Can we use pyroxene weathering textures to interpret aqueous alteration conditions? Yes and No.

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Abstract
Pyroxene minerals are a significant component of Shergottite-Nakhlate-Chassignite (SNC) meteorites (e.g., Velbel, 2012) and detected across large areas of Mars’ surface (e.g., Mustard, 2005). These minerals are associated with chloride, sulfate, and perchlorate salts that may represent briny waters present in Mars’ history. Previous textural analyses by Velbel and Losiak (2010) comparing pyroxenes and amphiboles from a variety of natural weathering environments showed no correlation between apparent apical angles (describing the morphology of denticular weathering textures) and mineralogy or aqueous alteration history in relatively dilute solutions. However, high salinity brines preferentially dissolve surface species, potentially leading to different textures dependent on the brine chemistry. In this study, we performed controlled pyroxene dissolution experiments in the laboratory on a well-characterized diopside to determine if aqueous alteration in different high salinity brines, representative of potential weathering fluids on Mars, produce unique textural signatures.

Following two months of dissolution in batch reactors, we observed denticles on etch pit margins and pyroxene chip boundaries in all of the solutions investigated: ultrapure water (18 MΩ cm\(^{-1}\); \(a_{\text{H}_2\text{O}}=1\)); low-salinity solutions containing 0.35 M NaCl (\(a_{\text{H}_2\text{O}}=0.99\)), 0.35 M Na\(_2\)SO\(_4\) (\(a_{\text{H}_2\text{O}}=0.98\)) and 2 M NaClO\(_4\) (\(a_{\text{H}_2\text{O}}=0.9\)); and near-saturated brines containing 1.7 M...
Na$_2$SO$_4$ ($a$H$_2$O=0.95), 3 M NaCl ($a$H$_2$O=0.75), and 4.5 M CaCl$_2$ ($a$H$_2$O=0.35). No systematic change in denticle length or apical angle was observed between any of the solutions investigated, even when altered in brines with significantly different salinity, activity of water, and anion composition. Based on these and previous results from natural systems, apical angle measurements are not a useful proxy for determining the extent or nature of aqueous alteration. However, since denticles form relatively slowly during weathering at circum-neutral pH, denticle length may be a useful proxy for chemical weathering duration. All of the experimental solutions produced median denticle lengths $\leq 1$ $\mu$m, likely due to the brief weathering experiments. However, perchlorate brines produced a significantly wider range of denticle lengths than those observed in all the other experimental solutions tested. Since perchlorate is likely a common constituent in martian soils (Glotch et al., 2016), denticle length measurements should be used cautiously as proxies for extent of aqueous alteration on Mars, particularly in samples which also contain perchlorate.

Key Words
weathering texture, pyroxene, denticles, apical angles, Mars, perchlorate, brines

Introduction
Interpreting the history of aqueous alteration on Mars relies on chemical, mineralogical, and textural clues recorded in rocks and minerals. Nano- to microscale textural features on primary rock-forming minerals frequently contribute to interpretations of mineral-fluid interactions in terrestrial samples (e.g., Hochella and Banfield, 1995). However, micro/nano-scale textural analyses of minerals from Mars remain mostly limited to observations of SNC meteorites. Pyroxene minerals are a significant component of SNC meteorites (McSween, 1994; Trieman, 2005; Velbel and Losiak, 2010; Velbel, 2012), indicative of their abundance in the martian crust.
They typically display indicators of weathering formed through aqueous alteration on Mars (Trieman, 2005; Velbel, 2012; Ling and Wang, 2015), including the formation of secondary clay minerals and Fe-oxides (Trieman et al., 1993; Ling and Wang, 2015) and dissolution textures on primary mineral phases. For example, jarosite, hematite, cristobalite, and iddingsite are observed in veins in the Miller Range meteorite MIL 03346 (Ling and Wang, 2015). In addition, denticles formed during pyroxene dissolution have been observed in the Allen Hills meteorite ALH 84001 (Thomas-Keptra et al., 2009; Velbel, 2012). Pre-terrestrial alteration in these meteorites has been established using cross-cutting relationships including impact-related features overprinting alteration textures and minerals, as well as weathering features predating the fusion crust (Gooding et al., 1988; Velbel, 2011).

In addition to alteration textures, salts are observed in SNC meteorites (Wentworth and Gooding, 1994; Velbel, 2012). Perchlorate salts were observed in Mars meteorite EETA 9001 (Kounaves et al., 2014). Sulfates, including gypsum, anhydrite, and epsomite, as well as chlorides, including halite, are common secondary minerals in SNC meteorites (Trieman, 1985; Gooding et al., 1988; Chatzitheodoridis and Turner, 1990; Gooding et al., 1991; Treiman et al., 1993; Wentworth and Gooding, 1994, 2005; Bridges and Grady, 1999, 2000; Bridges et al., 2001; Lee et al., 2013; Ling and Wang, 2015). These salts occur as coatings on fracture surfaces and as discontinuous veins in primary minerals, including pyroxene, in Chassigny (Wentworth and Gooding, 1994) and MIL 03346 (Ling and Wang, 2015). Sulfate salts and jarosite also occur along grain boundaries in MIL 03346 (Ling and Wang, 2015) and sulfate salts (gypsum, basanite, epsomite) and halite are intergrown with smectite in Nakhla (Gooding et al., 1991). Significant S and Cl are adsorbed to secondary clays and Fe-oxides in Lafayette (Trieman et al., 1993). The presence of these salts associated with secondary minerals in SNC meteorites
provides evidence of episodic weathering in saline waters on or near Mars’ surface (Trieman et al., 1993; McSween, 1994).

During chemical weathering, surface textures form on silicate minerals as a result of mineral dissolution (Berner et al., 1980; Velbel and Losiak, 2010). In most cases, the rate of silicate dissolution is controlled by chemical reactions at the mineral/solution interface (Berner, 1978), producing dissolution textures related to both mineral chemistry/structure and solution chemistry (Hochella and Banfield, 1995). Laboratory experiments (e.g., Berner et al., 1980) and field studies (e.g., Berner et al., 1980; Berner and Schott, 1982; Cremeens et al., 1992; Velbel and Barker, 2008; Phillips-Lander et al., 2014) of pyroxene weathering demonstrated the progressive development of distinctive dissolution textures, including lenticular etch pits lined with “hacksaw” or “sawtoothed” terminations called denticles. These surface weathering textures can be modified during transport and diagenesis; however, they may also be preserved through weathering, transportation, deposition, and cementation (Stieglitz and Rothwell 1978; Velbel, 2007; Velbel et al. 2007; Velbel and Losiak, 2010). Preservation of surface weathering textures may aid in the interpretation of aqueous alteration histories (Berner and Schott, 1982; Velbel, 2007; Andó et al. 2012).

Field-studies initially focused on etch pit sizes, morphologies, and distributions to understand the factors that influence mineral dissolution (Berner et al., 1980; Berner and Schott, 1982; Brantley et al., 1986; Cremeens et al., 1992; Brantley et al., 1993; MacInnis and Brantley, 1993; White and Brantley, 2003). Berner et al. (1980) demonstrated surface dissolution textures are primarily crystallographically controlled because textures observed from field studies were replicated in laboratory weathering experiments conducted under a wide range of pH and temperature conditions. However, individual etch pits observed in field-based studies are
generally larger than those observed in laboratory studies (Berner and Schott, 1982). Also, denticles are commonly observed in field-weathered chain silicates (e.g., Berner et al., 1980; Berner and Schott, 1982; Cremeens et al., 1992; Velbel and Barker, 2008; Phillips-Lander et al., 2014) but were only observed in laboratory-based dissolution experiments at elevated temperature (50-90 °C) and low pH (≤4) (Brantley and Chen, 1995; Chen and Brantley, 1998). Denticles likely only form in those experiments where alteration was accelerated due to temperature and pH effects since experiments are typically brief in duration (30 days). At neutral pH and low temperatures experiments with durations of ≤30 days, the extent of weathering may not have been sufficient to produce denticles due to slow pyroxene dissolution rates (Velbel, 2007). Therefore, previous short-term laboratory dissolution experiments suggest denticle formation correlates with extent of chemical weathering.

The correlation between denticle length and extent of chemical weathering has been further demonstrated in field studies examining amphiboles from a variety of glacial and periglacial systems (e.g., Hall and Michaud, 1988; Argast, 1991; Hall and Horn, 1993; Mikesell et al., 2004; Schatzel et al., 2006). Amphibole and pyroxene group minerals exhibit similar denticular dissolution textures in response to similar weathering conditions (Velbel, 2007). Dentine lengths decrease logarithmically with increasing depth in weathered soil profiles, which correlates with sediment age and degree of soil development (Hall and Michaud, 1988; Argast, 1991; Hall and Horn, 1993; Mikesell et al., 2004; Schatzel et al., 2006). However, these measurements only provide a relative indicator of weathering, as sediment size, mean annual precipitation, reactive fluid chemistry, and organic acids influence surface texture development in pyroxenes and amphiboles (Hall and Horn, 1993; Schaetzl et al., 2006). In addition to denticle lengths, the presence of microdenticles, denticles ≤1 μm in length observed on the surfaces of larger
denticles, have been previously interpreted as forming in low temperature solutions undersaturated with respect to pyroxene and amphibole (Velbel, 2011) or acidic solution conditions (Brantley et al., 1993). Therefore, microdenticles on pyroxenes in ALH 84001 may have formed during weathering in similar solutions (Velbel, 2012).

Based on these previous terrestrial studies, Velbel and Losiak (2010) examined whether SEM analysis, including quantitative measurements of denticle apparent apical angle (i.e. the angle subtended by a pair of denticle surfaces) could be used to determine the mineralogy of weathered grains and/or the weathering conditions that produced the observed morphologies. They sought to determine whether surface weathering textures on individual grains, like grain surface textures observed using atomic force microscopy (AFM) at the Phoenix landing site (Hecht et al., 2009), could be used to understand pyroxene weathering textures on another planetary body where both the mineralogy and aqueous alteration history may be unknown. Their results indicated denticle apical angles varied significantly, but apparently randomly, between mineral compositions (i.e. augite v. diopside), weathering conditions, and even different silicates (amphibole v. pyroxene) from the same terrestrially weathered rock unit, yielding no unique determining characteristics based on quantitative analysis of weathering textures. However, this survey of weathering textures was subject to the complications of studying natural pyroxenes from several localities that were influenced by several variables (mineralogy, solution chemistry, contact time with reactive solutions, temperature, saturation state, etc.) that may have affected denticle formation.

In order to reduce potential variability in textural weathering observations and measurements and extend the range of textural observations to brines, we conducted a series of experiments in which we reacted a diopside of known composition with different Mars-representative weathering solutions. A range of pyroxene compositions are common on the surface of Mars,
including diopside (e.g., Mustard, 2005). Previous studies of mineral weathering in Mars-
representative solutions have demonstrated solution chemistry (Elwood Madden et al., 2012;
Phillips-Lander et al., 2016; Parnell et al., 2016) and activity of water (Pritchett et al., 2012;
Legett et al., 2014; Olson et al., 2015; Miller et al., 2016; Parnell et al., 2016; Steiner et al.,
2016) influence mineral dissolution rates. We sought to determine if pyroxene dissolution in
brine solutions with different activities of water and solution chemistries would result in
quantifiable differences in denticle length and/or apparent apical angles. In other words, we seek
to determine whether diopside weathering textures vary in a systematic way during low-
temperature aqueous alteration. The results of this study will inform interpretations of pyroxene
weathering textures in meteorites and future studies of samples returned from Mars.

Methods

Pyroxene Characterization

We obtained a sample of diopside (Ca$_{0.96}$,Na$_{0.04}$,Fe$_{0.32}$,Mg$_{0.65}$,Al$_{0.04}$)Si$_{1.9}$O$_{6}$, a Ca-rich
pyroxene, from Wards Scientific (#466474). Bulk geochemistry was determined using energy-
dispersive X-ray spectroscopy (EDXA) in a Cameca SX-50 electron microprobe (EMPA)
operated at 20 kV and 10 nA, analyzing 160 x 160 μm areas (Supplemental Table 1).

Dissolution Experiments and Textural Analysis

After EMPA analysis, we coarsely crushed the diopside to ~2-4 mm chips. Resulting mineral
chips were sonicated, rinsed, and air-dried. We conducted batch dissolution experiments at 22 °C
and 1 atm using diopside chips added to solution at a ratio of 1 g pyroxene L$^{-1}$ solution. Pyroxene
was reacted with solutions with varying chemistry and salinity: 18 MΩ cm$^{-1}$ ultrapure water
(UPW) that has an activity of water ($a$H$_2$O=1); low-salinity solutions containing 0.35 M NaCl
($a$H$_2$O=0.99), 0.35 M Na$_2$SO$_4$ ($a$H$_2$O=0.98), and 2 M NaClO$_4$ ($a$H$_2$O=0.9); and near-saturated
brines containing 1.7 M Na$_2$SO$_4$ ($a$H$_2$O=0.95), 3 M NaCl ($a$H$_2$O=0.75), and 4.5 M CaCl$_2$ ($a$H$_2$O=0.35). We mixed the samples at 120 rpm on a shaker table over 60 days. These solutions were chosen to examine whether denticle length or apparent apical angle vary systematically with either changes in solution chemistry between dilute (0.35 M) and near-saturated (1.7 M Na$_2$SO$_4$ or 3 M NaCl) brines or decreasing activity of water.

At the end of the experiment, we filtered the contents of the reactor to retrieve the diopside chips, then rinsed the reacted diopside chips three times in 18 MΩ cm$^{-1}$ water and air-dried the samples. Chips from each experimental condition, including unreacted controls, were then placed on Al pin stubs in random orientations with carbon tape and iridium coated for imaging analysis on the Zeiss NEON 40EsB field-emission scanning electron microscope (SEM) at the University of Oklahoma’s Sam Noble Microscopy Laboratory. Images were collected at 15 kV and ~50 pA beam current with a vacuum of ~4x10$^{-6}$ torr using both in-lens and Everhart-Thornley secondary electron detectors.

We took SEM images at scales ranging from 100 nm to 10 µm in order to evaluate mineral weathering textures, including microdenticles. SEM images were imported into ImageJ (Schneider et al., 2012), an open source imaging software program, which has the capability to measure both denticle length and apparent denticle apical angles formed during dissolution. We measured denticle lengths from the initial parting on the mineral surface to the tip of the denticle (Figure 1A). Dentine lengths may be considered minimum values, due to the possibility that in some cases the base of a denticle is obscured by an overlapping denticle. We estimated our measurement precision based on measuring the same denticle three times to be ±0.13 µm. We also measured apparent apical angles using the angle measurement tool, which drops anchor points on each side of the denticle and at the tip. The precision of our apparent apical angle
measurements (1.3 °) was determined by measuring the same apical angle three times for a single
denticle. The number of images with etch pits and denticles was controlled by the degree of
dissolution of the mineral surface. However, we aimed to quantify denticles from a minimum of
five images per solution condition, including all visually distinguishable denticles in each image.
Statistical analysis of denticle measurements was performed by constructing box and whisker
plots. The number of denticle measurements and the boundary of each interquartile range is
presented in Table 1. We compared denticle lengths and apparent apical angles observed on
diopside surfaces in order to determine how these data vary with changes in fluid chemistry and
activity of water, which have been previously demonstrated to influence mineral dissolution
rates.

**Results**

Denticles are present along etch pit margins on diopside surfaces weathered under all
experimental conditions, with the exception of unreacted grains (Figure 1). Median denticle
lengths are approximately ≤1 μm; however, denticle length did not vary systematically with
decreasing activity of water (Table 1; Figure 2A). Denticle lengths in UPW (\(a_{H_2O}=1\)), 1.7 M
\(Na_2SO_4 (a_{H_2O}=0.95)\), and 2 M \(NaClO_4 (a_{H_2O}=0.93)\) are all very similar, with median lengths of
0.67-1.0 μm. However, the range (0.18-5.93 μm) of denticle lengths in 2 M \(NaClO_4\) is
significantly larger than the range of denticle lengths observed in all other experimental samples
(0.1-2.94 μm; Table 1; Figure 2A). Slightly shorter median denticle lengths were observed in
0.35 M \(NaCl (a_{H_2O}=0.99)\) and 4.5 M \(CaCl_2 (a_{H_2O}=0.35)\) with denticle lengths of 0.50 and 0.59
μm respectively. The shortest denticles were observed in 0.35 M \(Na_2SO_4 (a_{H_2O}=0.98)\) and 3 M
\(NaCl (a_{H_2O}=0.75)\) with median lengths of 0.14 and 0.36 μm respectively. Microdenticles
Median apparent apical angle measurements in UPW, 0.35 M Na$_2$SO$_4$, 2 M NaClO$_4$, and 4.5 M CaCl$_2$ range from 18.1 to 23.5º (Table 1; Figure 2B). However, apparent apical angles were significantly smaller in 0.35 M NaCl (9.5º) and 1.7 M Na$_2$SO$_4$ (11.1º). The range of apical angles (up to 40º) overlaps for experimental solutions with activities of water >0.9 (Figure 2B). Apparent apical angles are larger (42.4º) in 3 M NaCl. The range of apical angles for diopside chips weathered in near-saturated NaCl and CaCl$_2$ brines are greater than the range for more dilute solutions, if outlier data points are not considered (Figure 2B).

Discussion

Activity of water and weathering textures

Velbel and Losiak (2010) surveyed denticle apical angles of both amphiboles and pyroxenes with varying weathering histories to determine whether the mineralogy and alteration history of an unknown grain, like one imaged on Mars’ surface by the Phoenix lander (Hecht et al., 2009), could be obtained. Their study demonstrated apparent apical angles were not diagnostic of grain composition (Velbel and Losiak, 2010). Our research extends Velbel and Losiak’s (2010) work and demonstrates apparent apical angle also does not change systematically with activity of water. Median apparent apical angles, with the exception of those measured on diopside grains reacted with 3 M NaCl, overlap and have similar average values (Figure 2B).

Measured median denticle lengths in our study are also similar, with <1 μm difference in average values between experimental trials (Figure 2A), indicating activity of water also does not systematically influence denticle lengths. For example, our 0.35 M Na$_2$SO$_4$ ($a$H$_2$O=0.98) and 3 M NaCl ($a$H$_2$O=0.75) had the smallest median denticle lengths, but vary significantly in activity
of water (Figure 2A). In addition, while median denticle length decreased slightly with
decreasing activity of water in NaCl brines, the opposite trend was observed in NaSO₄ brines.
Therefore, our data indicate even when the parent material is well-constrained, neither denticle
length nor apparent apical angle are indicative of the activity of water of the weathering solution,
as similar denticle lengths and apparent apical angles can be formed under very different aqueous
alteration conditions.

Anion chemistry and weathering textures

In order to further clarify and distinguish the potential effects of different anions on denticle
formation, length, and apparent apical angles, we compared results of sodium chloride and
sodium sulfate experiments at different salt concentrations: low salinity (0.35 M) and near-
saturated brines (3 M NaCl and 1.7 M Na₂SO₄). We observed clear differences in the trends
between these two sets of solutions with different anion chemistries; however, overall quartile
ranges for the quantitative measurements overlap. In NaCl brines, median denticle lengths
decrease slightly (from 0.50 to 0.36 μm) and apical angles increase significantly (9.5 to 42.4º)
with increasing chloride salt concentration. However, the opposite trend is observed with
increasing concentration in Na₂SO₄ brines, where median denticle lengths increase significantly
(from 0.14 to 0.67 μm) and apical angles decrease slightly (from 23.5 to 11.1º). The contrasting
trends in measurements between the two solution sets suggests the dissolution mechanism may
be different between sodium chloride and sodium sulfate solutions at circum-neutral pH and/or
there is no clear trend in denticle length and apparent apical angle measurements with changing
anion chemistry. Given the non-systematic relationship between solution chemistry and denticle
length, as well as the general overlap in measurements between all the experiments, neither
apical angle nor denticle length are useful indicators of anion chemistry, particularly in more
complicated natural solutions that likely contain a mixture of different ions.

While perchlorate has been typically considered an “indifferent” electrolyte for investigations of mineral reactivity (e.g., Brown and Parks, 2001), we observed a much larger range of denticle lengths in 2 M NaClO₄ brine compared to our NaCl and Na₂SO₄ experiments. Sanemasa and Katsura (1973) stated that solutions containing up to 2 N HClO₄ and HCl had little effect on synthetic diopside dissolution rates and extent of cation release compared to H₂SO₄; however, they presented no data supporting their findings. In contrast, Sidhu et al. (1981) demonstrated a range of perchlorate concentrations up to 2 M had no influence on the dissolution rate of iron oxide minerals, while Cl⁻ ions produced faster dissolution rates. Our results show a much wider range in denticle lengths produced in the perchlorate dissolution experiments compared to all the other solution chemistries. This suggests perchlorate ions may interact differently with the diopside surface, producing a wider variety of denticle lengths. We hypothesize that this may be a result of redox reactions occurring at specific surface sites driven by sorption of highly oxidized perchlorate anions. Although redox reactions between perchlorate and ferrous iron-bearing minerals have not yet, to our knowledge, been demonstrated, it is well-established that redox reactions influence the dissolution of iron-bearing pyroxene (e.g., Siever and Woodford, 1979; Schott and Berner, 1983; White et al., 1985; Burns, 1993; Hoch et al. 1996). These redox-driven dissolution reactions may accelerate chemical weathering in specific locations on the diopside surface leading to formation of much longer denticles in some areas of the sample. The patchy development of protective iron (hydr)oxide and clay surface layers may influence diffusion of reactants, thus leading to variability in dissolution textures across the mineral surface (e.g., Siever and Woodford, 1979; Benzerara et al., 2005; Behrends et al., 2015). However, other studies suggest that protective surface layers may not ultimately control the overall dissolution
rate observed in natural weathering environments, depending on the ratio of molar volumes
between dissolving phases and secondary reaction products (Velbel, 1993) and the porosity of
the precipitates (e.g., Hodson, 2003; Lee et al., 2008). Therefore, individual measurements of
denticle lengths on weathered pyroxene minerals surfaces in systems exposed to perchlorate may
over-estimate the extent of aqueous alteration. Since perchlorate is commonly observed in Mars
surface samples (0.4-0.6 wt.%; Hecht et al., 2009; Navarro-Gonzalez et al., 2010; Glavin et al.,
2013), broader assessments of pyroxene weathering in the presence of perchlorate are needed to
provide context for any future denticle length measurements of pyroxene on/from Mars.

Denticle length as a quantitative assessment of weathering extent

Early laboratory studies conducted at either low pH (<4) and/or high temperature (50-90 ºC)
formed etch pits and denticle features similar to those observed in natural weathered soil profiles
(Brantley and Chen, 1995; Chen and Brantley, 1998). In contrast, 30-day dissolution experiments
at circumneutral pH and 22 ºC did not result in denticle formation (Werner et al., 1995), perhaps
due to the relatively short reaction times and slow reaction rates. However, etch pits and
denticles similar to those typically observed in natural systems formed in all of our 60 day
experiments, suggesting the duration of aqueous alteration may be the major control on denticle
formation. We observed microdenticles that have been previously linked to reactive solutions
that are acidic and/or undersaturated with respect to pyroxene (Velbel, 2011; Velbel, 2012) in
several of our experiments; however, we find no systematic variation with activity of water.

Previous studies have correlated pyroxene denticle length and extent of chemical weathering
in soil profiles, where denticle lengths decrease with increasing distance below the depth of first
chain silicate occurrence, reaching a minimum either where chemical weathering conditions
change (Argast, 1991) and/or as fresh bedrock surfaces are approached (Mikesell et al., 2004;
Schaetzl et al., 2006). For example, in amphibole-bearing soils developed on glacially-influenced sediments, denticle lengths ≥2 μm were common near the surface, but shorter denticles (<1 μm) were observed at greater depths approaching incipiently altered bedrock (Hall and Michaud, 1988; Hall and Horn, 1993; Mikesell et al., 2004; Schaetzl et al., 2006). Therefore, quantitative measures of median denticle lengths may be useful in constraining the duration of chemical weathering, with denticles ≤1 μm indicating relatively brief periods of aqueous alteration. Indeed, the relatively rapid formation of denticles observed in this study suggests even geologically brief aqueous alteration events can result in significant changes to pyroxene surface textures. In contrast, longer denticles would be expected to be observed on pyroxene and amphiboles that experienced longer weathering durations.

Implications

Our results demonstrate quantitative measurements of apical angles and denticle lengths do not correlate with changing solution chemistry or activity of water in chloride, perchlorate, and sulfate brines. Therefore, it is unlikely quantitative denticle measurements can be used to constrain past aqueous chemistry on Mars. As this supports Velbel and Losiak’s (2010) findings in dilute solutions, we recommend abandoning quantitative measures of apparent apical angles as a tool to determine aqueous alteration histories of pyroxene grains.

In contrast, quantitative comparisons of denticle lengths may provide insight into the duration of aqueous alteration. Small scale (<1 μm) denticles are commonly observed in martian meteorites, including ALH84001 (Thomas-Keptra et al., 2009; Velbel, 2011) and MIL 03346 (Velbel, 2012). These meteorites also contain veins with sulfate and chloride minerals, which may indicate martian meteorites experienced aqueous alteration in saline conditions, similar to those examined in this study, over relatively brief periods of geologic time.
However, perchlorate salts may complicate simple applications of denticle length measurements to interpret extent of weathering since a much wider range of measured denticle lengths (but similar average value ≤1 μm) were produced in perchlorate brines compared to the other solutions. Perchlorate brines may have been stable on the surface of Mars throughout its history, and may be active on Mars’ surface today (Chevrier et al., 2009; Ojha et al., 2015). Perchlorate salts have been detected in martian meteorite EETA 79001 at concentrations of 0.6±0.1 ppm (Kounaves et al., 2014). Perchlorate was also detected by the Phoenix lander at 0.5-0.7 wt.% (Hecht et al., 2009), suggesting it may be a common constituent in martian sediments. Therefore, care must be taken when using quantitative denticle lengths as proxies for the extent of aqueous alteration on Mars, including in returned samples, in order to ensure accurate interpretations of chemical weathering duration.

Laboratory studies using well-mixed reactors typically represent the ‘maximum’ weathering intensity possible; the ultimate lifetime and persistence of mineral grains in natural systems may be much longer than that predicted from short-term weathering rates (Velbel, 2007; Olsen and Rimstidt, 2007; Pritchett et al., 2012). For example, the relatively pristine clinopyroxene textures compared with more extensive olivine alteration observed in nakhlites may be due to fluid saturation with respect to pyroxene but remaining undersaturated with respect to olivine (Velbel, 2016). On the other hand, quantitative weathering rates from olivine laboratory experiments accurately predicted the time required to form etch pits in different laboratory experiments (Velbel, 2014), indicating that laboratory experiments do constrain the timing of mineral surface textural evolution.

Given these caveats, we recommend using qualitative comparisons of denticle lengths as proxies for relative extent of weathering on Mars only in areas where the mineralogy, including
salts associated with pyroxene grains, are well-constrained. We further recommend incorporating additional data, including qualitative weathering assessments that examine etch pit density, and secondary mineral coverage, including clays formed on the mineral surface (Phillips-Lander et al., 2017), to increase confidence in interpretations of weathering duration on Mars.

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Figure Captions

Figure 1: Diopside dissolution textures observed with SEM indicate denticles in all images are <1 μm. Denticle lengths and apparent apical angles were measured using ImageJ as shown in (A). Systematic changes in denticle lengths or apparent apical angles were not observable with increasing salinity between (B) 0.35 M NaCl and (E) 3 M NaCl or (C) 0.35 M Na₂SO₄ and (F) 1.7 M Na₂SO₄ or decreasing activity of water. Microdenticles are observed on pyroxene in almost all images, except (A) UPW, (B) 0.35 M NaCl, (F) 1.7 M Na₂SO₄, and (G) 4.5 M CaCl₂. These samples represent a very dilute solution (aH₂O=0.99) and a concentrated brine (aH₂O=0.35).

Figure 2: Box and whisker plots of diopside (A) denticle lengths and (B) apparent apical
angles display no clear trends with respect to changes in activity of water. (A) Dentine lengths are significantly longer in 2 M NaClO$_4$. (B) With the exception of 3 M NaCl, apparent apical angles are within range of each other. However, if outlier points are considered, apical angles in all samples are similar.
### Tables

Table 1: Measured Diopside Denticle Lengths (μm) and Apical Angles (°)

<table>
<thead>
<tr>
<th>Solution</th>
<th>UPW</th>
<th>0.35 M NaCl</th>
<th>0.35 M Na₂SO₄</th>
<th>1.7 M Na₂SO₄</th>
<th>2 M NaClO₄</th>
<th>3 M NaCl</th>
<th>4.5 M CaCl₂</th>
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<td>0.98</td>
<td>0.95</td>
<td>0.93</td>
<td>0.75</td>
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| Number of Measurements | 77  | 118         | 230           | 112          | 85         | 50      | 21         |

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<tr>
<th>Denticle Length (μm)</th>
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<tbody>
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<td>Maximum</td>
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<td>1.6</td>
<td>0.79</td>
<td>2.6</td>
<td>5.9</td>
<td>1.7</td>
<td>2.1</td>
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<tr>
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<td>0.27</td>
<td>0.94</td>
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<td><strong>Median</strong></td>
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<td>0.14</td>
<td>0.67</td>
<td>1.1</td>
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<tr>
<td>Lower Quartile</td>
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<td>0.30</td>
<td>0.075</td>
<td>0.49</td>
<td>0.60</td>
<td>0.22</td>
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<tr>
<td>Minimum</td>
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<td>0.069</td>
<td>0.028</td>
<td>0.17</td>
<td>0.18</td>
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<tr>
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<td>0.59</td>
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<th>Apparent Apical Angle (°)</th>
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<td>63.5</td>
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A. 18 MΩ H₂O
B. 0.35 M NaCl
C. 0.35 M Na₂SO₄
D. 2 M NaClO₄
E. 3 M NaCl
F. 1.7 M Na₂SO₄
G. 4.5 M CaCl₂

microdenticles
denticle

length
angle