

PYROXENE DISSOLUTION RATES IN HIGH SALINITY BRINES: IMPLICATIONS FOR POST-NOACHIAN AQUEOUS ALTERATION ON MARS C.M. Phillips-Lander¹, C. Legett¹, S. R. Parnell¹, A.S. Elwood Madden¹, and M.E. Elwood Madden¹ ¹School of Geology and Geophysics, University of Oklahoma, Norman, OK, USA, (charity.m.lander@ou.edu)

Introduction: 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 [1]. Chloride salts have also been observed in association with Noachian-Hesperian aged weathered deposits [2] and in Martian meteorites [3].

Pyroxene minerals have been shown to have similar weathering rates, regardless of changes in mineral composition [4]. In dilute solutions, pH and temperature influence pyroxene weathering [4, 5]. Dissolution rates are expected to be highest at low pH, reach a minimum near pH 4-5, and then increase more gradually than is observed in acidic solutions as the pH becomes alkaline [4, 6].

This study investigates pyroxene dissolution in near-saturated NaCl, Na₂SO₄, and CaCl₂ brines, to determine how pyroxene weathers in high salinity fluids. Previous research on labradorite weathering in brines indicates sulfate complexes Ca, which enhances weathering in sulfate brines [7]. In contrast, chloride complexes Fe during jarosite weathering, leading to preferential iron release from the mineral surface during dissolution and the subsequent precipitation of Fe-oxides [8]. However, the roles of decreasing water activity and anion complexation remain unknown for chain silicates such as pyroxene. Results from this study will inform models of mineral-water interactions on post-Noachian Mars, which may ultimately affect our assessment of martian surface geochemistry through time and Mars' potential habitability.

Methods: A diopside sample ((Ca_{0.96}, Na_{0.04})(Fe_{0.33}, Mg_{0.65}, Al_{0.01})(Si_{1.9}, Al_{0.03})₂O₆) obtained from Wards Scientific (#466474) was characterized using electron microprobe and BET surface area analysis. Pyroxene was crushed with a mortar and pestle, micronized, sonicated to clean mineral surfaces before reaction and dried. Batch experiments were conducted in triplicate with 1g pyroxene/L solution using 18 MΩ ultra-pure water (UPW) and near-saturated 333 g L⁻¹ NaCl (*a_w*=0.75), 174 g L⁻¹ Na₂SO₄ (*a_w*=0.95) and 1000 g L⁻¹ CaCl₂ (*a_w*=0.35) brines at 25°C [8, 10]. Samples were taken at ~7 day intervals for 60 days and acidified with high purity nitric acid. Cations (Ca, Mg, and Fe) were determined using flame atomic absorption analysis. Dissolved silica in solution was determined with UV-Vis [11].

Aqueous Si data were plotted and fitted with a polynomial trend line. The 1st-derivative of the trend line was used to determine the initial dissolution rate. These rates were normalized using the BET derived

surface area. Diopside mineral lifetimes were calculated using a shrinking sphere model [8,12]:

$$\Delta t = \frac{d}{2 V_m r}$$

where Δt is the lifetime of the particle (sec), d is the diameter of the particle (m; assumed 0.001 m), V_m is the molar volume of the mineral (m³ mol⁻¹), and r is the rate of dissolution (mol m⁻² s⁻¹).

Dissolution in Ultrapure Water: Cation concentrations at the end of the experiment were measured as follows Fe (3.6x10⁻⁴ M), Mg (1.3x10⁻⁴ M) Ca (5.2x10⁻⁴ M), resulting in Ca:Fe+Mg ratios of 4:1 indicating incongruent dissolution. Dissolved Si was measured at 2.3x10⁻⁴ M.

Dissolution in Brines: Dissolution in both NaCl and Na₂SO₄ brines outpaces dissolution in UPW by ~10x, based on average total dissolved Si (1.5x10⁻³ M in NaCl and 1.1x10⁻³ M in Na₂SO₄). Fe was preferentially released in NaCl brines (5.0x10⁻⁴ M, 1.4x10⁻⁴ M in Na₂SO₄). Calcium release is similar in both NaCl (2.4x10⁻³ M) and Na₂SO₄ (2.8x10⁻³ M). In contrast, Na₂SO₄ brines preferentially mobilized Mg (8.7x10⁻⁵ M in NaCl, 5.3x10⁻⁴ M in Na₂SO₄). These data suggest aqueous complexation of Fe by Cl⁻ and Mg by SO₄²⁻ may influence observed dissolution rates [13].

Initial pH for all experiments varied by <1 pH unit in UPW (6.5), NaCl (6.4) and Na₂SO₄ (6.5) brines, and therefore pH differences do not account for increased weathering rates in brine relative to UPW.

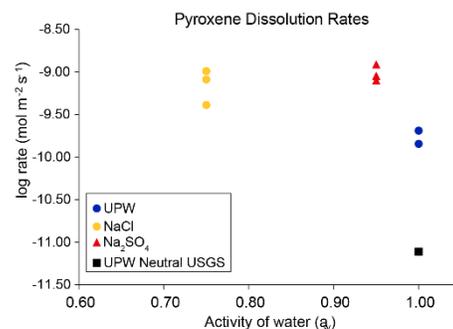


Figure 1: Log surface area normalized initial pyroxene dissolution rates for UPW, Na₂SO₄, and NaCl brines, indicate weathering rates in high salinity brines are ~10x faster than UPW.

Pyroxene Dissolution Rates: BET normalized log initial dissolution rates for UPW were -9.77 ± 0.11 on average, which is nearly an order of magnitude slower than either the NaCl (-9.16 ± 0.07) or Na₂SO₄ (-9.02 ± 0.10) brines (Figure 1). Higher UPW dissolution rates

observed in our experiments compared to dilute rates (~ 11.11) reported by the USGS [15] can be accounted for as the difference between batch (this study) and flow-through (USGS compilation) reactors. CaCl_2 dissolution rates were too slow to measure, as solute concentrations were below detection limits.

Pyroxene Lifetimes in Mars Relevant Brines: In UPW, a 1 mm diameter diopside particle is expected to persist for 117 yr, while NaCl and Na_2SO_4 brines reduce diopside lifetimes to 27 yr and 28 yr respectively.

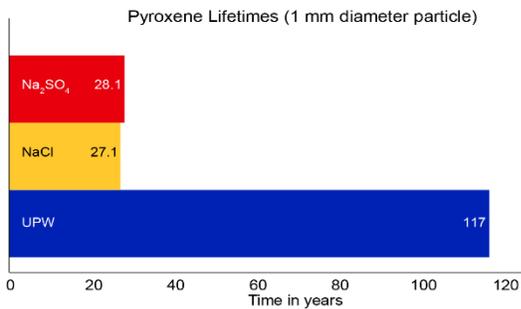


Figure 2: Pyroxene lifetimes in high salinity brines are significantly shorter ($\sim 100x$) than UPW.

Implications for Mars: Pyroxene weathering proceeds rapidly in both NaCl and Na_2SO_4 brines, indicating sustained contact between pyroxene and aqueous brines would result in conversion of pyroxene to secondary weathering products. These findings contrast with forsterite dissolution rates, which were observed to decrease by an order of magnitude in $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ brines [15,16]. This may be explained due to aqueous complexation of Fe by Cl^- and Mg by SO_4^{2-} respectively in pyroxene dissolution. However, the slow pyroxene weathering rates observed in CaCl_2 brines indicate that as salinity continues to increase (and activity of water decreases), slower water exchange at the mineral surface limits weathering [15,16].

Moreover, dissolution in chloride brines results in mobilization of Fe and Si 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 [2]. Ca- and Mg-sulfate veins associated with mudstones in Gale Crater, in contrast, may indicate pyroxene weathering in a sulfate-rich saline system [7, 17, 18].

However, the co-occurrence of sulfate and chloride salts with pyroxene grains on the Martian surface indicates that aqueous alteration was restricted throughout the post-Noachian, as long-term interaction between brines and pyroxene would cause weathering to progress rapidly.

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