DIVERSITY IN THE COMPOSITIONS OF FLUIDS GENERATED FROM THE SERPENTINIZATION OF OLIVINE- AND ORTHOPYROXENE-BEARING ROCKS.  J. M. Leong and E. L. Shock, Arizona State University (jmleong@asu.edu)

**Introduction:** The crust is directly involved in the habitability of a planet. Interaction between water and rocks that compose the crust mobilizes nutrients and facilitates the transfer of energy from the lithosphere to the biosphere. On Earth, a pertinent example is when serpentinization of ultramafic rocks yields reduced and alkaline fluids. These reduced fluids support chemotrophic communities [e.g., ref. 1] and the abiotic synthesis of organic compounds [e.g., ref. 2], and thus are attractive for their potential to support life outside our own planet – in ocean worlds in the outer solar system and in exoplanets beyond.

Spectroscopic surveys of stars in the solar neighborhood reveal variabilities in stellar elemental abundance [3, 4]. This diversity could potentially extend to the compositions of the interiors of terrestrial exoplanets [e.g., refs. 5, 6]. Variabilities in the mineral compositions (olivine- vs orthopyroxene-rich) predicted for the upper mantles of exoplanets hosted in stellar systems with differing Mg/Si ratios [6] can lead to varying crustal compositions. Ultimately, aqueous alteration of the crust of terrestrial exoplanets will yield diverse compositions of fluids and gases that can support chemotrophic life as well as contribute to differing atmospheric signatures. This work explores this diversity through simulations of water-rock interactions that involve olivine- and orthopyroxene-bearing igneous rocks of variable compositions.

**Methods:** We used the speciation and reaction path code, EQ3/6 [7], to simulate interactions between water and rock and track the evolution of fluids and minerals as aqueous alteration progresses. We first simulate systems with varying contributions from olivine and orthopyroxene to explore outcomes of the differing Mg/Si compositions of the reacting rocks [8]. To further explore contributions from other rock-forming elements, we then performed simulations involving numerous olivine- and pyroxene-bearing rock types with compositions ranging from what is known from harzburgitic to picritic rocks on Earth. These calculations include a model serpentine solid solution with various Fe$^{3+}$-bearing components as informed by Mössbauer and X-ray absorption spectroscopic measurements [e.g., refs. 9, 10]. Calculations simulate low-temperature conditions (<100°C) pervasive in most of serpentinizing aquifers on Earth, and perhaps in icy ocean worlds in the solar system.

**Results:** Results show that serpentine is stable at most simulated conditions and starting bulk compositions. These results allude to the pervasive occurrence of serpentine as observed in several terrestrial bodies, meteorites, and other planetary materials in our solar system. However, the compositions of fluids and gases arising from the serpentinization of various olivine- and orthopyroxene-bearing rocks differ. Alteration of olivine-rich rocks results in fluids that are more enriched in H$_2$ than those resulting from alteration of orthopyroxene-rich rocks. These predictions corroborate natural observations wherein fluids hosted in olivine-rich rocks are among the most H$_2$-rich and reduced in Earth. All rocks used in the model have similar ferrous iron content (FeO ∼ 10 wt %) and intuitively, similar potentials in generating H$_2$ as its production is tied to the coupled oxidation of Fe$^{2+}$ in rocks and the reduction of H$_2$O to H$_2$. However, redox reactions are also controlled by the abundance of non-redox-sensitive elements. Rocks enriched in Mg (olivine-rich rocks) favor the formation of Fe$^{3+}$-bearing serpentine and magnetite over Fe$^{2+}$-bearing serpentine and talc that are stable in orthopyroxene-rich rocks, and thus dictates how much of the starting iron can be oxidized and the amount of H$_2$ generated. Results of simulations also show a transition of the dominant precipitating secondary phases from serpentine to Fe$^{2+}$-bearing chloride and clay minerals as the reacting rocks become more picritic in composition. As a consequence, alteration of these rocks would result in much less H$_2$ than that resulting from alteration of ultramafic rocks.

**Concluding Thoughts:** Despite variations in rock compositions, all of the examples studied reveal a pattern wherein non-redox sensitive components of rocks (e.g., Mg, Si, Al) dictate the stabilities of Fe-bearing minerals and therefore the redox processes that generate reduced species during aqueous alteration. Fluxes of reduced gas from water-rock interactions could contribute to the compositions of exoplanetary atmospheres. Thus, these simulations can potentially inform future measurements of atmospheric biosignatures. For example, the alteration of the crust of Mg-rich (or olivine-rich) exoplanets would result in large fluxes of H$_2$ that can potentially draw O$_2$ to very low levels. On the other hand, a H$_2$-rich atmosphere would favor CH$_4$ formation, either microbially or abiotically. Aside from redox-sensitive species, calculations also reveal
lithological regimes that lead to contrasting aqueous compositions (e.g., pH, silica activity) and mineralization that can serve as tracers of water-rock interactions during planetary exploration. Ultimately this work provides a framework for exploring the origins of fluid and gas compositions, particularly their redox state, that can result from the varied crustal compositions of various water-bearing terrestrial bodies in the solar system and beyond.

References: