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

CHARITY M. PHILLIPS-LANDER^{1,*}, CAREY LEGETT IV¹, ANDREW S. ELWOOD MADDEN¹, AND MEGAN E. ELWOOD MADDEN¹

¹School of Geology and Geophysics, University of Oklahoma, 100 East Boyd Street, Room 710, Norman, Oklahoma, 73071, U.S.A.

ABSTRACT

Pyroxene minerals are a significant component of Shergottite-Nakhlite-Chassignite (SNC) meteorites (e.g., Velbel 2012) and detected across large areas of Mars' surface (e.g., Mustard et al. 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 various 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 M Ω cm⁻¹; $a_{H_{20}} = 1$); low-salinity solutions containing 0.35 M NaCl ($a_{H_{20}} = 0.99$), 0.35 M Na₂SO₄ ($a_{H_{20}} = 0.98$), and 2 M NaClO₄ ($a_{H_{20}} = 0.9$); and near-saturated brines containing 1.7 M Na₂SO₄ ($a_{H_{20}} = 0.95$), 3 M NaCl ($a_{H_{20}} = 0.75$), and 4.5 M CaCl₂ ($a_{H_{20}} = 0.35$). 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 that also contain perchlorate.

Keywords: 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-/nanoscale 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; Treiman 2005; Velbel and Losiak 2010; Velbel 2012), indicative of their abundance in the martian crust (Bandfield et al. 2000). They typically display indicators of weathering formed through aqueous alteration on Mars (Treiman 2005; Velbel 2012; Ling and Wang 2015), including the formation of secondary clay minerals and Fe-oxides (Treiman 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-Keprta 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

^{*} E-mail: charity.m.lander@ou.edu

secondary minerals in SNC meteorites (Treiman 1985; Gooding et al. 1988, 1991; Chatzitheodoridis and Turner 1990; Treiman et al. 1993; Wentworth and Gooding 1994; 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 (Treiman 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 (Treiman 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, 1993; Cremeens et al. 1992; 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 lowtemperature 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 various glacial and periglacial systems (e.g., Hall and Michaud 1988; Argast 1991; Hall and Horn 1993; Mikesell et al. 2004; Schaetzl et al. 2006). Amphibole and pyroxene group minerals exhibit similar denticular dissolution textures in response to similar weathering conditions (Velbel 2007). Denticle 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; Schaetzl 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 $\leq 1 \mu m$ 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 vs. diopside), weathering conditions, and even different silicates (amphibole vs. 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.

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



concentrated brine ($a_{\rm H_{2O}} = 0.35$).

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 (no. 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 × 160 μ m areas (Supplemental¹ 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 advitivy of water ($a_{H_{20}} = 1$); low-salinity solutions containing 0.35 M NaCl ($a_{H_{20}} = 0.99$), 0.35 M Na₂SO₄ ($a_{H_{20}} = 0.98$), and 2 M NaClO₄ ($a_{H_{20}} = 0.9$); and near-saturated brines containing 1.7 M Na₂SO₄ ($a_{H_{20}} = 0.95$), 3 M NaCl ($a_{H_{20}} = 0.75$), and 4.5 M CaCl₂ ($a_{H_{20}} = 0.35$). 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 $\rm Na_2SO_4$ 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 ~4 \times 10⁻⁶ torr using both in-lens and Everhart-Thornley secondary electron.

We took SEM images at scales ranging from 100 nm to 10 μm 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 (Fig. 1a). Denticle 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

¹Deposit item AM-17-96155, Supplemental Material. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2017/Sep2017_data/Sep2017_data.html).

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Solution	UPW	0.35 M NaCl	0.35 M Na₂SO₄	1.7 M Na ₂ SO ₄	2 M NaClO ₄	3 M NaCl	4.5 M CaCl₂
a _{H₂O}	1.0	0.99	0.98	0.95	0.93	0.75	0.35
Number of measurements	77	118	230	112	85	50	21
		D	Denticle length (μn	ו)			
Maximum	2.9	1.6	0.79	2.6	5.9	1.7	2.1
Upper Quartile	1.6	0.70	0.27	0.94	2.8	0.47	1.3
Median	0.76	0.50	0.14	0.67	1.1	0.36	0.59
Lower Quartile	0.50	0.30	0.075	0.49	0.60	0.22	0.40
Minimum	0.14	0.069	0.028	0.17	0.18	0.10	0.20
Mean	1.1	0.54	0.19	0.76	1.9	0.41	0.88
St.dev.	0.79	0.32	0.15	0.43	1.5	0.28	0.59
		Ар	parent apical angle	e (°)			
Maximum	78.3	61.7	63.5	55.0	45.0	79.8	57.5
Upper Quartile	23.4	13.6	27.7	16.3	22.5	55.2	38.7
Median	18.6	9.52	23.6	11.1	18.1	41.6	21.4
Lower Quartile	14.8	6.81	19.8	8.30	14.4	33.6	15.3
Minimum	6.71	3.21	5.84	3.40	8.40	11.5	11.8
Mean	21.2	12.2	24.3	14.4	19.3	43.1	26.5
St.dev.	12.1	8.84	7.55	10.1	7.10	16.1	13.2

TABLE 1. Measured diopside denticle lengths (µm) and apical angles (°)



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**) Denticle 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.

range is presented in Table 1. We compared denticle lengths and apparent apical angles observed on diopside surfaces 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 (Fig. 1). Median denticle lengths are approximately $\leq 1 \mu$ m; however, denticle length did not vary systematically with decreasing activity of water (Table 1; Fig. 2a). Denticle lengths in UPW ($a_{H_{20}} = 1$), 1.7 M Na₂SO₄ ($a_{H_{20}} = 0.95$), and 2 M NaClO₄ ($a_{H_{20}} = 0.9$) 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 NaClO₄ is significantly larger than the range of denticle lengths observed in all other experimental samples (~0.1–2.94 µm; Table 1; Fig. 2a). Slightly shorter median denticle lengths were observed in 0.35 M NaCl ($a_{H_{20}} = 0.99$) and 4.5 M CaCl₂ ($a_{H_{20}} = 0.35$) with denticle lengths of 0.50 and 0.59 m, respectively. The shortest denticles were observed in 0.35 M Na₂SO₄ $(a_{\rm H_{2O}} = 0.98)$ and 3 M NaCl $(a_{\rm H_{2O}} = 0.75)$ with median lengths of 0.14 and 0.36 µm, respectively. Microdenticles (Velbel 2011) are observed in Figure 1 in part (c) 0.35 M Na₂SO₄, (d) 2 M NaClO₄, and (e) 3 M NaCl.

Median apparent apical angle measurements in UPW, 0.35 M Na_2SO_4 , 2 M $NaClO_4$, and 4.5 M $CaCl_2$ range from 18.1 to 23.5° (Table 1; Fig. 2b). However, apparent apical angles were significantly smaller in 0.35 M NaCl (9.5°) and 1.7 M Na_2SO_4 (11.1°). The range of apical angles (up to 40°) overlaps for experimental solutions with activities of water >0.9 (Fig. 2b). Apparent 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 (Fig. 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 (Fig. 2b).

Measured median denticle lengths in our study are also similar, with <1 µm difference in average values between experimental trials (Fig. 2a), indicating activity of water also does not systematically influence denticle lengths. For example, our 0.35 M Na₂SO₄ ($a_{H_{2O}} = 0.98$) and 3 M NaCl ($a_{H_{2O}} = 0.75$) had the smallest median denticle lengths, but vary significantly in activity of water (Fig. 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

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 μ m) and apical angles increase significantly (9.5 to 42.4°) 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 11.1°). 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; Behrens 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 overestimate the extent of aqueous alteration. Since perchlorate is commonly observed in Mars surface samples (0.4-0.6 wt%; Hecht et al. 2009; Navarro-González 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 °C) 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 °C 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, 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 $\geq 2 \mu m$ 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 $\leq 1 \mu m$ 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 μ m) denticles are commonly observed in martian meteorites, including ALH84001 (Thomas-Keprta 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 $\leq 1 \mu$ m) 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, 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, to increase confidence in interpretations of weathering duration on Mars.

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REFERENCES CITED

- Andò, S., Garzanti, E., Padoan, M., and Limonta, M. (2012) Corrosion of heavy minerals during weathering and diagenesis: A catalog for optical analysis. Sedimentary Geology, 280, 165–178.
- Argast, S. (1991) Chlorite vermiculitization and pyroxene etching in an aeolian periglacial sand dune, Allen County, Indiana. Clays and Clay Minerals, 39(6), 622–633.
- Bandfield, J.L., Hamilton, V.E., and Christensen, P.R. (2000) A global view of Martian surface compositions from MGS-TES. Science, 287, 1626–1630.
- Behrens, R., Bouchez, J., Schuessler, J.A., Dultz, S., Hewawasam, T., and von Blanckenburg, F. (2015) Mineralogical transformations set slow weathering rates in low-porosity metamorphic bedrock on mountain slopes in a tropical climate. Chemical Geology, 411, 283–298.
- Benzerara, K., Yoon, T., Menguy, N., Tyliszczak, T., and Brown, G. (2005) Nanoscale environments associated with bioweathering of a Mg-Fe-pyroxene. Proceedings of the National Academy of Sciences, 102, 979–982.
- Berner, R.A. (1978) Rate control of mineral dissolution under earth surface conditions. American Journal of Science, 278(9), 1235–1252.
- Berner, R.A., and Schott, J. (1982) Mechanism of pyroxene and amphibole weathering; II, Observations of soil grains. American Journal of Science, 282(8), 1214–1231.
- Berner, R.A., Sjöberg, E.L., Velbel, M.A., and Krom, M.D. (1980) Dissolution of pyroxenes and amphiboles during weathering. Science, 207, 1205–1206.
- Brantley, S.L., and Chen, Y. (1995) Chemical weathering rates of pyroxenes and amphiboles. Reviews in Mineralogy and Geochemistry, 31, 119–172.
- Brantley, S.L., Crane, S.R., Crerar, D.A., Hellmann, R., and Stallard, R. (1986) Dissolution at dislocation etch pits in quartz. Geochimica et Cosmochimica Acta, 50(10), 2349–2361.
- Brantley, S.L., Blai, A.C., Cremeens, D.L., MacInnis, I., and Darmody, R.G. (1993) Natural etching rates of feldspar and hornblende. Aquatic Sciences, 55(4), 262–272.
- Bridges, J.C., and Grady, M.M. (1999) A halite-siderite-anhydrite-chlorapatite assemblage in Nakhla: Mineralogical evidence for evaporites on Mars. Meteoritics and Planetary Science, 34, 407–415.
- (2000) Evaporite mineral assemblages in the nakhlite (martian) meteorites. Earth and Planetary Science Letters, 176(3), 267–279.
- Bridges, J.C., Catling, D.C., Saxton, J.M., Swindle, T.D., Lyon, I.C., and Grady, M.M. (2001) Alteration assemblages in Martian meteorites: Implications for near-surface processes. In R. Kallenbach, J. Geiss, and W.K. Hartmann, Eds., Chronology and Evolution of Mars, p. 365–392. Springer, Netherlands.
- Brown, G.E. Jr., and Parks, G.A. (2001) Sorption of trace elements on mineral surfaces: modern perspectives from spectroscopic studies, and comments on sorption in the marine environment. International Geology Review, 43(11), 963–1073.
- Burns, R.G. (1993) Rates and mechanisms of chemical weathering of ferromagnesian silicate minerals on Mars. Geochimica et Cosmochimica Acta, 57, 4555–4574.
- Chatzitheodoridis, E., and Turner, G. (1990) Secondary minerals in the Nakhla meteorite. Meteoritics, 25, 354–354.
- Chen, Y., and Brantley, S.L. (1998) Diopside and anthophyllite dissolution at 25 and 90 °C and acid pH. Chemical Geology, 147(3), 233–248.
- Chevrier, V.F., Hanley, J., and Altheide, T.S. (2009) Stability of perchlorate hydrates

and their liquid solutions at the Phoenix landing site, Mars. Geophysical Research Letters, 36(10), L10202.

- Cremeens, D.L., Darmody, R.G., and Norton, L.D. (1992) Etch-pit size and shape distribution on orthoclase and pyriboles in a loess catena. Geochimica et Cosmochimica Acta, 56(9), 3423–3434.
- Elwood Madden, M.E., Madden, A.S., Rimstidt, J.D., Zahrai, S., Kendall, M.R., and Miller, M.A. (2012) Jarosite dissolution rates and nanoscale mineralogy. Geochimica et Cosmochimica Acta, 91, 306–321.
- Glavin, D.P., Freissinet, C., Miller, K.E., Eigenbrode, J.L., Brunner, A.E., Buch, A., Sutter, B., Archer, P.D., Atreya, S.K., Brinckerhoff, W.B., and Cabane, M. (2013) Evidence for perchlorates and the origin of chlorinated hydrocarbons detected by SAM at the Rocknest aeolian deposit in Gale Crater. Journal of Geophysical Research: Planets, 118(10), 1955–1973.
- Glotch, T., Bandfield, J., Wolff, M., Arnold, J., and Che, C. (2016) Constraints on the composition and particle size of chloride salt-bearing deposits on Mars. Journal of Geophysical Research: Planets, 121, 454–471.
- Gooding, J.L., Wentworth, S.J., and Zolensky, M.E. (1988) Calcium carbonate and sulfate of possible extraterrestrial origin in the EETA 79001 meteorite. Geochimica et Cosmochimica Acta, 52(4), 909–915.
- ——(1991) Aqueous alteration of the Nakhla meteorite. Meteoritics and Planetary Science, 26(2), 135–143.
- Hall, R.D., and Horn, L.L. (1993) Rates of hornblende etching in soils in glacial deposits of the northern Rocky Mountains (Wyoming-Montana, USA): Influence of climate and characteristics of the parent material. Chemical Geology, 105(1-3), 17–29.
- Hall, R.D., and Michaud, D. (1988) The use of hornblende etching, clast weathering, and soils to date alpine glacial and periglacial deposits: a study from southwestern Montana. Geological Society of America Bulletin, 100(3), 458–467.
- Hecht, M.H., Kounaves, S.P., Quinn, R.C., West, S.J., Young, S.M.M., Ming, D.W., Catling, D.C., Clark, B.C., Boynton, W.V., Hoffman, J., and DeFlores, L.P. (2009) Detection of perchlorate and the soluble chemistry of martian soil at the Phoenix lander site. Science, 325, 64–67.
- Hoch, A.R., Reddy, M.M., and Drever, J.I. (1996) The effect of iron content and dissolved O₂ on dissolution rates of clinopyroxene at pH 5.8 and 25°C: preliminary results. Chemical Geology, 132, 151–156.
- Hochella, M.F., and Banfield, J.F. (1995) Chemical weathering of silicates in nature; a microscopic perspective with theoretical considerations. Reviews in Mineralogy and Geochemistry, 31, 353–406.
- Hodson, M.E. (2003) The influence of Fe-rich coatings on the dissolution of anorthite at pH 2.6. Geochimica et Cosmochimica Acta, 67, 3355–3363.
- Kounaves, S.P., Carrier, B.L., O'Neil, G.D., Stroble, S.T., and Claire, M.W. (2014) Evidence of martian perchlorate, chlorate, and nitrate in Mars meteorite EETA79001: Implications for oxidants and organics. Icarus, 229, 206–213.
- Lee, M.R., Brown, D.J., Hodson, M.E., MacKenzie, M., and Smith, C.L. (2008) Weathering microenvironments on feldspar surfaces: implications for understanding fluid-mineral reactions in soils. Mineralogical Magazine, 72, 1319–1328.
- Lee, M.R., Tomkinson, T., Mark, D.F., Stuart, F.M., and Smith, C.L. (2013) Evidence for silicate dissolution on Mars from the Nakhla meteorite. Meteoritics and Planetary Science, 48(2), 224–240.
- Legett, C., Pritchett, B.N., Elwood Madden, A.S., and Elwood Madden, M.E. (2014) Measuring mineral dissolution rates in perchlorate brines: Method development and applications. Lunar and Planetary Sciences Conference, p. 2492.
- Ling, Z., and Wang, A. (2015) Spatial distributions of secondary minerals in the Martian meteorite MIL 03346, 168 determined by Raman spectroscopic imaging. Journal of Geophysical Research: Planets, 120(6), 1141–1159.
- MacInnis, I.N., and Brantley, S.L. (1993) Development of etch pit size distributions on dissolving minerals. Chemical Geology, 105(1-3), 31–49.
- McSween, H.Y. (1994) What we have learned about Mars from SNC meteorites. Meteoritics, 29(6), 757–779.
- Mikesell, L.R., Schaetzl, R.J., and Velbel, M.A. (2004) Hornblende etching and quartz/ feldspar ratios as weathering and soil development indicators in some Michigan soils. Quaternary Research, 62(2), 162–171.
- Miller, J.L., Madden, A.E., Phillips-Lander, C.M., Pritchett, B.N., and Madden, M.E. (2016) Alunite dissolution rates: Dissolution mechanisms and implications for Mars. Geochimica et Cosmochimica Acta, 172, 93–106.
- Mustard, J.F., Poulet, F., Gendrin, A., Bibring, J.-P., Langevin, Y., Gondet, B., Mangold, N., Bellucci, G., and Altieri, F. (2005) Olivine and pyroxene diversity in the crust of Mars. Science, 307, 1594–1597.
- Navarro-González, R., Vargas, E., de La Rosa, J., Raga, A.C., and McKay, C.P. (2010) Reanalysis of the Viking results suggests perchlorate and organics at midlatitudes on Mars. Journal of Geophysical Research, 115, E12010.
- Ojha, L., Wilhelm, M.B., Murchie, S.L., McEwen, A.S., Wray, J.J., Hanley, J., Massé, M., and Chojnacki, M. (2015) Spectral evidence for hydrated salts in recurring slope lineae on Mars. Nature Geoscience, 8(11), 829–832.
- Olsen, A.A., and Rimstidt, J.D. (2008) Oxalate-promoted forsterite dissolution at low pH. Geochimica et Cosmochimica Acta, 72(7), 1758–1766.
- Olsen, A.A., Hausrath, E.M., and Rimstidt, J.D. (2015) Forsterite dissolution rates in Mg-sulfate-rich Mars-analog brines and implications of the aqueous history of Mars. Journal of Geophysical Research: Planets, 120(3), 388–400.
- Parnell, S.P., Phillips-Lander, C.M., McGraw, L.E., and Elwood Madden, M.E. (2016) Carbonate dissolution rates in high salinity brines. Lunar and Planetary

Sciences, 1460.

- Phillips-Lander, C.M., Fowle, D.A., Taunton, A., Hernandez, W., Mora, M., Moore, D., Shinogle, H., and Roberts, J.A. (2014) Silicate dissolution in Las Pailas thermal field: Implications for microbial weathering in acidic volcanic hydrothermal spring systems. Geomicrobiology Journal, 31(1), 23–41.
- Phillips-Lander, C.M., Legett, C. IV, Elwood Madden, A.S., and Elwood Madden, M.E. (2016) Pyroxene dissolution rates in high salinity brines: Implications for post-Noachian aqueous alteration on Mars. 47th Lunar and Planetary Science Conference, Contribution no. 1903, p. 1313.
- Pritchett, B.N., Madden, M.E., and Madden, A.S. (2012) Jarosite dissolution rates and maximum lifetimes in high salinity brines: Implications for Earth and Mars. Earth and Planetary Science Letters, 357, 327–336.
- Sanemasa, I., and Katsura, T. (1973) The dissolution of CaMg(SiO₃)₂ in acid solutions. Bulletin of the Chemical Society of Japan, 46(11), 3416–3422.
- Schaetzl, R.J., Mikesell, L.R., and Velbel, M.A. (2006) Soil characteristics related to weathering and pedogenesis across a geomorphic surface of uniform age in Michigan. Physical Geography, 27(2), 170–188.
- Schneider, C.A., Rasband, W.S., and Eliceiri, K.W. (2012) NIH Image to ImageJ: 25 years of image analysis. Nature Methods, 9, 671–675.
- Schott, J., and Berner, R. (1983) X-ray photoelectron studies of the mechanism of iron silicate dissolution during weathering. Geochimica et Cosmochimica Acta, 47, 2233–2240.
- Sidhu, P.S., Gilkes, R.J., Cornell, R.M., Posner, A.M., and Quirk, J.P. (1981) Dissolution of iron oxides and oxyhydroxides in hydrochloric and perchloric acids. Clays and Clay Minerals, 29, 269–276.
- Siever, R., and Woodford, N. (1979) Dissolution kinetics and the weathering of mafic minerals. Geochimica et Cosmochimica Acta, 43, 717–724.
- Stieglitz, R.D., and Rothwell, B. (1978) Surface microtextures of freshwater heavy mineral grains. Geoscience Wisconsin, 3, 21–34.
- Steiner, M.H., Hausrath, E.M., Madden, M.E., Tschauner, O., Ehlmann, B.L., Olsen, A.A., Gainey, S.R., and Smith, J.S. (2016) Dissolution of nontronite in chloride brines and implications for the aqueous history of Mars. Geochimica et Cosmochimica Acta, 195, 259–276.
- Thomas-Keprta, K.L., Clemett, S.J., McKay, D.S., Gibson, E.K., and Wentworth, S.J. (2009) Origins of magnetite nanocrystals in Martian meteorite ALH84001. Geochimica et Cosmochimica Acta, 73, 6631–6677.
- Treiman, A.H. (2005) The nakhlite meteorites: Augite-rich igneous rocks from Mars. Chemie der Erde-Geochemistry, 65(3), 203–270.
- Treiman, A.H., Barrett, R.A., and Gooding, J.L. (1993) Preterrestrial aqueous alteration of the Lafayette (SNC) meteorite. Meteoritics, 28(1), 86–97.
- Velbel, M.A. (1993) Formation of protective surface layers during silicate-mineral weathering under well-leached, oxidizing conditions. American Mineralogist, 78, 405–405.
- (2007) Surface textures and dissolution processes of heavy minerals in the sedimentary cycle: examples from pyroxenes and amphiboles. Developments in Sedimentology, 58, 113–150.
- ——(2011) Microdenticles on naturally weathered hornblende. Applied Geochemistry, 26(8), 1594–1596.
- (2012) Aqueous alteration in Martian meteorites: Comparing mineral relations in igneous-rock weathering of Martian meteorites and in the sedimentary cycle of Mars. Sedimentary Geology of Mars, SEPM. Society for Sedimentary Geology Special Publication, 102, 97–117.
- ——(2014) Terrestrial weathering of ordinary chondrites in nature and continuing during laboratory storage and processing: Review and implications for Hayabusa sample integrity. Meteoritics & Planetary Science, 49(2), 154–171.
- (2016) Aqueous corrosion of olivine in the Mars meteorite Miller Range (MIL) 03346 during Antarctic weathering: Implications for water on Mars. Geochimica et Cosmochimica Acta, 180, 126–145.
- Velbel, M.A., and Barker, W.W. (2008) Pyroxene weathering to smectite: conventional and cryo-field emission scanning electron microscopy, Koua Bocca ultramafic complex, Ivory Coast. Clays and Clay Minerals, 56(1), 112–127.
- Velbel, M.A., and Losiak, A.I. (2010) Denticles on chain silicate grain surfaces and their utility as indicators of weathering conditions on Earth and Mars. Journal of Sedimentary Research, 80(9), 771–780.
- Wentworth, S.J., and Gooding, J.L. (1994) Carbonates and sulfates in the Chassigny meteorite: Further evidence for aqueous chemistry on the SNC parent planet. Meteoritics, 29(6), 860–863.
- Werner, A.J., Hochella, M.F., Guthrie, G.D., Hardy, J.A., and Aust, A.E. (1995) Asbestiform riebeckite (crocidolite) dissolution in the presence of Fe chelators: implications for mineral-induced disease. American Mineralogist, 80(11-12), 1093–1103.
- White, A.F., and Brantley, S.L. (2003) The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field? Chemical Geology, 202(3), 479–506.
- White, A., Yee, A., and Flexser, S. (1985) Surface oxidation-reduction kinetics associated with experimental basalt-water reaction at 25°C. Chemical Geology, 49, 73–86.

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