FROM LOW-TEMPERATURE, SERPENTINIZING FLUIDS. J. Leong, A. Howells, K. Robinson, and E. Shock, GEOPIG, Arizona State University (jmleong@asu.edu), Tempe, AZ

Introduction: Serpentinization occurs across the solar system owing to the ubiquity of ultramafic silicates and the existence of aqueous fluids that can drive alteration [1]. Highly reduced and hyperalkaline fluids seeping from ultramafic bodies on Earth provide analogs for serpentinized fluids on Ocean Worlds such as Europa and Enceladus. These reduced fluids provide energy for many metabolic processes [2] and thus have profound implications for the habitability of water-rock systems, including those of Ocean Worlds [1].

Thermodynamically guided mass-transfer calculations provide insights into fluid/rock reactions that drive the transformation of near-neutral surface fluids (*e.g.*, rain and seawater) into high-pH fluids. However, deviations from predictions will likely occur, especially at low-temperatures where the approach to equilibrium can be sluggish. We compared predicted fluid compositions to actual serpentinizing fluids analyzed from the Samail Ophiolite in Oman and found concentrations of several aqueous species that deviate from predictions. To understand processes that can account for these deviations, we conducted further calculations (*e.g.*, mixing calculations, sensitivity to changes in temperature, dissolved inorganic carbon (DIC) content, mineral solid solutions, and salinity) that can reconcile predicted compositions with actual measurements.

Predicting Hyperalkaline Fluids: We used the speciation-reaction path code, EQ36 [3], to simulate the evolution of rainwater (pH 5.6) as it reacts with ultramafic rocks representative of the Samail Ophiolite at ambient conditions (25°C, 1 bar). The earliest stage of reaction progress is dominated by the dissolution of primary minerals driving increases in pH and concentrations of dissolved species. This results in fluid compositions close to those measured from surface streams and shallow groundwater wells (pH 7-9), suggesting that the compositions of these surficial and shallow subsurficial fluids result from early stages of reaction progress. Further reaction with ultramafic rocks would saturate serpentine, carbonates, and brucite, driving numerous aqueous species to very dilute concentrations. At advanced stages of reaction progress, fluid compositions reach equilibrium with serpentine, brucite and diopside (srp-brc-dp eq). Predicted pH for the srp-brc-dp eq at 25°C is 12.3, which is close to the maximum pH measured from serpentinizing fluids in the Tablelands Ophiolite [4]. However, measured pH in the Oman springs and many other similar continental settings are mostly within the pH range of 11-12. Fur-

thermore, measured Si and Mg concentrations are variable and are higher than those imposed by fluid in equilibrium with serpentine and brucite. Additional calculations show that the deviations between predicted and measured fluid compositions cannot be accounted for by variations in fluid temperature and salinity. Accounting for mineral solid solutions more closely predicts environmental compositions, but does not fully reconcile models with actual measurements.

Reconciling Predictions with Reality:

Influence of DIC. As discharging deep-seated hyperalkaline fluids ascend back to the surface, DIC concentrations can increase due to infiltrating atmospheric CO₂ or contact with carbonate veins in the shallow subsurface. Minor addition of DIC can drive fluid compositions from the srp-brc-dp eq to those in equilibrium with serpentine, brucite, and calcite. Such carbonate-controlled equilibria yield pH and Ca concentrations that are consistent with measured values.

Fluid Mixing. Deep-seated hyperalkaline fluids can also mix with shallow groundwater during upflow. Our calculations show that mixing can account for the variabilities in the Si and Mg measured from discharging hyperalkaline springs. Calculated mixing extents of 0.1-5% shallow subsurficial/surficial influence are consistent with values determined using ³H isotopes [5].

Lessons from Oman: We demonstrated that predicted and measured chemistry of low-temperature serpentinizing fluids can be successfully reconciled using a combination of reaction-path, mixing, and sensitivity calculations. Moreover, our calculations also highlight potential imprints of *shallow* subsurficial processes on the deep-seated signature of discharging hyperalkaline fluids through (1) fluid mixing and (2) addition of DIC. Shallow portions of the fluid pathway could be hotspots for subsurface life which may bloom where reduced deep-seated fluids encounter oxidized shallow aquifer fluids [6]. As systems with contrasting oxidation-reduction potentials meet, habitability will be defined by the extent to which such systems fail to equilibrate abiotically, leaving opportunities for microbial communities to exploit.

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