

**CAN WE USE PYROXENE WEATHERING TEXTURES TO INTERPRET AQUEOUS ALTERATION CONDITIONS? YES AND NO.** C. M. Phillips-Lander<sup>1</sup>, C. Legett IV<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 are a significant component of SNC meteorites [1,2,3,4]. These meteorites provide a window into Mars' aqueous alteration history. Pyroxene minerals in SNC meteorites typically display weathering textures indicative of aqueous alteration on Mars [1,2,3,4,6,7]. Pyroxene minerals are observed associated with chloride and sulfate salts on the surface Mars [5], suggesting that these anions may play an important role in pyroxene weathering [8,9].

Lab experiments [e.g., 10,11] and field studies [e.g., 12,13,14] of pyroxene weathering demonstrated the progressive development of distinctive dissolution textures: crystallographically controlled etch pits and tooth-shaped 'denticles'. The presence of microdenticles (denticles with lengths of micron-submicron range) on pyroxenes in SNC meteorites have been previously interpreted to result from weathering in extremely undersaturated solutions [4,15]. However, previous meta-analysis of pyroxene dissolution textures reported in the literature suggested that no systematic interpretations relating textures to aqueous conditions can be determined based on quantitative textural analyses of denticle lengths or apical angles [3].

Our previous research on diopside dissolution in brines indicates Na and SO<sub>4</sub> complexes enhance dissolution when the activity of water ( $a_w$ ) > 0.9 [16]. However, our results indicate significantly less dissolution occurred in near-saturated NaCl and CaCl<sub>2</sub> brines. This study qualitatively and quantitatively examines diopside dissolution textures and the formation of alteration minerals and textures in ultrapure water (UPW), dilute 0.35 M NaCl and Na<sub>2</sub>SO<sub>4</sub>, 2M NaClO<sub>4</sub>, and near-saturated 1.7M Na<sub>2</sub>SO<sub>4</sub>, 3M NaCl, and 4.5M CaCl<sub>2</sub> brines, in order to determine whether pyroxene dissolution varies systematically with activity of water.

**Methods:** A diopside 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. Diopside was coarsely crushed to a ~2-4 mm size fraction, sonicated and washed to clean mineral surfaces prior to reaction, and air-dried. Batch experiments were conducted with 1g pyroxene/L solution using 18 MΩ ultra-pure water (UPW), 0.35M NaCl brine ( $a_w$ =0.99), 0.35M Na<sub>2</sub>SO<sub>4</sub> ( $a_w$ =0.98), 2M NaClO<sub>4</sub> brine ( $a_w$ =0.93) and near-saturated 1.7M Na<sub>2</sub>SO<sub>4</sub> ( $a_w$ =0.95), 3M NaCl ( $a_w$ =0.75), and 4.5M CaCl<sub>2</sub> ( $a_w$ =0.35) brines at 25°C. All batch reactors were placed on a shaker table operating at 60 rpm for 60 days. Upon completion of the experiment, we retrieved the diopside chips from solution via filtration. We rinsed the reacted diopside chips three times in 18 MΩ water and air-dried the samples.

Chips from each experimental condition were then placed on SEM stubs and iridium coated for imaging analysis on the Zeiss NEON 40 EsB at the University of Oklahoma's Sam Noble Microscopy Laboratory.

SEM images were taken at a variety of scales from 10 μm to 100 nm to evaluate mineral weathering textures (including denticles) and secondary alteration minerals. Qualitative assessment was conducted by ranking the degree of dissolution based on formation of etch pits and denticles, as well as the percent coverage of secondary minerals. This data was tabulated and used to qualitatively assess weathering assessment for each experimental condition.

Microdenticle length and apical angles formed during dissolution were quantified using ImageJ. We used at least 5 SEM images containing visible denticles from each experimental condition. Dissolution textures were evaluated in comparison with surface textures observed in unreacted control samples. The results from qualitative and quantitative assessments of diopside weathering were compared to previously determined aqueous dissolution rates [16].

**Results:** Qualitative assessment of etch pit density on diopside surfaces indicates the greatest degree of alteration was observed in 0.35M NaCl, where clay minerals cover weathered pyroxene surfaces in some areas and most pyroxene surfaces display significant dissolution and denticle formation. Dissolution is less pervasive in the other dilute (UPW, 0.35M Na<sub>2</sub>SO<sub>4</sub>) solutions with high activity of water (>0.95) and in near-saturated CaCl<sub>2</sub> brines with low activities of water (0.35). Both UPW and dilute Na<sub>2</sub>SO<sub>4</sub> appear less dissolved than 0.35 M NaCl, as is also observed in our quantitative aqueous rate determinations based on solute measurements [16]. Dissolution in 2 M NaClO<sub>4</sub> is similar to UPW and dilute Na<sub>2</sub>SO<sub>4</sub>, however the extent of clay coverage is similar to dilute NaCl. Concentrated (1.7M) Na<sub>2</sub>SO<sub>4</sub> appears more weathered than UPW and dilute Na<sub>2</sub>SO<sub>4</sub>, which is also observed in our aqueous rate data [16]. Large denticles comprised of smaller denticles typify dissolution in 3M NaCl. Both clay minerals and SiO<sub>2</sub> spherules are detected in concentrated NaCl, which may explain the variability in aqueous rate measurements in this solution [16]. Minimal dissolution was observed in near-saturated CaCl<sub>2</sub>, including only a few chains of etch pits on mineral surfaces and limited alteration of the pyroxene surface to clay. Together these data suggest that  $a_w$  does not solely control pyroxene dissolution, as the highest degrees of alteration were observed in 0.35M NaCl and

1.7M Na<sub>2</sub>SO<sub>4</sub>, while pyroxene reacted in both more dilute (UPW and 0.35M Na<sub>2</sub>SO<sub>4</sub>) and more saturated (3M NaCl and 4.5M CaCl<sub>2</sub>) solutions appeared less altered.

Clay textures observed in all weathering experiments are similar to those previously observed in SNC meteorites [7,11]. Clay minerals are commonly observed in etch pits, while, on other surfaces, denticles appear to be transforming to clay in situ. Therefore, while clays are useful for the assessment of weathering extent, their textures are not specifically related to aqueous solution composition or activity of water.

Microdenticles were detected in all samples, indicating they form in a wide range of aqueous alteration conditions. This contrasts with previous research that indicated microdenticles form predominantly in undersaturated solutions [4,14]. Denticle length did not vary systematically with decreasing activity of water. This suggests that no empirical relationship exists between denticle length and diopside aqueous alteration histories.

Median apparent apical angle measurements indicate that apical angles are similar in UPW, 2M NaClO<sub>4</sub>, 0.35M Na<sub>2</sub>SO<sub>4</sub>, and 4.5M CaCl<sub>2</sub> ranging from 18.1–23.5. However, apparent apical angles were significantly smaller in 0.35M NaCl (9.5°) and 1.7M Na<sub>2</sub>SO<sub>4</sub> (11.1°), which likely reflects the rapid dissolution occurring in these brines [15]. Apparent apical angles are significantly larger (42.4°) in 3M NaCl. These data suggest that apparent apical angles are similar in both high and very low a<sub>w</sub> solutions, which limits their utility as a weathering indicator.

**Discussion and Implications for Mars:** Qualitative weathering analyses can provide additional context to aqueous dissolution data. Textural analyses confirmed minimal dissolution occurred in CaCl<sub>2</sub> brine (a<sub>w</sub>=0.35). We were unable to measure solute-based dissolution rates in NaClO<sub>4</sub> brines due to analytical constraints; however, textural analysis demonstrated NaClO<sub>4</sub> (a<sub>w</sub>=0.93) dissolution rates are relatively fast, similar to other high a<sub>w</sub> (>0.9) solutions. Considering all solutions investigated in this study, general textural analysis accurately reflects the solute-based dissolution rates derived for pyroxene and may provide an effective means to rank the extent of aqueous alteration on Mars where the aqueous alteration environment is likely unknown.

High salinity 3M NaCl Si-based dissolution rates were challenging to interpret due to highly variable Si<sub>aq</sub> concentrations [16]. Si-spherules observed in high salinity NaCl brines likely accounts for this variability and results from the “salting out” of Si as chloride concentration increases [16, 17]. This process may account for the co-association of Cl-enrichments and siliceous rocks near “Home Plate”, Gusev Crater, Mars [18]. In con-

trast, Ca- and Mg-sulfate veins associated with mudstones in Gale Crater may have formed due to pyroxene weathering in a sulfate-rich saline system [19,20].

While qualitative weathering assessments were useful for interpreting extent of weathering and supported aqueous dissolution rates, quantitative analysis of pyroxene denticle characteristics yielded overlapping data over a wide range of solution chemistry and water activity even when the mineralogy was identical. Thus, denticle length and apparent apical angle are not indicative of alteration environment. Results of these experiments examining pyroxene weathering textures under varying aqueous conditions support Velbel and Losiak’s previous assessment of denticle apical angles from natural systems, which also concluded that qualitative assessments of denticle length and angle vary significantly, but indiscriminately across a wide range of weathering conditions [3]. Therefore, aqueous alteration conditions cannot be differentiated from unknown samples based on apical angle and denticle length. Based on the results of this study, combined with previous work, we recommend abandoning quantitative analysis of pyroxene minerals as a means of determining aqueous alteration conditions.

**References:** [1] Meyer (2005) Mars Meteorite Compendium, 2<sup>nd</sup> Ed. [2] Treiman (2005) *Chemie der Erde*, 65, 203–270. [3] Velbel and Losiak (2010) *JSR*, 80, 771–780. [4] Velbel (2012) *Sedimentary Geology of Mars*, 102, 97–117. [5] Bibring et al. (2006) *Science*, 312, 400–404. [6] Ling and Wang (2015) *JGR Planets*, 120, 1141–1159. [7] Wentworth et al. (2005) *Icarus*, 174, 383–395. [8] Squyres et al. (2004) *Science*, 306, 1709–1714. [9] Haskin et al. (2005) *Nature*, 436, 66–59. [10] Berner et al. (1980) *Science*, 207, 1205–1206. [11] Velbel and Barker (2008) *Clay and Clay Min.*, 56, 112–127. [12] Berner and Schott (1982) *Am. J. Sci.*, 282, 1214–1231. [13] Creameens et al. (1992) *GCA*, 56, 3423–3434. [14] Phillips-Lander et al. (2014) *Geomicro. J.*, 31, 23–41. [15] Velbel (2011) *Applied Geochem.*, 26, 1594–1596. [16] Phillips-Lander et al. (2016) *LPSC Abstract #1313*. [17] Tanaka and Takahashi (2005) *J. of Soln. Chem.*, 34, 617–631. [18] Squyres et al. (2008) *Science*, 320, 1063–1067. [19] Grotzinger et al. (2015) *Science*, 343, 5–14. [20] Nachon et al. (2014) *JGR Planets*, 119, 1991–2016.

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