

**PYROXENE DISSOLUTION IN SULFATE AND CHLORIDE BRINES: IMPLICATIONS FOR POST-NOACHIAN AQUEOUS ALTERATION ON MARS** C.M. Phillips-Lander<sup>1</sup>, C. Legett<sup>1</sup>, A.S. Elwood Madden<sup>1</sup>, and M.E. Elwood Madden<sup>1</sup> <sup>1</sup>School of Geology and Geophysics, University of Oklahoma, Norman, OK, USA, (charity.m.lander@ou.edu)

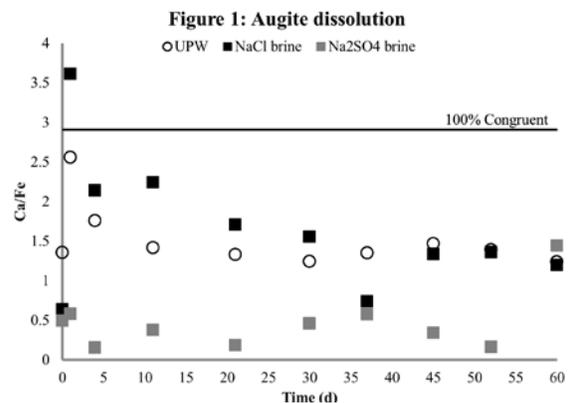
**Introduction:** Pyroxene minerals, which are a common constituent in basalts, have been shown to have similar weathering rates, regardless of changes in mineral composition [1]. In dilute solutions, pyroxene weathering is influenced by pH and temperature [1, 2] and weathers relatively rapidly over geologic time scales compared to many other silicates. Dissolution rates are expected to be highest at low pH, reach a minimum near pH 4-5, and then increase at a lower rate than is observed in acidic solutions as the pH becomes more more alkaline [1, 3]. Despite relatively fast chemical weathering rates under terrestrial conditions, pyroxene grains are detected by OMEGA in dune fields on the surface of Mars, often in association with sulfate minerals [4]. Chloride salts have also been observed in association with Noachian-Hesperian aged weathered deposits [5] and in Martian meteorites [6]. These mineral associations may be indicators of progressive dessication of the post-Noachian Martian surface.

Limited data exists on pyroxene weathering in brines. This knowledge gap handicaps our ability to effectively model the geochemistry of the Martian surface as it evolved from a relatively water-rich hydrologic system to a water-restricted, brine dominated system near the end of the Noachian. This study investigates pyroxene dissolution in post-Noachian analog NaCl and Na<sub>2</sub>SO<sub>4</sub> brines, to determine how pyroxene weathers in high salinity fluids. Previous research on jarosite weathering in brines indicates chloride complexes iron, leading to preferential iron release from the mineral surface during dissolution and the subsequent precipitation of Fe-oxides [6]. Fe rapidly oxidizes during weathering in dilute solutions, resulting in preferential Fe removal from M2 sites in pyroxene and precipitates as Fe-oxides [3]. However, Fe-oxidation rates decrease in high ionic strength solutions, which should reduce brine weathering rates [3, 7]. Fe-oxidation rates also decrease in sulfate versus chloride solutions, which would indicate that mineral lifetimes on Mars should increase if sulfate brines are present [3]. Results from this study will inform models of mineral-water interactions on post-Noachian Mars, which may ultimately affect our assessment of Mars' potential habitability.

**Methods:** A augite sample ((Ca<sub>0.96</sub>, Na<sub>0.04</sub>)(Fe<sub>0.33</sub>, Mg<sub>0.65</sub>, Al<sub>0.01</sub>)(Si<sub>1.9</sub>, Al<sub>0.03</sub>)<sub>2</sub>O<sub>6</sub>) obtained from Wards Scientific (#466474) was characterized using electron

microprobe and BET surface area analysis. Pyroxene was crushed with a mortar and pestle, sonicated to clean mineral surfaces before reaction and dried. Batch experiments were conducted in triplicate with 1g pyroxene/L solution using ultra pure water (UPW) and saturated NaCl (*a<sub>w</sub>*=0.75) and Na<sub>2</sub>SO<sub>4</sub> (*a<sub>w</sub>*=0.15) brines at 25°C [8, 9]. Samples were taken at ~7 day intervals for 60 days and acidified with high purity nitric acid. Cations (Fe and Ca) were determined using flame atomic absorption analysis. Dissolution textures were evaluated in UPW and NaCl using AFM and SEM.

**Dissolution in Dilute Solution:** Pyroxene dissolution in UPW is initially incongruent with Ca:Fe = 2.5 (Figure 1). During this time period, pH increased ~1 pH unit, from 6.5 to 7.5, which corresponds to initial dissolution of pyroxene due to proton attack [7], resulting in initial releases of 1.1x10<sup>-4</sup> M Ca and 2.3x10<sup>-5</sup> M Fe. Over the course of the experiment Fe-release increased, resulting in steady state Ca:Fe ratios of ~1.4 and final Ca and Fe concentrations of 4.8x10<sup>-4</sup> M and 2.8x10<sup>-4</sup> M respectively.



**Dissolution in Brines:** Despite Ca:Fe ratios of 2.9 in the starting material, total molar release of Ca was only ~0% greater than Fe in NaCl brine, with final Ca concentrations of 6.0x10<sup>-4</sup> M and Fe concentrations of 3.6x10<sup>-4</sup> M respectively. Steady state Ca:Fe ratios were similar in NaCl brine (1.3) and UPW (1.4). In contrast, pyroxene dissolution was impeded in Na<sub>2</sub>SO<sub>4</sub> brines, with final Ca concentrations of 1.4x10<sup>-4</sup> M and Fe concentrations of 1.8x10<sup>-4</sup> M. Sulfate stability constants for Ca and Fe are relatively weak in water ( $\beta_{Ca}$ =2.91 v.  $\beta_{Fe}$ =2.25 in water) [10] and expected to decrease in low water activity Na<sub>2</sub>SO<sub>4</sub> brine, therefore little SO<sub>4</sub><sup>2-</sup>

complexation of Ca or Fe is expected to occur. However, gypsum precipitation may account for some reduction in Ca concentrations in solution, and precipitation of secondary sulfate salts may explain the co-occurrence of sulfates, pyroxene, and other silicate grains in dunes on Mars. Future analysis of secondary reaction products is expected to elucidate the weathering processes occurring within brine solutions.

Similar dissolution textures were observed in UPW and NaCl brine samples with AFM and SEM. Both UPW and NaCl brines displayslight etching at particle edges, typical for the incipient formation of “denticles” due to preferential removal of cations along the direction of the silicate chains [11]. Linear features along prismatic surfaces could not be distinguished from cleavage partings observed on unreacted grains.

**Implications for Mars:** Despite decreased water activity in NaCl brines, observed dissolution rates approach those measured in UPW once the reactors reached steady state. In contrast, olivine dissolution rates were observed to decrease by an order of magnitude in NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O brines [12]. Therefore, olivine grain lifetimes may exceed pyroxene in high salinity brines. Moreover, dissolution in in chloride brines results in mobilization of Ca and Fe into solution, which may facilitate the formation of Fe-oxides and silica-rich deposits. These processes may account for the co-association of Cl-enrichments, siliceous rocks, and Fe-oxides near “Home Plate”, Gusev Crater, Mars [4].

In contrast, the co-occurrence of sulfate minerals and pyroxene grains on the Martian surface may be linked to decreased pyroxene dissolution rates in sulfate brines. Decreased dissolution rates in sulfate brines may be due to (1) decreased water activity, (2) precipitation of gypsum, which would remove Ca from solution or (3) decreased Fe-oxidation and removal of Fe from the M2 site [3, 7]. Future analysis of reaction products should further elucidate the pyroxene dissolution process in sulfate brines.

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