1   **Revision 2**

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

4   By: Charity M. Phillips-Lander[1][*], Carey Legett IV[1], Andrew S. Elwood Madden[1], and

5   Megan E. Elwood Madden[1]

6   [1]School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd Street, Room

7   710, Norman, OK, 73071; *charity.m.lander@ou.edu

8   **Abstract**
9   Pyroxene minerals are a significant component of Shergottite-Nakhlite-Chassignite (SNC)

10   meteorites (e.g., Velbel, 2012) and detected across large areas of Mars' surface (e.g., Mustard,

11   2005). These minerals are associated with chloride, sulfate, and perchlorate salts that may

12   represent briny waters present in Mars' history. Previous textural analyses by Velbel and Losiak

13   (2010) comparing pyroxenes and amphiboles from a variety of natural weathering environments

14   showed no correlation between apparent apical angles (describing the morphology of denticular

15   weathering textures) and mineralogy or aqueous alteration history in relatively dilute solutions.

16   However, high salinity brines preferentially dissolve surface species, potentially leading to

17   different textures dependent on the brine chemistry. In this study, we performed controlled

18   pyroxene dissolution experiments in the laboratory on a well-characterized diopside to determine

19   if aqueous alteration in different high salinity brines, representative of potential weathering fluids

20   on Mars, produce unique textural signatures.

21   Following two months of dissolution in batch reactors, we observed denticles on etch pit

22   margins and pyroxene chip boundaries in all of the solutions investigated: ultrapure water (18

23     $M\Omega$ cm^{-1}; $aH_2O=1$); low-salinity solutions containing 0.35 M NaCl ($aH_2O=0.99$), 0.35 M

24   Na_2SO_4 ($aH_2O=0.98$) and 2 M $NaClO_4$ ($aH_2O=0.9$); and near-saturated brines containing 1.7 M

25   Na_2SO_4 (aH_2O=0.95), 3 M NaCl (aH_2O=0.75), and 4.5 M $CaCl_2$ (aH_2O=0.35). No systematic

26   change in denticle length or apical angle was observed between any of the solutions investigated,

27   even when altered in brines with significantly different salinity, activity of water, and anion

28   composition. Based on these and previous results from natural systems, apical angle

29   measurements are not a useful proxy for determining the extent or nature of aqueous alteration.

30   However, since denticles form relatively slowly during weathering at circum-neutral pH, denticle

31   length may be a useful proxy for chemical weathering duration. All of the experimental solutions

32   produced median denticle lengths ≤1 μm, likely due to the brief weathering experiments.

33   However, perchlorate brines produced a significantly wider range of denticle lengths than those

34   observed in all the other experimental solutions tested. Since perchlorate is likely a common

35   constituent in martian soils (Glotch et al., 2016), denticle length measurements should be used

36   cautiously as proxies for extent of aqueous alteration on Mars, particularly in samples which also

37   contain perchlorate.

38   **Key Words**

39   weathering texture, pyroxene, denticles, apical angles, Mars, perchlorate, brines

40   <div align="center">**Introduction**</div>
41   Interpreting the history of aqueous alteration on Mars relies on chemical, mineralogical, and

42   textural clues recorded in rocks and minerals. Nano- to microscale textural features on primary

43   rock-forming minerals frequently contribute to interpretations of mineral-fluid interactions in

44   terrestrial samples (e.g., Hochella and Banfield, 1995). However, micro/nano-scale textural

45   analyses of minerals from Mars remain mostly limited to observations of SNC meteorites.

46   Pyroxene minerals are a significant component of SNC meteorites (McSween, 1994; Trieman,

47   2005; Velbel and Losiak, 2010; Velbel, 2012), indicative of their abundance in the martian crust

48   (Bandfield et al., 2000). They typically display indicators of weathering formed through aqueous

49   alteration on Mars (Trieman, 2005; Velbel, 2012; Ling and Wang, 2015), including the

50   formation of secondary clay minerals and Fe-oxides (Trieman et al., 1993; Ling and Wang,

51   2015) and dissolution textures on primary mineral phases. For example, jarosite, hematite,

52   cristobalite, and iddingsite are observed in veins in the Miller Range meteorite MIL 03346 (Ling

53   and Wang, 2015). In addition, denticles formed during pyroxene dissolution have been observed

54   in the Allen Hills meteorite ALH 84001 (Thomas-Keptra et al., 2009; Velbel, 2012). Pre-

55   terrestrial alteration in these meteorites has been established using cross-cutting relationships

56   including impact-related features overprinting alteration textures and minerals, as well as

57   weathering features predating the fusion crust (Gooding et al., 1988; Velbel, 2011).

58   In addition to alteration textures, salts are observed in SNC meteorites (Wentworth and

59   Gooding, 1994; Velbel, 2012). Perchlorate salts were observed in Mars meteorite EETA 9001

60   (Kounaves et al., 2014). Sulfates, including gypsum, anhydrite, and epsomite, as well as

61   chlorides, including halite, are common secondary minerals in SNC meteorites (Trieman, 1985;

62   Gooding et al., 1988; Chatzitheodoridis and Turner, 1990; Gooding et al., 1991; Treiman et al.,

63   1993; Wentworth and Gooding, 1994, 2005; Bridges and Grady, 1999, 2000; Bridges et al.,

64   2001; Lee et al., 2013; Ling and Wang, 2015). These salts occur as coatings on fracture surfaces

65   and as discontinuous veins in primary minerals, including pyroxene, in Chassigny (Wentworth

66   and Gooding, 1994) and MIL 03346 (Ling and Wang, 2015). Sulfate salts and jarosite also occur

67   along grain boundaries in MIL 03346 (Ling and Wang, 2015) and sulfate salts (gypsum,

68   basanite, epsomite) and halite are intergrown with smectite in Nakhla (Gooding et al.,

69   1991). Significant S and Cl are adsorbed to secondary clays and Fe-oxides in Lafayette (Trieman

70   et al., 1993). The presence of these salts associated with secondary minerals in SNC meteorites

71 provides evidence of episodic weathering in saline waters on or near Mars' surface (Trieman et

72 al., 1993; McSween, 1994).

73   During chemical weathering, surface textures form on silicate minerals as a result of mineral

74 dissolution (Berner et al., 1980; Velbel and Losiak, 2010). In most cases, the rate of silicate

75 dissolution is controlled by chemical reactions at the mineral/solution interface (Berner, 1978),

76 producing dissolution textures related to both mineral chemistry/structure and solution chemistry

77 (Hochella and Banfield, 1995). Laboratory experiments (e.g., Berner et al., 1980) and field

78 studies (e.g., Berner et al., 1980; Berner and Schott, 1982; Cremeens et al., 1992; Velbel and

79 Barker, 2008; Phillips-Lander et al., 2014) of pyroxene weathering demonstrated the progressive

80 development of distinctive dissolution textures, including lenticular etch pits lined with

81 "hacksaw" or "sawtoothed" terminations called denticles. These surface weathering textures can

82 be modified during transport and diagenesis; however, they may also be preserved through

83 weathering, transportation, deposition, and cementation (Stieglitz and Rothwell 1978; Velbel,

84 2007; Velbel et al. 2007; Velbel and Losiak, 2010). Preservation of surface weathering textures

85 may aid in the interpretation of aqueous alteration histories (Berner and Schott, 1982; Velbel,

86 2007; Andó et al. 2012).

87   Field-studies initially focused on etch pit sizes, morphologies, and distributions to understand

88 the factors that influence mineral dissolution (Berner et al., 1980; Berner and Schott, 1982;

89 Brantley et al., 1986; Cremeens et al., 1992; Brantley et al., 1993; MacInnis and Brantley, 1993;

90 White and Brantley, 2003). Berner et al. (1980) demonstrated surface dissolution textures are

91 primarily crystallographically controlled because textures observed from field studies were

92 replicated in laboratory weathering experiments conducted under a wide range of pH and

93 temperature conditions. However, individual etch pits observed in field-based studies are

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94   generally larger than those observed in laboratory studies (Berner and Schott, 1982). Also,

95   denticles are commonly observed in field-weathered chain silicates (e.g., Berner et al., 1980;

96   Berner and Schott, 1982; Cremeens et al., 1992; Velbel and Barker, 2008; Phillips-Lander et al.,

97   2014) but were only observed in laboratory-based dissolution experiments at elevated

98   temperature (50-90 ºC) and low pH ($\leq$4) (Brantley and Chen, 1995; Chen and Brantley, 1998).

99   Denticles likely only form in those experiments where alteration was accelerated due to

100   temperature and pH effects since experiments are typically brief in duration (30 days). At neutral

101   pH and low temperatures experiments with durations of $\leq$30 days, the extent of weathering may

102   not have been sufficient to produce denticles due to slow pyroxene dissolution rates (Velbel,

103   2007). Therefore, previous short-term laboratory dissolution experiments suggest denticle

104   formation correlates with extent of chemical weathering.

105   The correlation between denticle length and extent of chemical weathering has been further

106   demonstrated in field studies examining amphiboles from a variety of glacial and periglacial

107   systems (e.g., Hall and Michaud, 1988; Argast, 1991; Hall and Horn, 1993; Mikesell et al., 2004;

108   Schatzel et al., 2006). Amphibole and pyroxene group minerals exhibit similar denticular

109   dissolution textures in response to similar weathering conditions (Velbel, 2007). Denticle lengths

110   decrease logarithmically with increasing depth in weathered soil profiles, which correlates with

111   sediment age and degree of soil development (Hall and Michaud, 1988; Argast, 1991; Hall and

112   Horn, 1993; Mikesell et al., 2004; Schatzel et al., 2006). However, these measurements only

113   provide a relative indicator of weathering, as sediment size, mean annual precipitation, reactive

114   fluid chemistry, and organic acids influence surface texture development in pyroxenes and

115   amphiboles (Hall and Horn, 1993; Schaetzl et al., 2006). In addition to denticle lengths, the

116   presence of microdenticles, denticles $\leq$1 µm in length observed on the surfaces of larger

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117   denticles, have been previously interpreted as forming in low temperature solutions

118   undersaturated with respect to pyroxene and amphibole (Velbel, 2011) or acidic solution

119   conditions (Brantley et al., 1993). Therefore, microdenticles on pyroxenes in ALH 84001 may

120   have formed during weathering in similar solutions (Velbel, 2012).

121   Based on these previous terrestrial studies, Velbel and Losiak (2010) examined whether SEM

122   analysis, including quantitative measurements of denticle apparent apical angle (i.e. the angle

123   subtended by a pair of denticle surfaces) could be used to determine the mineralogy of weathered

124   grains and/or the weathering conditions that produced the observed morphologies. They sought

125   to determine whether surface weathering textures on individual grains, like grain surface textures

126   observed using atomic force microscopy (AFM) at the Phoenix landing site (Hecht et al., 2009),

127   could be used to understand pyroxene weathering textures on another planetary body where both

128   the mineralogy and aqueous alteration history may be unknown. Their results indicated denticle

129   apical angles varied significantly, but apparently randomly, between mineral compositions (i.e.

130   augite v. diopside), weathering conditions, and even different silicates (amphibole v. pyroxene)

131   from the same terrestrially weathered rock unit, yielding no unique determining characteristics

132   based on quantitative analysis of weathering textures. However, this survey of weathering

133   textures was subject to the complications of studying natural pyroxenes from several localities

134   that were influenced by several variables (mineralogy, solution chemistry, contact time with

135   reactive solutions, temperature, saturation state, etc.) that may have affected denticle formation.

136   In order to reduce potential variability in textural weathering observations and measurements

137   and extend the range of textural observations to brines, we conducted a series of experiments in

138   which we reacted a diopside of known composition with different Mars-representative

139   weathering solutions. A range of pyroxene compositions are common on the surface of Mars,

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140 including diopside (e.g., Mustard, 2005). Previous studies of mineral weathering in Mars-

141 representative solutions have demonstrated solution chemistry (Elwood Madden et al., 2012;

142 Phillips-Lander et al., 2016; Parnell et al., 2016) and activity of water (Pritchett et al., 2012;

143 Legett et al., 2014; Olson et al., 2015; Miller et al., 2016; Parnell et al., 2016; Steiner et al.,

144 2016) influence mineral dissolution rates. We sought to determine if pyroxene dissolution in

145 brine solutions with different activities of water and solution chemistries would result in

146 quantifiable differences in denticle length and/or apparent apical angles. In other words, we seek

147 to determine whether diopside weathering textures vary in a systematic way during low-

148 temperature aqueous alteration. The results of this study will inform interpretations of pyroxene

149 weathering textures in meteorites and future studies of samples returned from Mars.

150 ## Methods
151 ### Pyroxene Characterization

152 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

153 pyroxene, from Wards Scientific (#466474). Bulk geochemistry was determined using energy-

154 dispersive X-ray spectroscopy (EDXA) in a Cameca SX-50 electron microprobe (EMPA)

155 operated at 20 kV and 10 nA, analyzing 160 x 160 μm areas (Supplemental Table 1).

156 ### Dissolution Experiments and Textural Analysis

157 After EMPA analysis, we coarsely crushed the diopside to ~2-4 mm chips. Resulting mineral

158 chips were sonicated, rinsed, and air-dried. We conducted batch dissolution experiments at 22 ºC

159 and 1 atm using diopside chips added to solution at a ratio of 1 g pyroxene L^{-1} solution. Pyroxene

160 was reacted with solutions with varying chemistry and salinity: 18 MΩ cm^{-1} ultrapure water

161 (UPW) that has an activity of water (aH_2O=1); low-salinity solutions containing 0.35 M NaCl

162 (aH_2O=0.99), 0.35 M Na_2SO_4 (aH_2O=0.98), and 2 M $NaClO_4$ (aH_2O=0.9); and near-saturated

163   brines containing 1.7 M Na_2SO_4 (aH$_2$O=0.95), 3 M NaCl (aH$_2$O=0.75), and 4.5 M $CaCl_2$

164   (aH$_2$O=0.35). We mixed the samples at 120 rpm on a shaker table over 60 days. These solutions

165   were chosen to examine whether denticle length or apparent apical angle vary systematically

166   with either changes in solution chemistry between dilute (0.35 M) and near-saturated (1.7 M

167   Na_2SO_4 or 3 M NaCl) brines or decreasing activity of water.

168   At the end of the experiment, we filtered the contents of the reactor to retrieve the diopside

169   chips, then rinsed the reacted diopside chips three times in 18 MΩ cm^{-1} water and air-dried the

170   samples. Chips from each experimental condition, including unreacted controls, were then placed

171   on Al pin stubs in random orientations with carbon tape and iridium coated for imaging analysis

172   on the Zeiss NEON 40EsB field-emission scanning electron microscope (SEM) at the University

173   of Oklahoma's Sam Noble Microscopy Laboratory. Images were collected at 15 kV and ~50 pA

174   beam current with a vacuum of ~4x10^{-6} torr using both in-lens and Everhart-Thornley secondary

175   electron detectors.

176   We took SEM images at scales ranging from 100 nm to 10 μm in order to evaluate mineral

177   weathering textures, including microdenticles. SEM images were imported into ImageJ

178   (Schneider et al., 2012), an open source imaging software program, which has the capability to

179   measure both denticle length and apparent denticle apical angles formed during dissolution. We

180   measured denticle lengths from the initial parting on the mineral surface to the tip of the denticle

181   (Figure 1A). Denticle lengths may be considered minimum values, due to the possibility that in

182   some cases the base of a denticle is obscured by an overlapping denticle. We estimated our

183   measurement precision based on measuring the same denticle three times to be ±0.13 μm. We

184   also measured apparent apical angles using the angle measurement tool, which drops anchor

185   points on each side of the denticle and at the tip. The precision of our apparent apical angle

186   measurements (1.3 º) was determined by measuring the same apical angle three times for a single

187   denticle. The number of images with etch pits and denticles was controlled by the degree of

188   dissolution of the mineral surface. However, we aimed to quantify denticles from a minimum of

189   five images per solution condition, including all visually distinguishable denticles in each image.

190   Statistical analysis of denticle measurements was performed by constructing box and whisker

191   plots. The number of denticle measurements and the boundary of each interquartile range is

192   presented in Table 1. We compared denticle lengths and apparent apical angles observed on

193   diopside surfaces in order to determine how these data vary with changes in fluid chemistry and

194   activity of water, which have been previously demonstrated to influence mineral dissolution

195   rates.

196   **Results**

197   Denticles are present along etch pit margins on diopside surfaces weathered under all

198   experimental conditions, with the exception of unreacted grains (Figure 1). Median denticle

199   lengths are approximately ≤ 1 µm; however, denticle length did not vary systematically with

200   decreasing activity of water (Table 1; Figure 2A). Denticle lengths in UPW (aH$_2$O=1), 1.7 M

201   Na$_2$SO$_4$ (aH$_2$O=0.95), and 2 M NaClO$_4$ (aH$_2$O=0.93) are all very similar, with median lengths of

202   0.67-1.0 µm. However, the range (0.18-5.93 µm) of denticle lengths in 2 M NaClO$_4$ is

203   significantly larger than the range of denticle lengths observed in all other experimental samples

204   (~0.1-2.94µm; Table 1; Figure 2A). Slightly shorter median denticle lengths were observed in

205   0.35 M NaCl (aH$_2$O=0.99) and 4.5 M CaCl$_2$ (aH$_2$O=0.35) with denticle lengths of 0.50 and 0.59

206   µm respectively. The shortest denticles were observed in 0.35 M Na$_2$SO$_4$ (aH$_2$O=0.98) and 3 M

207   NaCl (aH$_2$O=0.75) with median lengths of 0.14 and 0.36 µm respectively. Microdenticles

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208   (Velbel, 2011) are observed in Figure 1 in (C) 0.35 M Na_2SO_4, (D) 2 M $NaClO_4$, and (E) 3 M

209   NaCl.

210   Median apparent apical angle measurements in UPW, 0.35 M Na_2SO_4, 2 M $NaClO_4$, and 4.5

211   M $CaCl_2$ range from 18.1 to 23.5º (Table 1; Figure 2B). However, apparent apical angles were

212   significantly smaller in 0.35 M NaCl (9.5º) and 1.7 M Na_2SO_4 (11.1º). The range of apical angles

213   (up to 40º) overlaps for experimental solutions with activities of water >0.9 (Figure 2B).

214   Apparent apical angles are larger (42.4º) in 3 M NaCl. The range of apical angles for diopside

215   chips weathered in near-saturated NaCl and $CaCl_2$ brines are greater than the range for more

216   dilute solutions, if outlier data points are not considered (Figure 2B).

217   **Discussion**

218   **Activity of water and weathering textures**

219   Velbel and Losiak (2010) surveyed denticle apical angles of both amphiboles and pyroxenes

220   with varying weathering histories to determine whether the mineralogy and alteration history of

221   an unknown grain, like one imaged on Mars' surface by the Phoenix lander (Hecht et al., 2009),

222   could be obtained. Their study demonstrated apparent apical angles were not diagnostic of grain

223   composition (Velbel and Losiak, 2010). Our research extends Velbel and Losiak's (2010) work

224   and demonstrates apparent apical angle also does not change systematically with activity of

225   water. Median apparent apical angles, with the exception of those measured on diopside grains

226   reacted with 3 M NaCl, overlap and have similar average values (Figure 2B).

227   Measured median denticle lengths in our study are also similar, with <1 μm difference in

228   average values between experimental trials (Figure 2A), indicating activity of water also does not

229   systematically influence denticle lengths. For example, our 0.35 M Na_2SO_4 ($a$$H_2O$=0.98) and 3

230   M NaCl ($a$$H_2O$=0.75) had the smallest median denticle lengths, but vary significantly in activity

231 of water (Figure 2A). In addition, while median denticle length decreased slightly with

232 decreasing activity of water in NaCl brines, the opposite trend was observed in NaSO$_4$ brines.

233 Therefore, our data indicate even when the parent material is well-constrained, neither denticle

234 length nor apparent apical angle are indicative of the activity of water of the weathering solution,

235 as similar denticle lengths and apparent apical angles can be formed under very different aqueous

236 alteration conditions.

237 ### Anion chemistry and weathering textures

238 In order to further clarify and distinguish the potential effects of different anions on denticle

239 formation, length, and apparent apical angles, we compared results of sodium chloride and

240 sodium sulfate experiments at different salt concentrations: low salinity (0.35 M) and near-

241 saturated brines (3 M NaCl and 1.7 M Na$_2$SO$_4$). We observed clear differences in the trends

242 between these two sets of solutions with different anion chemistries; however, overall quartile

243 ranges for the quantitative measurements overlap. In NaCl brines, median denticle lengths

244 decrease slightly (from 0.50 to 0.36 µm) and apical angles increase significantly (9.5 to 42.4º)

245 with increasing chloride salt concentration. However, the opposite trend is observed with

246 increasing concentration in Na$_2$SO$_4$ brines, where median denticle lengths increase significantly

247 (from 0.14 to 0.67 µm) and apical angles decrease slightly (from 23.5 to 11.1º). The contrasting

248 trends in measurements between the two solution sets suggests the dissolution mechanism may

249 be different between sodium chloride and sodium sulfate solutions at circum-neutral pH and/or

250 there is no clear trend in denticle length and apparent apical angle measurements with changing

251 anion chemistry. Given the non-systematic relationship between solution chemistry and denticle

252 length, as well as the general overlap in measurements between all the experiments, neither

253 apical angle nor denticle length are useful indicators of anion chemistry, particularly in more

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254   complicated natural solutions that likely contain a mixture of different ions.

255   While perchlorate has been typically considered an "indifferent" electrolyte for investigations

256   of mineral reactivity (e.g., Brown and Parks, 2001), we observed a much larger range of denticle

257   lengths in 2 M $NaClO_4$ brine compared to our NaCl and Na_2SO_4 experiments. Sanemasa and

258   Katsura (1973) stated that solutions containing up to 2 N $HClO_4$ and HCl had little effect on

259   synthetic diopside dissolution rates and extent of cation release compared to H_2SO_4; however,

260   they presented no data supporting their findings. In contrast, Sidhu et al. (1981) demonstrated a

261   range of perchlorate concentrations up to 2 M had no influence on the dissolution rate of iron

262   oxide minerals, while Cl^- ions produced faster dissolution rates. Our results show a much wider

263   range in denticle lengths produced in the perchlorate dissolution experiments compared to all the

264   other solution chemistries. This suggests perchlorate ions may interact differently with the

265   diopside surface, producing a wider variety of denticle lengths. We hypothesize that this may be

266   a result of redox reactions occurring at specific surface sites driven by sorption of highly

267   oxidized perchlorate anions. Although redox reactions between perchlorate and ferrous iron-

268   bearing minerals have not yet, to our knowledge, been demonstrated, it is well-established that

269   redox reactions influence the dissolution of iron-bearing pyroxene (e.g., Siever and Woodford,

270   1979; Schott and Berner, 1983; White et al., 1985; Burns, 1993; Hoch et al. 1996). These redox-

271   driven dissolution reactions may accelerate chemical weathering in specific locations on the

272   diopside surface leading to formation of much longer denticles in some areas of the sample. The

273   patchy development of protective iron (hydr)oxide and clay surface layers may influence

274   diffusion of reactants, thus leading to variability in dissolution textures across the mineral surface

275   (e.g., Siever and Woodford, 1979; Benzerara et al., 2005; Behrends et al., 2015). However, other

276   studies suggest that protective surface layers may not ultimately control the overall dissolution

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277 rate observed in natural weathering environments, depending on the ratio of molar volumes

278 between dissolving phases and secondary reaction products (Velbel, 1993) and the porosity of

279 the precipitates (e.g., Hodson, 2003; Lee et al., 2008). Therefore, individual measurements of

280 denticle lengths on weathered pyroxene minerals surfaces in systems exposed to perchlorate may

281 over-estimate the extent of aqueous alteration. Since perchlorate is commonly observed in Mars

282 surface samples (0.4-0.6 wt.%; Hecht et al., 2009; Navarro-Gonzalez et al., 2010; Glavin et al.,

283 2013), broader assessments of pyroxene weathering in the presence of perchlorate are needed to

284 provide context for any future denticle length measurements of pyroxene on/from Mars.

285 **Denticle length as a quantitative assessment of weathering extent**

286 Early laboratory studies conducted at either low pH (<4) and/or high temperature (50-90 ºC)

287 formed etch pits and denticle features similar to those observed in natural weathered soil profiles

288 (Brantley and Chen, 1995; Chen and Brantley, 1998). In contrast, 30-day dissolution experiments

289 at circumneutral pH and 22 ºC did not result in denticle formation (Werner et al., 1995), perhaps

290 due to the relatively short reaction times and slow reaction rates. However, etch pits and

291 denticles similar to those typically observed in natural systems formed in all of our 60 day

292 experiments, suggesting the duration of aqueous alteration may be the major control on denticle

293 formation. We observed microdenticles that have been previously linked to reactive solutions

294 that are acidic and/or undersaturated with respect to pyroxene (Velbel, 2011; Velbel, 2012) in

295 several of our experiments; however, we find no systematic variation with activity of water.

296 Previous studies have correlated pyroxene denticle length and extent of chemical weathering

297 in soil profiles, where denticle lengths decrease with increasing distance below the depth of first

298 chain silicate occurrence, reaching a minimum either where chemical weathering conditions

299 change (Argast, 1991) and/or as fresh bedrock surfaces are approached (Mikesell et al., 2004;

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300   Schaetzl et al., 2006). For example, in amphibole-bearing soils developed on glacially-influenced

301   sediments, denticle lengths ≥ 2 μm were common near the surface, but shorter denticles (<1 μm)

302   were observed at greater depths approaching incipiently altered bedrock (Hall and Michaud,

303   1988; Hall and Horn, 1993; Mikesell et al., 2004; Schaetzl et al., 2006). Therefore, quantitative

304   measures of median denticle lengths may be useful in constraining the duration of chemical

305   weathering, with denticles ≤ 1 μm indicating relatively brief periods of aqueous alteration.

306   Indeed, the relatively rapid formation of denticles observed in this study suggests even

307   geologically brief aqueous alteration events can result in significant changes to pyroxene surface

308   textures.   In contrast, longer denticles would be expected to be observed on pyroxene and

309   amphiboles that experienced longer weathering durations.

310   **Implications**
311   Our results demonstrate quantitative measurements of apical angles and denticle lengths do

312   not correlate with changing solution chemistry or activity of water in chloride, perchlorate, and

313   sulfate brines. Therefore, it is unlikely quantitative denticle measurements can be used to

314   constrain past aqueous chemistry on Mars. As this supports Velbel and Losiak's (2010) findings

315   in dilute solutions, we recommend abandoning quantitative measures of apparent apical angles as

316   a tool to determine aqueous alteration histories of pyroxene grains.

317   In contrast, quantitative comparisons of denticle lengths may provide insight into the

318   duration of aqueous alteration. Small scale (<1 μm) denticles are commonly observed in martian

319   meteorites, including ALH84001 (Thomas-Keptra et al., 2009; Velbel, 2011) and MIL 03346

320   (Velbel, 2012). These meteorites also contain veins with sulfate and chloride minerals, which

321   may indicate martian meteorites experienced aqueous alteration in saline conditions, similar to

322   those examined in this study, over relatively brief periods of geologic time.

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323   However, perchlorate salts may complicate simple applications of denticle length

324   measurements to interpret extent of weathering since a much wider range of measured denticle

325   lengths (but similar average value $\leq$1 μm) were produced in perchlorate brines compared to the

326   other solutions. Perchlorate brines may have been stable on the surface of Mars throughout its

327   history, and may be active on Mars' surface today (Chevrier et al., 2009; Ojha et al., 2015).

328   Perchlorate salts have been detected in martian meteorite EETA 79001 at concentrations of

329   0.6$\pm$0.1 ppm (Kounaves et al., 2014). Perchlorate was also detected by the Phoenix lander at 0.5-

330   0.7 wt.% (Hecht et al., 2009), suggesting it may be a common constituent in martian sediments.

331   Therefore, care must be taken when using quantitative denticle lengths as proxies for the extent

332   of aqueous alteration on Mars, including in returned samples, in order to ensure accurate

333   interpretations of chemical weathering duration.

334   Laboratory studies using well-mixed reactors typically represent the 'maximum' weathering

335   intensity possible; the ultimate lifetime and persistence of mineral grains in natural systems may

336   be much longer than that predicted from short-term weathering rates (Velbel, 2007; Olsen and

337   Rimstidt, 2007; Pritchett et al., 2012). For example, the relatively pristine clinopyroxene

338   textures compared with more extensive olivine alteration observed in nakhlites may be due to

339   fluid saturation with respect to pyroxene but remaining undersaturated with respect to olivine

340   (Velbel, 2016). On the other hand, quantitative weathering rates from olivine laboratory

341   experiments accurately predicted the time required to form etch pits in different laboratory

342   experiments (Velbel, 2014), indicating that laboratory experiments do constrain the timing of

343   mineral surface textural evolution.

344   Given these caveats, we recommend using qualitative comparisons of denticle lengths as

345   proxies for relative extent of weathering on Mars only in areas where the mineralogy, including

15

346   salts associated with pyroxene grains, are well-constrained. We further recommend incorporating

347   additional data, including qualitative weathering assessments that examine etch pit density, and

348   secondary mineral coverage, including clays formed on the mineral surface (Phillips-Lander et

349   al., 2017), to increase confidence in interpretations of weathering duration on Mars.

Acknowledgements

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543

544   **Figure Captions**

545   Figure 1: Diopside dissolution textures observed with SEM indicate denticles in all images

546   are ≤ 1 μm. Denticle lengths and apparent apical angles were measured using ImageJ as shown in

547   (A). Systematic changes in denticle lengths or apparent apical angles were not observable with

548   increasing salinity between (B) 0.35 M NaCl and (E) 3 M NaCl or (C) 0.35 M Na_2SO_4 and (F)

549   1.7 M Na_2SO_4 or decreasing activity of water. Microdenticles are observed on pyroxene in

550   almost all images, except (A) UPW, (B) 0.35 M NaCl, (F) 1.7 M Na_2SO_4, and (G) 4.5 M $CaCl_2$.

551   These samples represent a very dilute solution (aH$_2$O=0.99) and a concentrated brine

552   (aH$_2$O=0.35).

553   Figure 2: Box and whisker plots of diopside (A) denticle lengths and (B) apparent apical

554   angles display no clear trends with respect to changes in activity of water. (A) Denticle lengths

555   are significantly longer in 2 M $NaClO_4$. (B) With the exception of 3 M NaCl, apparent apical

556   angles are within range of each other. However, if outlier points are considered, apical angles in

557   all samples are similar.

558

559

Tables

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

Solution	UPW	0.35 M NaCl	0.35 M Na$_2$SO$_4$	1.7 M Na$_2$SO$_4$	2 M NaClO$_4$	3 M NaCl	4.5 M CaCl$_2$
*a*H$_2$O	1.0	0.99	0.98	0.95	0.93	0.75	0.35
Number of Measurements	77	118	230	112	85	50	21
Denticle Length (μm)							
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
Stnd. Dev.	0.79	0.32	0.15	0.43	1.5	0.28	0.59
Apparent Apical Angle (º)							
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
Stnd. Dev.	12.1	8.84	7.55	10.1	7.10	16.1	13.2

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