Shallow subsurface influence on serpentinization: Insights from hyperalkaline springs. J.M. Leong[1], A. Cox[2], V. Debes[1], K. Fecteau[1], A. Howells[1], P. Prapaipong[1], K. Robinson[1], and E. L. Shock[1], [1]GEOPIG, Arizona State University (jmleong@asu.edu), Tempe, AZ, [2] LEGEND, Montana Tech of the University of Montana, Butte, MT

Introduction: Serpentinization occurs across the solar system owing to the ubiquity of ultramafic silicates and the existence of aqueous fluids that can drive alteration [1,2]. The generation of highly reduced fluids during serpentinization has profound implications for the habitability of water-rock systems. H_2-rich and hyperalkaline fluids seeping from ultramafic bodies in continental settings on Earth provide analogs for serpentinized fluids on Mars, Europa and Enceladus. By sampling and analyzing these fluids we can decipher the various reaction paths occurring as a starting fluid (in this case, rainwater) is transformed to a H_2-rich and hyperalkaline solution. Fluid and gas measurements were coupled with thermodynamic calculations to understand the various fluid-mineral controls on the generation of these fluids. Ultimately, these analyses will provide a framework for testing ideas about cycling of volatiles and bio-essential elements during serpentinization and locating where in a serpentinization fluid pathway is most likely to be habitable.

Methods: Fluids were sampled from several streams, springs and wells located in the Samail Ophiolite in Oman, which hosts one of the largest continental exposures of ultramafic rocks on Earth and is considered one of the best natural laboratories to study serpentinization [3]. pH, conductivity, and redox-sensitive species were measured in the field. Fluids and gases were sampled for further chemical (fluid major and trace element chemistry, gas chemistry) and isotopic (water isotope, radiogenic Sr isotope) characterization. Calculations on fluid-mineral equilibria were done using the EQ3/6 speciation-reaction path code [4] and the SUPCRT software package [5] using the latest standard state data from GEOPIG (slop16).

Results: We observed that numerous factors can influence the composition of hyperalkaline fluids such as the type of host rock (peridotite *vs.* gabbro), geological setting of the springs (basal thrust *vs.* inner part of the ophiolite), fluid-mineral equilibria, and influences from the shallow subsurface. This study focuses on the latter two factors.

Controls imposed by fluid-mineral equilibria are evident especially for Si, Mg and Ca. Equilibrium thermodynamic calculations simulating serpentinization predict high-pH fluids controlled by the serpentine-brucite-diopside equilibria. However, we observed that spring chemistry does not coincide with this prediction. For instance, silica measured from peridotite-hosted springs lies between that controlled by serpentine-brucite precipitation and that governed by forsterite dissolution. Brucite seems to buffer the Mg content as it never reaches a value where brucite is undersaturated. Total Ca and dissolved inorganic carbon content are in equilibrium with calcite, an indication that these elements are already controlled by surficial or shallow subsurficial processes. Moreover, a diverging trend in the Na/Cl ratio observed between fluids sampled from surface seeps and those from wells suggests surficial and/or shallow subsurficial modifications. Furthermore, radiogenic Sr isotope ratios ($^{87}Sr/^{86}Sr$) measured from the hyperalkaline fluids reflect values closer to those measured from Oman serpentinized peridotites, carbonate veins, and travertines [6], rocks common in the altered shallow subsurface. We suggest that these shallow subsurficial to surficial influences could have caused a divergence from a deep-seated fluid controlled by the serpentine-brucite-diopside equilibria. Calculations show that this divergence could be brought about if a surfacing deep-seated hyperalkaline fluid mixes with circumneutral shallow groundwater, interacts with altered rocks in the shallow subsurface, or by a combination of these processes.

Hyperalkaline springs are thought to be windows into the deep subsurface. Our study shows and quantifies how much the *shallow* subsurface can influence the deep subsurface signature. Shallow portions of the fluid pathway could be hotspots for subsurface life, which may bloom where deep-seated, reductant-rich hyperalkaline fluids encounter oxidant-rich shallow groundwaters or oxidized and carbonate-rich shallow subsurface lithologies. In these environments where 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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