**AQUEOUS CORROSION OF OLIVINE IN THE MARS METEORITE MILLER
RANGE (MIL) 03346 DURING ANTARCTIC WEATHERING:
IMPLICATIONS FOR WATER ON MARS**

Michael A. Velbel^{1,2*}

¹Division of Meteorites, Department of Mineral Sciences
National Museum of Natural History, Smithsonian Institution
10th and Constitution Avenues NW, Washington, DC 20560-0119

²Permanent address:

Department of Geological Sciences
206 Natural Science Building, 288 Farm Lane
Michigan State University
East Lansing, MI 48824-1115

*Corresponding author. E-mail address: velbel@msu.edu (M.A. Velbel).

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ABSTRACT

Several nakhlites (clinopyroxenite meteorites from Mars) contain olivine phenocrysts with corrosion features identical in size, shape and distribution to the smaller etch-pits of well-characterized weathered terrestrial olivine. Miller Range (MIL) 03346 is an Antarctic nakhlite find, recovered after long exposure to Antarctic conditions. The distribution of discrete olivine etch-pits almost exclusively within a few hundred microns of allocation MIL 03346,171's documentably exposed surface suggests that they formed by terrestrial weathering in Antarctica. The small size of olivine etch-pits in MIL 03346,171 relative to commonly much larger etch-pits in even incipiently weathered terrestrial examples suggests that the duration of its exposure to weathering conditions was short, or the weathering conditions to which it was exposed did not favor olivine corrosion (in the form of etch-pit formation), or both. Time-scales for the formation of etch-pits, estimated from experimentally determined dissolution rates of olivine over a range of pHs, are comparable to the measured terrestrial age of the meteorite and short relative to the time available for possible similar corrosion on Mars. Etch-pits of the observed size on MIL 03346 olivine phenocrysts would be relatively easy to form supraglacially under brief episodic acidic Antarctic conditions, but the terrestrial age of MIL 03346 is long enough that its olivine might have been weathered to the observed state by englacial films of alkaline Antarctic water. The paucity of similar etch-pits in olivine from the interior of MIL 03346 suggests that olivine in this Mars meteorite was exposed to even less aqueous alteration after iddingsitization during its 1.3 billion years on Mars than its exterior was subjected to during its Pleistocene-Holocene exposure to Antarctic weathering conditions.

1. INTRODUCTION

Olivine dissolution during weathering requires aqueous solutions that are undersaturated with respect to olivine. Etch-pits are site-selective, crystallographically distributed, and crystallographically oriented mineral-surface dissolution and corrosion features of negative relief (e.g., Berner, 1978; Brantley et al., 1986). Correspondingly distributed and oriented conical or domical features of positive relief include those formerly known as mammillary surfaces (e.g., Velbel and Ranck, 2008). Etch-pits and anhedral positive-relief features are widely recognized textural indicators of site-selective mineral-surface destruction during corrosive dissolution (etching; Velbel, 2009). The presence of etch-pits or other corrosion features on olivine-product interfaces distinguishes aqueous alteration environments in which the solutions were thermodynamically and kinetically favorable to olivine destruction (e.g., undersaturated with respect to olivine dissolution at conditions favoring reaction) from those in which solutions were not destructive of olivine, and corrosion features are absent. Etch-pits may form either before or concurrently with other alteration products, and both unmodified olivine and etched olivine may subsequently serve as a passive substrate for precipitation of secondary minerals (Velbel, 2012).

Nakhlites (clinopyroxenite meteorites from Mars) are one of several groups of Mars meteorites that contain olivine (e.g., Treiman 2005), and the site on Mars from which nakhlites were ejected is inferred to have contained a range of mineral-water interaction microenvironments (Gooding et al., 1991; Treiman et al., 1993; Bridges and Grady, 1999, 2000; Bridges et al., 2001; Tosca and McLennan, 2006; Tosca et al., 2008; Velbel, 2012; Lee et al., 2013, 2015a,b; Stopar et al., 2013; Tomkinson et al., 2013; Needham et al., 2013). In Nakhla (a witnessed meteorite fall, and the namesake of the nakhlite group), abundant evidence for pre-terrestrial phyllosilicate-like phases, carbonates, sulfates, and halite indicates Nakhla was

McCoy et al. (2011) provide an excellent short overview of the many important scientific contributions enabled by study of Mars meteorites (used here to mean “meteorites from Mars” rather than “meteorites found on Mars”); Velbel (2012) provides a longer review specific to aqueous alteration phenomena in Mars meteorites. This section summarizes the fundamentals of distinguishing terrestrial from pre-terrestrial aqueous alteration of stony meteorites, important attributes of the category of meteorites from which one was selected for this study, and previous work on olivine corrosion during weathering. Some of this background material is updated from Velbel (2009, 2012).

2.1 Olivine in Mars Meteorites

Olivine is a major constituent of several groups of Mars meteorites. The chassignites consist almost entirely of olivine, the lherzolithic shergottites contain up to 60 vol % olivine, and the nakhlites contain up to 20 vol % ferroan olivine with compositions ranging (due mainly to compositional zoning) between Fo_{~14-43} (Treiman 2005; Meyer 2009, his Table 1; Corrigan et al., 2015). Many Mars meteorites contain small quantities of aqueous alteration minerals, some of which are associated with olivine (Reid and Bunch, 1975; Gooding, 1986a,b; Gooding and Muenow, 1986; Gooding et al., 1988, 1991; Treiman et al., 1993; Wentworth and Gooding, 1993, 1994; Bridges and Grady, 1999, 2000; Bridges et al., 2001; Treiman, 2005; Wentworth et al., 2005; Leshin and Vicenzi, 2006; Fisk et al., 2006; McSween, 2008; Meyer, 2009; Noguchi et al., 2009; Changela and Bridges, 2011; Hallis and Taylor, 2011; Velbel, 2012; Bridges and Schwenzer, 2012; Lee et al., 2013, 2015a,b; Stopar et al., 2013; Tomkinson et al., 2013; Needham et al., 2013; Kuebler, 2013; Hallis et al., 2014; Hicks et al., 2014).

2.2 The Nakhrites

Nakhrites (nine examples presently known) are clinopyroxenites with radiometric crystallization ages of ~1.3 Ga (Treiman, 2005). Chassignites (presently known from three examples) are dunites with radiometric crystallization ages ~1.3 Ga (McSween, 1994, 2002; Meyer, 2009). At present, the best estimate for the age of the Hesperian-Amazonian boundary is ~3.2-2.0 Ga (Hartmann, 2005; Soderblom and Bell, 2008); thus, igneous crystallization ages of nakhrites and chassignites fall within the Amazonian, the most recent of the three major intervals of Mars' geologic time. Nakhrites are the largest and longest known group of Mars meteorites to contain noteworthy abundances of phyllosilicate-like minerals; consequently, their aqueous alteration features are well-studied (Reid and Bunch, 1975; Gooding et al., 1991; Treiman et al., 1993; Treiman and Lindstrom, 1997; Bridges and Grady, 2000; Bridges et al., 2001; Gillet et al., 2002; Treiman, 2005; Leshin and Vicenzi, 2006; Noguchi et al., 2009; Hallis and Taylor, 2011; Changela and Bridges, 2011; Velbel, 2012; Lee et al., 2013, 2015a,b; Stopar et al., 2013; Tomkinson et al., 2013; Kuebler 2013; Hallis et al., 2014; Hicks et al., 2014).

Ejection (cosmic-ray exposure) ages of the two longest-known chassignites (Chassigny and Northwest Africa 2737) and all of the longer-known and, therefore, most thoroughly studied nakhrites (Nakhla, Governador Valadares, Lafayette, the Yamato 000593 pairing group, and Northwest Africa 817) are similar (10.1-12.2 Myr; Fritz et al., 2005; Herzog, 2005; Eugster et al., 2006; McSween, 2008; Korochantseva et al., 2011); ejection ages have not yet been

determined for all of the most recently recovered nakhlites. The ejection ages suggest that all the nakhlite and chassignite meteorites for which CRE ages are known from the cited references not only have essentially identical igneous crystallization ages ($\sim 1.3 \pm 0.1$ Ga; McSween, 1994, 2008; Treiman, 2005) but were also all ejected together with one another, at a different time than the ejection of other Mars meteorites (Fritz et al., 2005; Herzog, 2005; Eugster et al., 2006; McSween, 2008; Korochantseva et al., 2011).

The insight that multiple nakhlites and chassignites may sample the same source locality on Mars led petrologists to interpret the longest-known nakhlites as different samples of the same thick flow or shallow sill (Harvey and McSween, 1992; Friedman Lentz et al., 1999; Lentz et al., 2011; Corrigan et al., 2015). With the subsequent recovery, recognition, and study of more nakhlite finds, systematic variations among nakhlites in compositional zoning or homogeneity of olivine and pyroxenes crystals have been revealed. Together with the degree of crystallization and devitrification of interstitial igneous glass, these features are interpreted to indicate that different nakhlites sample different emplacement depths, up to tens of meters from the cooling surfaces of the flow or sill (Mikouchi et al., 2003, 2005, 2006, 2012; McKay et al., 2007; Corrigan et al., 2015). Nakhlites with interstitial glass and compositionally zoned olivine and pyroxene crystals are interpreted to have cooled quickly, near the chilled margins of the emplacement unit, while nakhlites with devitrified interstitial glass and compositionally homogenous olivines and pyroxenes cooled slowly in its interior (Mikouchi et al., 2003, 2005, 2006; Treiman, 2005; McKay et al., 2007; Corrigan et al., 2015). The inferred solidification products of this magma body (Friedman Lentz et al., 1999) are collectively referred to as the “nakhlite stack” (Mikouchi et al., 2003, 2005, 2006; McKay et al., 2007; Corrigan et al., 2015).

Thus, the nakhlites with ~11 Ma ejection ages may all represent samples of different parts of the same emplacement unit on Mars, all ejected at the same time during the same impact.

2.3 Distinguishing Pre-terrestrial from Terrestrial Aqueous Alteration in Meteorites from Mars

Fusion crust on stony (silicate) meteorites is the last (quenched) remnant of the outermost melted and ablated surface, produced by frictional heating during the high-temperature, bright-flight episode of the meteoroid's passage through Earth's atmosphere (Bevan and de Laeter, 2002). The fusion crust is a relative-age datum for distinguishing pre-terrestrial (including parent-body) from terrestrial (post-arrival) phenomena (e.g., Gooding, 1986a). Only one nakhlite (Nakhla) is a *fall*, recovered promptly after witnessed arrival and with minimal post-fall terrestrial aqueous alteration. Most Mars meteorites available for scientific study (including all nakhlites other than Nakhla) are *finds*, recovered after unwitnessed arrival and some exposure to the terrestrial surface environment, often over millennial or longer timescales. In both falls and finds, aqueous alteration minerals crosscut by or metamorphosed (used in this context to mean mineral and textural consequences of heating during the high-temperature interval of the meteoroid's passage through Earth's atmosphere) immediately beneath the fusion crust are pre-terrestrial and record aqueous alteration on their parent body; Reid and Bunch (1975), Gooding et al. (1991), Treiman et al. (1993), and Wentworth et al. (2005) discuss this phenomenon specifically with respect to nakhlites. In finds, effects of terrestrial aqueous weathering and contamination that crosscut and/or are superimposed upon the fusion crust are of terrestrial

origin, and may indicate modification of pre-terrestrial aqueous-alteration mineral assemblages near the fusion crust as well. Such phenomena are broadly understood for stony meteorites in general (Gooding, 1986a,b; Velbel and Gooding, 1990; Velbel et al., 1991; Losiak and Velbel, 2011; Velbel and Palmer, 2011; Velbel, 2014a), achondritic meteorites (Gooding, 1986a), and Mars meteorites in particular (Gooding and Muenow, 1986; Gooding et al., 1988, 1991; Schwandt, 2005; Treiman, 2005; Hallis and Taylor, 2011; Velbel, 2012; Hallis, 2013; Stopar et al., 2013).

Alteration veins dominated by poorly crystalline silicate material with phyllosilicate-like compositions occur widely in the olivine of most (but not all) nakhlites. The vein material is called “iddingsite” by nakhlite specialists (following Reid and Bunch, 1975), mainly on the basis of the veins’ elemental composition and association with olivine. Sparsely distributed domains in the iddingsite veins of some nakhlites exhibit lattice fringes in transmitted electron microscopy, indicating that nakhlite iddingsite contains minor crystalline phyllosilicate and opal-A, and is closely associated with carbonates and/or sulfates (see review by Velbel, 2012 and primary references therein; also, Lee et al., 2013, 2015a,b; Hicks et al., 2014).

Examination of Mars-meteorite falls presumably sheds light on pre-terrestrial (Martian) aqueous alteration of Mars meteorite primary minerals. Nakhla is the only witnessed fall among the nakhlites, and was, therefore, exposed to the terrestrial weathering environment for the shortest amount of time. Heating and devolatilization effects exhibited by “iddingsite” veins, and annealing of the host olivine, immediately beneath fusion crust indicate that iddingsite veins pre-date the fusion crust and are thus pre-terrestrial (most likely martian) in origin in Nakhla (Gooding et al., 1991; Wentworth et al., 2005). Nevertheless, even Nakhla shows evidence of

terrestrial effects; Hallis et al. (2012) showed that the D/H ratio of Nakhla “iddingsite” has been substantially modified by isotopic exchange with the terrestrial environment.

All nakhlites other than Nakhla are finds, recovered after exposure to the terrestrial surface environment that may have modified pre-terrestrial aqueous-alteration mineral assemblages and produced new (terrestrial) weathering-product assemblages (Treiman et al., 1993; Treiman, 2005; Hallis and Taylor, 2011; Velbel, 2012; Hallis, 2013; Stopar et al., 2013). Both pre-terrestrial and terrestrial alteration are inferred to have occurred in the nakhlite examined here, Miller Range (MIL) 03346 (Hallis and Taylor, 2011; Lee et al., 2013; Stopar et al., 2013; Kuebler, 2013), and its putative pair MIL 090032 (Hallis et al., 2014). Iddingsite veins that are vesiculated (devolatilized) immediately beneath fusion crust in MIL 03346 (Stopar et al., 2013, their Fig. 9) were present when fusion crust formed, therefore pre-date the meteoroid’s entry into Earth’s atmosphere, and are of preterrestrial origin. Veins that crosscut (fill fractures in) fusion crust in MIL 03346 (Velbel, 2012, Fig. 3; Stopar et al., 2013, Fig. 10A) are not vesicular, post-date Earth arrival, and are terrestrial in origin. Systematic study to distinguish pre-terrestrial from terrestrial aqueous alteration features and products is required to derive the maximum scientific value for Mars science from Mars meteorites finds.

This study takes advantage of the natural long-term Antarctic cold-desert weathering to which one nakhlite find was exposed, as a “natural experiment” to evaluate the response of Mars’ olivine (one of the two primary igneous major minerals of nakhlites) to weathering in the presence of small quantities of cold, dilute water over sub-million-year timescales. The insight gained may shed some new light on how similar cold-desert conditions may affect olivine during weathering on post-Hesperian Mars.

2.4 Olivine Corrosion During Weathering of Terrestrial Olivine

Etch-pits produced during weathering of terrestrial olivine were previously examined in detail by Velbel (2009) and are summarized here. Naturally weathered olivine crystals in a variety of terrestrial igneous and metamorphic rocks are all similarly corroded. Etch-pits tens of microns or larger in size occur on forsterite in a variety of weathered rocks and geomorphic settings. These include olivines in weathered Paleozoic dunites exposed and weathered long after crystallization, in minimally weathered corestones in spheroidally weathered Plio-Pleistocene extrusive igneous rocks exposed and weathered long after eruption and emplacement, and on minimally weathered surfaces of Holocene extrusive flows exposed continuously since eruption (Patino et al., 2003; Velbel, 2009). Ample time evidently exists in these diverse terrestrial geomorphic settings and weathering environments for episodes of exposure to terrestrial weathering and consequent etching of olivine.

Conical (funnel-shaped) etch-pits occur as individual pits, base-to-base (biconical) pairs of cone-shaped pits (joined at their bases, resembling funnels joined mouth-to-mouth), or *en echelon* arrays. Velbel (2009) noted that experimentally dissolved fayalite exhibits etch-pits similar to those of naturally weathered forsterite. Cross-sections through entire biconical etch-pits (pairs of cones joined at their bases) are rhombic (diamond-shaped). In backscattered-electron images of polished thin sections, cross-sections through conical etch-pits of all sizes, or portions of biconical etch-pits, at grain boundaries, fractures, and contacts with veins of alteration products or inclusions are triangular (wedge-shaped) notches (Figure 1; see also Velbel, 2009 for other examples). Wedges or wedge-shaped notches are the observed features in (two-dimensional) cross-sections of etch pits along fracture margins, from which the occurrence

of (three-dimensional) etch-pits is inferred, based on the relationships described by Velbel (2009). Serrated margins, or more jagged shapes, form by the coalescence of multiple diamond-shaped pits nucleated on dislocation arrays (Figure 2; see also Velbel, 2009; Nowicki and Velbel, 2011). The conical surfaces of naturally weathered olivine etch-pits on terrestrial olivines examined to date do not conform to individual crystal planes and faces of the dissolving olivine's crystal structure (Velbel, 2009).

The etch-pits on naturally weathered terrestrial olivines studied by Velbel (2009) are commonly as large as 100 μm in diameter, with the smallest pits below the limit of scanning electron microscope (SEM) resolution (~ 20 nm). Etch-pit shapes and orientations in the smallest etch-pit arrays visible in conventional SEM resemble even smaller features reported from transmission electron microscope (TEM) investigations of aqueous olivine weathering (Eggerton, 1986; Banfield et al., 1990) and serpentinization (Boudier et al., 2010; Plümper et al., 2012). Similarity of corrosion forms resulting from naturally weathered olivine from multiple parent-rock bodies suggests that olivine weathers in the same manner regardless of its specific crystallization/recrystallization history, eruption/weathering/exposure ages of the olivine's host rock, and the local regolith.

The theory for the development of etch-pits at dislocation outcrops is well developed, and the role of strain energy in the locally distorted crystal structure around a screw or edge dislocation is well understood to affect both the dissolution kinetics of silicate minerals and etch-pit morphology. With increasing undersaturation of the aqueous medium into which minerals dissolve, both the activation-energy barrier to etch-pit nucleation and the size of critical etch-pits decrease, and etch-pit morphologies change (Brantley et al., 1986; Lasaga and Blum, 1986; Blum and Lasaga, 1987; Lasaga, 1998). Geometric relationships among etch-pits and other

textural features on olivine-void and olivine-product interfaces yield insight into the nature of the crystal imperfection with which etching is associated (Velbel, 2009, 2012). Corrosion of olivine, and/or corrosive replacement of olivine by veins of alteration products, originating along a dislocation array to the extent that etch-pits overlap and coalesce (Figure 3 in Velbel, 2009) results in mirror-image counterpart wedges and/or serrations or crenulations on the opposite interfaces of an empty cavity in the case of corrosion, or of veins of alteration products in the case of corrosive replacement (Figures 1, 2) (Velbel, 2009; Boudier et al., 2010; Plümper et al., 2012). However, corrosion of olivine, corrosive replacement of olivine by veins of alteration products, or both, originating on opposing surfaces of a fracture through olivine result in wedges or serrations *without* counterparts on opposing interfaces of cavities or veins of alteration products (Figure 1) (Velbel, 2009).

Velbel et al. (2007) and Velbel (2014b) calculated timescales of etch-pit formation on naturally weathered garnet and experimentally dissolved olivine grains, respectively, using experimentally determined dissolution rates to estimate the time required to form etch-pits of observed dimensions. For simplicity, as a first approximation, hemispherical etch-pit geometry is assumed. This approach assumes that all dissolution occurs at the walls of etch-pits; in other words, that all reactive surface area on naturally corroded olivines is within etch-pits, and that the olivine surface between etch-pits is not reactive. This assumption is invoked because it is consistent with observed grain-surface morphologies of garnet and olivine after overlap and coalescence of etch-pits (Velbel et al., 2007; Velbel, 2014b). The inferred dominance of mass loss by dissolution from etch-pit walls over other surfaces is embodied in the equations used by Velbel et al. (2007) and Velbel (2014b). (This approach is slightly different from that of Stopar et al., 2006, and Olsen and Rimstidt, 2007. Their equations are for reduction of grain size, and

corresponding decrease of surface area, by areally averaged dissolution. This process is not the same as the site-selective removal of volume that produces etch pits, during which process the surface area of the etch pit *increases* as its wall dissolves radially outward from its surface-nucleation site. Calculations using the two approaches differ only by a small integer.) Different assumptions about the specific geometry of an etch-pit result in surface-area estimates that vary by less than a factor of two from a simple hemispherical pit (Velbel, 2014b). Given that other sources of uncertainty in mass-time relationships of silicate-mineral dissolution rates during natural weathering can be up to four orders-of-magnitude, the factor-of-two or -three effects of differing geometric assumptions about the shapes and surface areas of the etch-pits are trivial for this application. Only if other parameters are known to within much less than a factor of three will details of etch-pit shape discernably affect etch-pit formation times estimated using the approach of Velbel et al. (2007) and Velbel (2014b).

3. MATERIALS AND METHODS

3.1 Miller Range (MIL) 03346

MIL 03346 is an Antarctic nakhlite find. The original recovered mass was 715.2 g. The U.S. Antarctic Meteorite Classification Database (Astromaterials Curation at NASA JSC website, <http://curator.jsc.nasa.gov/antmet/>) classifies MIL 03346 as the most fractured U.S. Antarctic Mars meteorite recovered to date and, at weathering category B, it is more weathered than at least half of all other U.S. Antarctic Mars meteorites. Its main constituents are clinopyroxene, olivine, and mesostasis; several papers provide detailed descriptions and

interpretations of its igneous petrology and petrogenesis (Treiman, 2005; Dyar et al., 2005; Day et al., 2006; Imae and Ikeda, 2007; Hallis and Taylor, 2011; Udry et al., 2012; Corrigan et al., 2015). MIL 03346 has glassy mesostasis rather than the crystalline groundmass of most other nakhlites, shows a range of compositions in its compositionally zoned olivine, and has the highest mean Al_2O_3 content in the cores of its zoned augites; taken together these characteristics all suggest that MIL 03346 cooled more rapidly than any of the other nakhlites (except possibly the recently recognized NWA 5790), and may therefore be one of the uppermost samples available from the “nakhlite stack” (Mikouchi et al., 2003, 2005, 2006, 2012; McKay et al., 2007).

Hallis and Taylor (2011) examined both primary and secondary minerals and features in thin-sections of MIL 03346. They mentioned but did not image etch-pits in olivine. Also, in contrast to their treatment of how secondary minerals are distributed among different allocations originating from various distances from the exterior of the as-found meteorite, Hallis and Taylor (2011) did not describe the distribution of the olivine etch-pits relative to the meteorite’s exterior. In the absence of knowing the spatial distribution of the etch-pits throughout the meteorite, hypotheses of pre-terrestrial (on Mars) or terrestrial (weathering after the meteorite’s fall) etching of the olivine cannot be distinguished from one another. However, by selecting a sample with intact fusion crust, this study explicitly narrows this knowledge gap.

Allocation MIL 03346,171 was examined for this study. It was prepared from split MIL 03346,23, and includes fusion crust along part of one long edge. The relationship of specific alteration features to fusion crust allows terrestrial alteration minerals and features to be distinguished from those formed by pre-terrestrial aqueous alteration (Reid and Bunch, 1975; Gooding and Muenow, 1986; Gooding et al., 1988, 1991; Treiman et al., 1993; Schwandt, 2005;

Treiman, 2005; Wentworth et al., 2005; Velbel, 2012). Although some other allocations of MIL 03346 may also have originated near the surface of the main mass, the preserved fusion crust indicates unequivocally that split ,23 was at the surface of the main mass between fall and recovery. Assuming that thin section MIL 03346,171 was cut perpendicular to the fusion crust, the most distal portion of the section is ~4 mm from the fusion crust.

3.2 Methods

Polished thin-section MIL 03346,171 was examined using transmitted polarized-light microscopy, and scanning electron microscopy (SEM) in backscattered-electron imaging (BEI) mode with energy-dispersive spectroscopy (EDS) using a JEOL 6400 SEM at the Center for Advanced Microscopy at Michigan State University. This instrument was equipped with a conventional (LaB₆) emitter, digital image acquisition, and Noran and Oxford energy dispersive spectroscopy (EDS) systems, with point-to-point spatial resolution of ~20 nm in imaging mode. BEI is used here to examine two-dimensional (cross-section) slices through grains, and gives insight into the penetration of corrosion features from grain boundaries and trans-mineral fractures into grain interiors.

4. RESULTS

MIL 03346,171 contains only two olivine phenocrysts. This is consistent with previous petrographic work on MIL 03346 in that MIL 03346 contains a lower modal abundance of olivine than any other previously described nakhlite (Treiman, 2005; Day et al., 2006; Imae and Ikeda, 2007; Udry et al., 2012; Corrigan et al., 2015), including the other three members of its

proposed pairing group: MIL 090030, MIL 090032, and MIL 090136 (Hallis and Taylor, 2011; Udry et al., 2012; Corrigan et al., 2015). Both olivine phenocrysts in MIL 03346,171 are truncated remnants of more or less equant, possibly circular sections slightly more than 1 mm in diameter, as preserved and transected. The one approximately 3 mm below the fusion crust is truncated by the bounding fracture of the rock chip from which the thin-section was cut, and is referred to as the interior or inner olivine phenocryst of this MIL 03346 allocation; the other is transected by the fusion crust (Figure 3) and is referred to as the exterior or outer olivine phenocryst. Alteration features in the interior olivine phenocryst are similar to olivine alteration features described in previous work on other nakhlites (Reid and Bunch, 1975; Gooding et al., 1991; Treiman et al., 1993; Bridges and Grady, 2000; Bridges et al., 2001; Gillet et al., 2002; Treiman, 2005; Leshin and Vicenzi, 2006; Noguchi et al., 2009; Changela and Bridges, 2011; Velbel, 2012; Lee et al., 2013, 2015a,b; Tomkinson et al., 2013; Hallis et al., 2014; Hicks et al., 2014) and in other (all interior) allocations of MIL 03346 examined by previous workers (Hallis and Taylor, 2011; Stopar et al., 2013; Kuebler, 2013). In the interest of brevity, these common features are referred to as occurring in interior olivines of this and previously examined allocations of MIL 03346, and their characteristics are not re-described here.

The exterior olivine phenocryst (Figure 3) hosts several melt inclusions, has grown around unzoned augite cores, and is surrounded by compositionally zoned clinopyroxene and mesostasis. The host olivine phenocryst, the largest preserved melt inclusion, and alteration-product veins, are all transected by fusion crust (Figure 3).

The maximum perpendicular distance from fusion crust to the distal edge of the exterior olivine phenocryst is approximately 600 μm (Figure 3). The vein material most distal from the fusion crust has homogenous atomic-number contrast (electron backscattering properties) at the

imaged resolution (see vein adjacent to “H” in Figure 4) and is in this regard identical to veins of alteration products in the interior olivine phenocryst of this allocation (Velbel, 2012, Figure 5a therein) and in other previously reported olivine phenocrysts in other interior allocations of MIL 03346 (Hallis and Taylor, 2011; Stopar et al., 2013). Between approximately 500-300 μm from the fusion crust, micron-scale laminar variations in atomic-number contrast appear (see “L” in Figure 4). Veins of alteration products less than approximately 300-200 μm from the fusion crust are vesiculated, and the solid material exhibits variegated atomic-number contrast (Figure 5).

Individual wedge-shaped notches up to 2 μm in long dimension occur on olivine along olivine-vein interfaces within a few hundred microns of the meteorite’s surface (Figures 5-8). Counterpart wedges or notches do not occur on the opposite interfaces symmetrically across the veins of alteration products. Some such notches or wedges are associated with vesicular alteration product in exterior olivine phenocryst (Figures 5-7); others occur along fractures that appear to lack alteration products (Figure 8).

5. DISCUSSION

5.1 Olivine Corrosion Textures in MIL 03346

5.1.1 Pre-terrestrial alteration

Pre-terrestrial alteration features in terrestrially unweathered olivine >3 mm inward from the fusion crust of MIL 03346,171 are identical to alteration features at olivine-vein interfaces that have been illustrated (often without comment in early papers) from other nakhlites

(Lafayette; Nakhla; Governador Valadares; Y-000593 and one of the two other members of its pairing group, Y-000749); other thin-sections of MIL 03346 at undetermined distances from fusion crust; and the three other members of the MIL 03346 pairing group, MIL 090030, MIL 090032, and MIL 090132), by numerous workers (Treiman et al., 1993; Bridges and Grady, 2000; Bridges et al., 2001; Treiman, 2005; Leshin and Vicenzi, 2006; Noguchi et al., 2009; Changela and Bridges, 2011; Hallis and Taylor, 2011; Velbel, 2012; Lee et al., 2013, 2015a,b; Stopar et al., 2013; Tomkinson et al., 2013; Kuebler, 2013; Hicks et al., 2014; Hallis et al., 2014).

Veins of alteration products petrographically similar to those in interior olivine phenocrysts in this and other allocations of MIL 03346 (e.g., Hallis and Taylor, 2011; Velbel, 2012; Stopar et al., 2013; Kuebler, 2013) are crosscut by and metamorphosed near the fusion crust (Figures 3-5). The veins of alteration products most distal from the fusion crust have homogenous atomic-number contrast and are visually identical to vein material in the interior olivine phenocrysts of this and other MIL 03346 allocations (Hallis and Taylor, 2011; Velbel, 2012; Stopar et al., 2013; Kuebler, 2013). Between approximately 600-300 μm from the fusion crust, laminar atomic-number contrast variations appear (Figure 4). Closer to (within approximately 300-200 μm of) the fusion crust the main vein of alteration products is vesiculated and exhibits variegated atomic-number contrast (Figures 5-7); smaller branching veins are also vesiculated but exhibit homogenous atomic-number contrast (Figures 5-7). These variations with proximity to the fusion crust suggest that the vein of alteration products was devolatilized by heating, during passage of the meteoroid through Earth's atmosphere, and further suggest the vein material was volatile-bearing prior to the meteoroid's arrival at Earth. The evidence suggests that the volatile-bearing vein material was pre-terrestrial and almost certainly Martian,

consistent with the inferences of previous workers from other nakhlites and previous work on MIL 03346 (Stopar et al., 2013) and other members of its pairing group (Hallis, 2013). Characterization of individual phases in iddingsite veins and branching veins, and veins cross-cutting fusion crust, including their compositions, textures, and parageneses, continues and will be the subject of a future contribution.

5.1.2 Terrestrial alteration

Individual wedge-shaped notches up to 2 μm in their long dimension occur in the exterior olivine phenocryst of MIL 03346,171 (Figures 5-8). They resemble cross-sections through individual etch-pits of typical form for olivine produced by incipient crystallographically controlled corrosion of olivine from weathered terrestrial basalt and dunite as reported and illustrated by Velbel (2009, 2012). These small etch-pit cross-sections are common along olivine-vein interfaces in the MIL 03346,171 exterior olivine phenocryst within a few hundred microns of the meteorite's surface (Figures 5-8), were not previously reported from olivine phenocrysts in other interior allocations (Stopar et al., 2013), were not observed on the interior olivine of the MIL 03346 allocation examined here (Velbel, 2012), and are smaller than serrations and notches associated with vein material in the olivine phenocrysts of interior MIL 03346 allocations (Hallis and Taylor, 2011; Stopar et al., 2013). The fact that mirror-image counterpart wedges or notches do not occur on the opposite olivine interfaces across the veins of alteration products suggests that corrosion of olivine and/or corrosive replacement of olivine by alteration products originated on opposing surfaces of a fracture through olivine, not along a dislocation array. Perfect fit of opposing surfaces along the narrowest etched surfaces in the exterior olivine phenocryst (Figures 5, 8) is similar to the perfect fit of opposing surfaces along

recent product-free fractures in the interior olivine phenocrysts of this and other MIL 03346 allocations (Hallis and Taylor, 2011; Stopar et al., 2013) and also consistent with fracturing. Some such notches or wedges are associated with veins of vesicular alteration products in the exterior olivine phenocryst (Figure 5-7); others occur along fractures apparently lacking discrete alteration products or veins of alteration products (Figure 8).

In contrast to the empty olivine-vein gaps in the olivine phenocrysts of some interior allocations of MIL 03346 (Hallis and Taylor, 2011; Velbel, 2012), near the fusion crust the exterior olivine phenocryst contains no empty gaps or fractures between olivine and veins; instead, veins completely fill the space between olivine volumes with material of variegated atomic-number contrast (Figures 5-7). Fully occupied fractures (excluding fractures clearly resulting from sample processing) near the weathering-exposed surface suggest that the pre-terrestrial veins of iddingsitic alteration products were thermally metamorphosed near the fusion crust (Stopar et al., 2013), and that associated sulfates were precipitated, after the last episode of fracture dilation. This stands in contrast to iddingsite veins in this allocation's interior, in which volume change produced vacant olivine-vein fractures after the most recent event that formed or modified the vein mineral(s) themselves. By this textural reasoning, some vein mineralization in the exterior olivine phenocryst of MIL 03346,171 postdates that of the interior olivine phenocrysts in this and other previously examined (interior) MIL 03346 allocations. Possible compositional variations among different vein materials with similar atomic-number contrast remain to be established by future work, but olivine-hosted iddingsite alteration veins and sulfates in MIL 03346,171 resemble those reported from other MIL 03346 allocations by Hallis and Taylor (2011), Hallis (2013), Stopar et al. (2013), and Kuebler (2013), and from Y-000749 by Changela and Bridges (2011). In general, small etch-pits along such veins of alteration

products may have formed before, concurrently with, or after vein mineralization; however, given that the evidence presented here suggests that vein-margin mineralization in the outermost exterior olivine phenocryst post-dates both the alteration products in interior olivine phenocrysts of this and other MIL 03346 allocations and the last post-product fracturing, the etch-pits along thermally metamorphosed iddingsite veins near the fusion crust may be among the most recently formed aqueous alteration features in the thin-section. The occurrence of these small etch-pits predominantly within a few hundred microns of fusion crust and exclusively along thermally metamorphosed vein material or unmineralized fractures is consistent with a terrestrial (late) origin. These etch-pits are likely to be among the most recently formed aqueous alteration features in the thin-section.

Association of these small etch-pits with proximity to fusion crust (as distinct from uniform distribution of larger serrations and/or wedge-shaped notches throughout the meteorite at greater, but uncertain, distance from the weathering-exposure surface; Hallis and Taylor, 2011; Stopar et al., 2013; Kuebler, 2013), with late-stage fractures, and with late-stage aqueous alteration minerals that occur exclusively near the fusion-crust datum marking the terrestrial exposure surface, suggests that surface-proximal olivine corrosion is no older than the fusion crust, consistent with it being a terrestrial weathering effect, and not exclusively the result of aqueous alteration of olivine on Mars. It also suggests that small quantities of cold water are sufficient to weather olivine in Martian igneous rocks.

5.2 Environments of Aqueous Alteration of Antarctic Meteorites

5.2.1 Physical Environment

Antarctic meteorites spend much of their terrestrial history encased in ice where chemical weathering is likely minimal; consequently, the duration of surface exposure to aqueous solutions and atmosphere, and consequent supraglacial weathering, may be much shorter than a meteorite's terrestrial age (Gooding, 1981, 1989; Burns et al., 1995; Welten, 1999; Velbel, 2014a). Nevertheless, oxidation proceeds readily even in the cold-desert weathering environment of Antarctica; only 4% of ANSMET stony meteorites have the lowest possible oxidation grade (Harvey, 2003; Losiak and Velbel, 2011; Velbel, 2014a). Furthermore, meteorite weathering in Antarctica may not be restricted to episodes of exposure to atmosphere and insolation heating at the ice surface. ALH 82102 (H5) was recovered still encased in ice that showed no petrographic indications of recrystallization near the meteorite's surface, suggesting that the meteorite was just emerging for the first time since becoming entombed in the ice (Antarctic Meteorite Newsletter, 1983; Nishiizumi et al., 1989). The terrestrial age determined for ALH 82102 by ^{14}C is $11,000 \pm 1,300$ yrs (Nishiizumi et al., 1989). ALH 82102 is classified as weathering category B/C (Antarctic Meteorite Newsletter, 1984), the second-most weathered category in the Antarctic Meteorite Working Group's five-part weathering classification. While it is possible that ALH 82012 was extensively oxidized and rusted prior to being encased in glacial ice and remained in that state without further weathering until recovery, it is also possible that weathering proceeds under the influence of thin layers of unfrozen water on mineral surfaces while the meteorite is fully encased in glacial ice (Gooding, 1986a,b; Velbel and Gooding, 1990). The full range of possible hydrocryogenic terrestrial aqueous-alteration environments includes "periglacial" (supraglacial pre- and/or post-entombment, and possibly multiple episodes of supraglacial exposure between initial entombment and the most recent pre-recovery exposure) and "glacial" (englacial, hydrocryogenic, in the presence of small quantities of unfrozen water)

environments (*sensu* Gooding, 1986a,b). All must be considered in interpreting aqueous-alteration phenomena in Antarctic finds.

5.2.2 Chemical Environment

The morphology of olivine etch-pits in MIL 03346,171, including those inferred to have formed by terrestrial weathering, is identical to that of common weathering of terrestrial olivine under a variety of terrestrial environmental conditions (Velbel, 2009). The etch-pits observed in MIL 03346,171 indicate that, despite the generally more fayalitic compositions of Mars-meteorite olivine than common forsteritic terrestrial olivines, fayalitic Mars-meteorite olivine is etched in the same manner as terrestrial forsterite when exposed to similar weathering solutions, and that the same kinds of insight retrievable from the size, shape and distribution of etch-pits on terrestrial olivine can be expected to be retrievable from olivine in other Mars meteorites. Terrestrial etch-pits on olivine in MIL 03346,171 demonstrate that olivine in MIL 03346 could have corroded in the presence of suitable solutions undersaturated with respect to olivine on Mars, had such solutions existed. Such features would be especially informative if some were eventually found to be pre-terrestrial in Mars meteorite finds, more so in Mars meteorite falls (e.g., Nakhla; Velbel, 2012; Lee et al., 2013, 2015b), and even more so in mission-returned Mars samples.

5.3 Inferring Aqueous-Alteration Conditions for Olivine Etch-Pit Formation in MIL 03346

Textural evidence of silicate alteration has been previously used to infer the pH of the aqueous alteration environment (Schaefer et al., 2006; Velbel and Barker, 2008; McAdam et al.,

2008; Hausrath et al., 2008a,b). Qualitative relations between the relative weathering rates of two coexisting minerals in the same sample (“mineral A is more weathered over a given exposure time than mineral B”) can be compared with known pH dependences of the minerals (“mineral A dissolves faster than mineral B when pHs are less than [a value known from experimental dissolution kinetics literature]”) to place empirical bounds on the pH of the solution environment, even if the duration of the alteration episode is unknown. Velbel and Barker (2008) inferred relative weathering rates of two coexisting compositionally different pyroxenes from their relative persistence in a naturally weathered pyroxenite sample, compared the empirical relative weathering rates with experimentally determined dissolution rates, and found the observed natural relative rates consistent with experimental rates if the pH of the natural weathering environment was high ($\text{pH} > \sim 5\text{-}6$). Similarly, where the extents of alteration can be quantified, the equal durations of alteration of the mineral pair allow the ratio of alteration extents to be treated as a ratio of rates, which can be compared with ratios of experimentally determined rates to constrain environmental conditions (Schaetzl et al., 2006; McAdam et al., 2008; Hausrath et al., 2008a,b). Schaetzl et al. (2006) demonstrated that hornblende subjected to different soil pH conditions at different depths in post-glacial soils in Michigan was 6-10 times more corroded in more acidic soil horizons than in soil horizons less acidic by 2-3 pH units. If the within-profile gradient of pHs (not necessarily the absolute values of pH) has existed since deglaciation, the observed difference in corrosion implies that hornblende corroded 6-10 times more in the more acidic horizons compared to the less acidic soil horizons over the same duration of exposure to profile-variant weathering conditions (Schaetzl et al., 2006). This magnitude of difference in time-integrated hornblende etching at different pHs in a natural soil conforms to the difference in experimentally determined

dissolution rates of hornblende at different pHs (Brantley and Chen, 1995). Several recent papers (McAdam et al., 2008; Hausrath et al., 2008a,b) applied a similar approach to Mars-relevant observations and kinetics, comparing observed relative persistence for pairs of minerals in natural materials with experimental dissolution rates of the same minerals over a range of pHs in order to constrain pH. All these studies assumed that the multiple coexisting phases examined were exposed to the same aqueous solution for the same amount of time, and responded to the aqueous alteration environment differently because the dissolution rates of the different phases have different pH-dependences. In the present study, only one mineral is altered (pyroxene was examined but, contrary to the erroneous interpretation of the igneous quench crystallization texture shown in Fig. 7a in Velbel, 2012, exhibits no alteration features, for reasons explained in section 5.3.4 below), and therefore both exposure time (which cannot be constrained to be equal to the exposure time of a coexisting mineral if no such co-existing altered mineral occurs) and pH are unknowns. However, if exposure time can be independently constrained and the amount of dissolved mineral can be quantified, pH can be estimated.

Both acidic and alkaline conditions can exist in Antarctic weathering environments. Some constraints on the pH of the solution and the associated aqueous-alteration environments can be established by considering whether MIL 03346,171 was exposed to specified Antarctic conditions for sufficient time to form olivine etch-pits of the observed dimension at the pH-dependent olivine dissolution rates constrained from experimental literature. The terrestrial (^{36}Cl) age of MIL 03346 is 25 ± 15 kyr (Nishiizumi and Caffee, 2010; Nishiizumi, written communication, 11 January 2013).

5.3.1 Estimating timescales of olivine etch-pit formation in MIL 03346

Olivine etch-pits formed by terrestrial weathering in MIL 03346,171 as reported here, and by pre-terrestrial aqueous alteration in Nakhla (Velbel, 2012; Lee et al., 2013), are comparable in size ($\sim 2 \mu\text{m}$) to the smallest etch-pits visible in terrestrially weathered terrestrial forsteritic olivine using SEM, and identical in morphology to etch-pits of all sizes (up to $100 \mu\text{m}$) reported from terrestrially weathered terrestrial forsteritic olivine (Velbel, 2009). Ferroan Mars-meteorite olivine corrodes in the same manner as common terrestrial forsteritic olivine when exposed to similar weathering solutions, suggesting that the same kinds of insight retrievable from etch-pits on terrestrial olivine (Velbel, 2009) are transferable to olivine in Mars meteorites. The small size of olivine etch-pits in MIL 03346,171 relative to commonly much larger etch-pits in even incipiently weathered terrestrial examples (Velbel, 2009) suggests that the duration of MIL 03346,171's exposure to weathering conditions was short, the weathering conditions to which MIL 03346,171 was exposed did not favor olivine corrosion, terrestrial weathering was heterogeneously distributed in MIL 03346,171, or some combination of these factors must be considered.

Timescales for formation of small etch-pits near the fusion crust during terrestrial weathering of olivine in MIL 03346,171 (as argued above) are estimated here from the measured maximum size of terrestrial (Antarctic) etch-pits ($\sim 2 \mu\text{m}$; Figures 5-8) and compilations of dissolution rates from the extensive body of literature on the experimental geochemical dissolution kinetics of olivine in water at ambient temperatures using an approach (Velbel et al., 2007; Velbel, 2014b) that is similar to published approaches to mineral-lifetime estimates (Stopar et al., 2006; Olson and Rimstidt, 2007). Similar modeling of formation times of *pre-*terrestrial olivine replacement features and associated secondary phases is not yet attempted here because (1) unlike Antarctic alteration of MIL 03346, for which there exists a measured

terrestrial age with which to compare, there exists no independent information about (a) specific narrow ranges of Mars-surface or near-surface exposure temperatures (e.g., Changela and Bridges, 2011; Lee et al., 2013; Tomkinson et al., 2013) for constraining olivine reaction rates or (b) exposure times on Mars with which to compare calculated estimates, and (2) the Martian serrated margins most likely formed simultaneously with the veins of carbonate- and silicate-bearing products (e.g., Velbel, 2012; Lee et al., 2013, 2015a,b; Tomkinson et al., 2013), which involves different conditions of, for example, temperature and most likely solution composition, than for the somewhat better constrained terrestrial Antarctic case.

The time required to form etch-pits of a defined geometry and measured characteristic dimension can be determined if the dissolution rate of the mineral in a natural system can be determined for the specific natural regolith being studied from geochemical mass-balance (e.g., Velbel, 1985), or estimated by adjusting experimentally determined dissolution rates for known differences between laboratory and field rates (e.g. Velbel, 1993a; White and Brantley, 2003). In the absence of field-based studies of Antarctic nakhlite weathering rates, this study applies the latter approach. The experimentally determined forsterite dissolution rates used here are those compiled by Olsen and Rimstidt (2007) and Rimstidt et al. (2012).

Most room-temperature dissolution kinetics experiments are undertaken using dilute solutions at standard temperature and pressure (STP). This yields maximum limiting rates that result in minimum lifetimes of specified mineral volumes (whole grains in the applications of Stopar et al., 2006, and Olsen and Rimstidt, 2007; etch-pits in the present case). For application to natural weathering at conditions other than STP and extreme solution undersaturation with respect to the dissolving mineral, experimentally determined maximum rates must be adjusted. Terrestrial weathering of Antarctic meteorites takes place at lower temperatures (even during

brief episodes of insolation heating of a meteorite exposed at the ice surface to T as high as 5°C ; Schultz, 1986) than those at which mineral dissolution rates are experimentally determined in the laboratory, and reaction rates between silicate minerals and aqueous solutions are slower at lower temperatures (e.g., Velbel, 1990, 1993b). Kinetic rate laws require mineral-solution reaction rates to slow as equilibrium is approached (e.g., Sposito, 1994; Velbel, 1989). Solute-rich aqueous solutions (brines) suppress olivine dissolution rates in acidic solutions by up to an order of magnitude relative to olivine dissolution in dilute aqueous solutions, due to the lower thermodynamic activity of water in brines (Hausrath and Brantley, 2010; Olsen et al., 2015). All of these effects will tend to make weathering in chemically evolved, lower-temperature aqueous solution slower, and estimated time-scales of mineral-grain-surface modification longer, than the rates measured in common room-temperature laboratory experiments. Comparison of abundant published silicate-mineral weathering rates determined experimentally with those determined from weathering in natural systems reveals a systematic lab/field rate discrepancy; field rates are commonly up to three (and in a few instances, up to four) orders of magnitude slower than experimentally determined rates (Velbel, 1993a; White and Brantley, 2003). Most of the aforementioned factors, as well as variations in rate with olivine composition (fayalite content), grain size, pH, hydrodynamics, and the lab/field rate discrepancy, are taken into account graphically by Olsen et al. (2015) in their Figure 4 (updated from Olsen and Rimstidt, 2007, their Figure 2).

Using the range of experimentally determined dissolution rates for forsteritic olivine reviewed by Olsen and Rimstidt (2007) and Rimstidt et al. (2012) and invoking the geometric assumptions about olivine volume and surface area in the samples examined (Velbel, 2014b) allows determination of the time, t_d , required to form (by dissolution) an hemispherical etch-pit

of radius r or diameter d , dissolving radially outward from its surface-nucleation site using equation (1)

$$t_d = r / (3 V^\circ J) = d / (6 V^\circ J)$$

(1)

where V° is the molar volume (cm^3/mol) and J is dissolution rate ($\text{mol}/\text{cm}^2/\text{s}$). This approach recovers experimental run durations at $\text{pH} = 2$ from imaged etch-pit sizes in Pokrovsky and Schott (2000) to within a factor of two (Velbel, 2014b). For forsterite (Mg_2SiO_4) and fayalite olivine (Fe_2SiO_4), $V^\circ_{\text{forsterite}} = 43.603 \text{ cm}^3/\text{mol}$ and $V^\circ_{\text{fayalite}} = 46.290 \text{ cm}^3/\text{mol}$ (Smyth and Bish, 1988). Poikilitic olivine in MIL 03346 is zoned with compositions of Fa_{57-87} (Treiman, 2005; Day et al., 2006; Imae and Ikeda, 2007; Udry et al., 2012). For simplicity, end-member molar volumes are interpolated linearly to the midpoint of the observed compositional range, giving a value of $V^\circ_{\text{MIL 033436 ol}} = 45.6 \text{ cm}^3/\text{mol}$.

Experimentally determined forsterite dissolution rates range from $1.0 \times 10^{-7} \text{ mol}/\text{m}^2/\text{s}$ ($= 1.0 \times 10^{-11} \text{ mol}/\text{cm}^2/\text{s}$) at $\text{pH} = 0$, to $1.0 \times 10^{-11} \text{ mol}/\text{m}^2/\text{s}$ ($= 1.0 \times 10^{-15} \text{ mol}/\text{cm}^2/\text{s}$) at $\text{pH} = 12$ (Olsen and Rimstidt, 2007; Rimstidt et al., 2012). Abundant evidence from natural terrestrial weathering and dissolution-kinetics experiments demonstrates that ferroan olivine weathers faster than forsterite (Velbel, 2009). In some naturally exposed terrestrial fragmental rocks such as volcanic breccias and tephra, olivines of more than one composition occur and weather together; in such occurrences, the more fayalitic olivine is more extensively weathered than the more forsteritic olivine (e.g., Hay, 1959). Because all constituents of these fragmental rocks were exposed to weathering for the same amount of time, the observed difference in extent of alteration over the same duration of exposure means that the more fayalitic olivine weathered faster than the forsteritic olivine. Laboratory dissolution-kinetics experiments (Wogelius and

Walther, 1992) and considerations of crystal-chemistry and bond strengths (Schott and Berner, 1985; Velbel, 1999) all yield results consistent with this observation from nature. Therefore, consideration must be given to the difference between the compositions of nakhlite olivine relative to forsterite for which abundant experimental data are available.

Under similar experimental conditions, near-end-member fayalitic olivine (Fo₆) may dissolve from six times (Wogelius and Walther, 1992) to up to two orders-of-magnitude (Westrich et al., 1993) faster than forsteritic (Fo₉₁₋₁₀₀) olivine. Assuming linear interpolation between the known rates for extreme olivine compositions as suggested by Wogelius and Walther (1992), olivine of the mean composition in MIL 03346 olivine (Fo₂₈) dissolves at 78% of the dissolution rate for near-end-member fayalite (or approximately 4.7 times faster than forsteritic olivine); the difference would be larger but still much less than an order-of-magnitude using the data of Westrich et al. (1993). However, insufficient experimental data exist on dissolution kinetics of ferroan olivine of intermediate composition to establish whether the dependence of dissolution rate on Fo content is linear over the compositional range. Given that dissolution rate/composition relationships for other better-studied silicate solid solution series are not linear with composition (e.g., plagioclase feldspars, Casey et al., 1991), it is assumed here that the possible less-than-one-order-of-magnitude difference between the dissolution rates of Fo₂₈ and Fo₉₁₋₁₀₀ does not justify using a poorly constrained interpolated value different from the forsterite dissolution rate; in other words, a possible error of up to a factor of five is accepted here. This error is minor given a range of four orders-of-magnitude variation due to pH (Olsen and Rimstidt, 2007; Rimstidt et al., 2012) and possible variation at any given pH of up to another four orders-of-magnitude due to other causes (discussed above; Velbel, 1993a; White and Brantley, 2003). Thus, before accounting for the dominant sources of variation, the dissolution

rate of olivine at different pHs ranges between $1.0 \times 10^{-11} \text{ mol/cm}^2/\text{s} > J > 1.0 \times 10^{-15} \text{ mol/cm}^2/\text{s}$.

So, for olivine, using rates determined experimentally, the shortest minimum etch-pit formation time is determined by the fastest dissolution rate (at extremely acidic pH):

$$t_d(\text{s}) = d(\text{cm}) / (6 \times 45.6 \text{ cm}^3/\text{mol} \times 1.0 \times 10^{-11} \text{ mol/cm}^2/\text{s})$$

$$t_d(\text{s}) = d(\text{cm}) / (2.74 \times 10^{-9} \text{ cm/s}) = d(\text{cm}) \times (3.65 \times 10^8 \text{ s/cm})$$

$$t_d(\text{s}) = d(\mu\text{m}) \times (3.65 \times 10^8 \text{ s/cm}) \times (10^{-4} \text{ cm}/\mu\text{m})$$

$$t_d(\text{s}) = d(\mu\text{m}) \times (3.65 \times 10^4 \text{ s}/\mu\text{m})$$

$$t_d(\text{hr}) = d(\mu\text{m}) \times (3.65 \times 10^4 \text{ s}/\mu\text{m}) \times (1 \text{ hr}/3600 \text{ s}) = d(\mu\text{m}) \times 10.2 \text{ hr}/\mu\text{m}$$

~0.4 day/ μm diameter, at acidic pH (pH = 0) and STP,

and the longest minimum etch-pit formation time is determined by the slowest dissolution rate (at extremely alkaline pH):

$$t_d(\text{s}) = d(\text{cm}) / (6 \times 45.6 \text{ cm}^3/\text{mol} \times 1.0 \times 10^{-15} \text{ mol/cm}^2/\text{s})$$

$$t_d(\text{s}) = d(\text{cm}) / (2.74 \times 10^{-13} \text{ cm/s}) = d(\text{cm}) \times (3.65 \times 10^{12} \text{ s/cm})$$

$$t_d(\text{s}) = d(\mu\text{m}) \times (3.65 \times 10^{12} \text{ s/cm}) \times (10^{-4} \text{ cm}/\mu\text{m})$$

$$t_d(\text{s}) = d(\mu\text{m}) \times (3.65 \times 10^8 \text{ s}/\mu\text{m})$$

$$t_d(\text{yr}) = d(\mu\text{m}) \times (3.65 \times 10^8 \text{ s}/\mu\text{m}) \times (1 \text{ yr}/3.15 \times 10^7 \text{ s}) = d(\mu\text{m}) \times 11.6 \text{ yr}/\mu\text{m}$$

~12 years/ μm diameter, at alkaline pH (pH = 12) and STP,

As noted above, the day-to-decade timescale estimated for etch-pit formation on olivine in MIL 03346,171 is a minimum with respect to expected variability in all rate-influencing parameters except olivine composition. Poikilitic olivine in MIL 03346 is Fa_{57-87} (Treiman, 2005; Day et al., 2006; Imae and Ikeda, 2007; Udry et al., 2012). Fayalitic olivine can weather

up to nearly two orders of magnitude faster than the forsterite from which experimental rates were determined (Olsen and Rimstidt, 2007), reducing the time required to form etch-pits of the observed size. In contrast, temperatures of Antarctic meteorites heated by insolation at the ice surface are several tens of degrees Centigrade lower than STP (Schultz, 1986), suppressing Antarctic olivine dissolution rates by up to a full two orders of magnitude relative to experimentally determined rates (Olsen and Rimstidt, 2007), and thus lengthening the time required to form etch-pits of the observed size. If it is assumed that the composition and temperature effects more or less cancel each other out, and that all other factors discussed above are embodied in the widely observed up-to-four-orders-of-magnitude discrepancy between field rates and experimentally determined rates (Velbel, 1993a; White and Brantley, 2003), the day-to-decade timescale is adjusted (lengthened) by four orders of magnitude. Under Antarctic conditions and pH = 0, an etch-pit on olivine can form in;

$$t_d(s) = d(\mu\text{m}) \times (3.65 \times 10^8 \text{ s}/\mu\text{m})$$

$$t_d(\text{hr}) = d(\mu\text{m}) \times (3.65 \times 10^8 \text{ s}/\mu\text{m}) \times (1\text{yr}/3.15 \times 10^7 \text{ s}) = d(\mu\text{m}) \times 116 \text{ yr}/\mu\text{m}$$

$$\sim 12 \text{ yr }/\mu\text{m diameter, at acidic pH,}$$

And at pH = 12,

$$t_d(s) = d(\mu\text{m}) \times (3.65 \times 10^{12} \text{ s}/\mu\text{m})$$

$$t_d(\text{yr}) = d(\mu\text{m}) \times (3.65 \times 10^{12} \text{ s}/\mu\text{m}) \times (1\text{yr}/3.15 \times 10^7 \text{ s}) = d(\mu\text{m}) \times 116 \text{ kyr}/\mu\text{m}$$

$$120 \text{ kyr years}/\mu\text{m diameter, at alkaline pH}$$

Given that etch-pits are dissolution features, some degree of undersaturation with respect to olivine must have been maintained long enough to form the observed etch-pits. Under the

circumstances described by the equations and parameter values used above, an olivine etch-pit of the 2 μm dimension observed in MIL 03346,171 requires a few decades to form under cold acidic conditions, up to some quarter of a million years under cold alkaline conditions.

5.3.2 Comparing estimated timescales for Antarctic corrosion of olivine with the terrestrial age of MIL 03346 to constrain the pH of the corroding solution

5.3.2.1 Exploring the acidic option – A case can be made that olivine in MIL 03346,171 corroded under acidic conditions over brief intervals of time. The decade timescale inferred for production of olivine etch-pits of the size observed in MIL 03346,171 under acidic conditions is very short compared with the time available as implied by the terrestrial age of MIL 03346 (10,000-40,000 yrs) reported by Nishiizumi and Caffee (2010) and Nishiizumi (written communication). One or more brief episodes combining supraglacial exposure to Antarctic liquid water and acidic ($\text{pH} = 0$) conditions would have been sufficient to produce the observed olivine etch-pits in MIL 03346,171. Because of the pH dependence of olivine dissolution (Grandstaff, 1986; Olsen and Rimstidt, 2007; Rimstidt et al., 2012), more numerous and/or longer-duration supraglacial exposure episodes would be required under less extreme (higher pH) acidic conditions.

Several lines of evidence other than olivine etch-pit formation-time estimates and the terrestrial age of MIL 03346 support the possibility that aqueous alteration took place under acidic conditions. Excess dissolved silica has been produced experimentally from cold acidic solutions reacting with basalt minerals (Hausrath and Brantley, 2010), and sulfate-rich rock varnish similar to that described from MIL 03346 by Hallis and Taylor (2011) and Stopar et al. (2013) has been reported on exposed surfaces of compositionally diverse igneous rocks in

Antarctica by Giorgetti and Baroni (2007). Giorgetti and Baroni (2007) attributed the varnish they observed to terrestrial additions by way of terrestrial atmospheric dust and subsequent redistributions of dissolved constituents by water from snowmelt, possibly under the influence of S-rich acidic aerosols from active Antarctic volcanoes. Corrosion of MIL 03346,171 olivine could have occurred quickly if temporary episodes of acidic conditions resulting from Antarctic volcanic emissions coincided with episodic exposure of the meteorite at the ice surface. However, Hallis (2013) attributes the sulfate in terrestrial weathering products in MIL 03346 and its pair MIL 090032 to terrestrial sea-spray sulfate; because sea-water is mildly alkaline (Berner and Berner, 2012), a sea-spray origin for sulfate on the Miller Range nakhlites would be inconsistent with acidic conditions.

5.3.2.2 Exploring the alkaline option – Exposure to Antarctic liquid water and alkaline (pH = 12) conditions would have taken hundreds of thousands of years to produce olivine etch-pits of the size observed in MIL 03346,171. Even such a long timescale is within an order of magnitude of the preliminary terrestrial age of MIL 03346 reported by Nishiizumi and Caffee (2010) and Nishiizumi (written communication). Consequently, there was sufficient time available for olivine corrosion in MIL 03346,171 under alkaline geochemical conditions by persistent thin films of unfrozen grain-boundary water (Gooding, 1986a,b; Velbel and Gooding, 1990) if this water remained undersaturated with respect to olivine over long timescales even while the meteorite was encased in Antarctic glacial ice.

Several lines of evidence other than olivine etch-pit formation time estimates and the terrestrial age of MIL 03346 support the possibility that Antarctic olivine corrosion in MIL 03346 may have occurred under alkaline geochemical conditions. (1) There is abundant literature on the pH of Antarctic streamwaters and meltwater ponds of glacial melt origin, that

800 have come into contact with the stream- and lake-bed minerals. The pH of bulk ice-melt water
 801 before contact with stream bed materials is not as extensively investigated or reported, but
 802 Stumpf et al (2012) report that the pH of the Clark Glacier meltwater stream is 9.00 nearest the
 803 glacier and decreases with distance from the glacier. Stratified Antarctic meltwater ponds
 804 commonly include depth intervals with pHs of ~8-9 (Green et al., 1988; Healy et al., 2006), and
 805 pHs up to 11 have been reported (Wait et al., 2006). (2) The surfaces of Mars-relevant mafic
 806 silicates such as olivine, clinopyroxene, and mesostasis react quickly with, and raise the pH of,
 807 small amounts of initially dilute solution. Abrasion pH is a long-used field test in mineral
 808 identification and soil science, that measures the pH of a small quantity of distilled water after
 809 contact with a slurry of mineral matter (Stevens and Carron, 1948) or soil (Grant, 1969).
 810 Abrasion pHs of 8-11 characterize Mars-relevant mafic silicate minerals (abrasion pH of
 811 hypersthene = 8, augite = 10, generic pyroxene = 10, diopside = 10-11, intermediate olivine =
 812 10-11). (3) Field-determined soil pHs for the deepest, least-weathered soil horizons developed
 813 by terrestrial basalt weathering fall within this range (Ziegler et al., 2003), as do the highest pHs
 814 attained at long durations during experimental batch (stagnant solution) weathering of
 815 compositionally Mars-relevant synthetic basalt (Tosca et al., 2004). (4) Weathering solutions
 816 associated with early-stage natural Earth-surface (low temperature) weathering of basaltic rocks,
 817 before appreciable quantities of primary minerals are replaced by weathering products, are
 818 commonly alkaline (Garrels, 1967; Gíslason and Eugster, 1987; Bricker and Rice, 1989;
 819 Gíslason and Arnórsson, 1990, 1993; Nesbitt and Wilson, 1992; Gíslason et al., 1996; Stefánsson
 820 et al., 2001; Stefánsson and Gíslason, 2001; Ziegler et al., 2003; Chadwick et al., 2003).
 821 Furthermore, pHs as high as 10.5 (within the range of abrasion pH values for basalt- and
 822 pyroxenite-relevant primary ferromagnesian silicates; Stevens and Carron, 1948) have been

reported from groundwaters in basalt isolated from Earth's atmosphere (Gíslason and Eugster, 1987; Gíslason and Arnórsson, 1990, 1993; Stefánsson et al., 2001). (5) Waters issuing from extensively serpentinized ultramafic rocks commonly have pHs in the 7.5-9 range, whereas partly serpentinized peridotites and dunites still containing unaltered olivine and pyroxene yield waters with pHs that commonly approach and often exceed 12 (Barnes et al., 1967, 1972, 1978; Barnes and O'Neil, 1969; Nesbitt and Bricker, 1978; Neal and Stanger, 1983, 1984, 1985; Neal and Shand, 2002).

Timescales in the longer part of the range of etch-pit formation timescales calculated above are estimated from experimentally determined slow dissolution rates of olivine at such high pHs (e.g., Olsen and Rimstidt, 2007; Hausrath et al., 2008a,b; Rimstidt et al., 2012).

5.3.2.3 Weighing the options – Comparing measured etch-pit size with the time required to dissolve the corresponding mineral mass extrapolated from experimental to field-relevant reaction conditions yields broadly reasonable results. A terrestrial age of MIL 00346 at the long-duration end of the estimated range of etch-pit formation times (tens of thousands of years or longer) would permit either rapid supraglacial weathering under the influence of acidic inputs or slow englacial weathering at alkaline conditions in the presence of unfrozen water. In contrast, a terrestrial age at the short-duration end of the estimated range of etch-pit formation times (a few thousand years or less) would militate against the latter and be consistent only with the former. Within large uncertainties of both terrestrial age and extrapolated dissolution rates, the known terrestrial age of MIL 03346 ($25,000 \pm 15,000$ yrs) falls within the range of allowable combinations of alteration timescale and alteration conditions – approximately three orders of magnitude longer than the few centuries required under extreme acidic conditions but

approximately an order of magnitude shorter than the few hundred thousand years required under extreme alkaline conditions.

Wedge-shaped cross-sections through etch-pits filled with alteration products have been reported from Nakhla (Velbel, 2012; Lee et al., 2013). Using different assumptions, including dissolution along the entire lateral extent of olivine along the margin of a vein (in contrast to site-specific dissolution at etch-pits as discussed by Velbel, 2014b, and used in the estimates discussed above) and accepting a consensus from previous work that aqueous alteration in nakhlites took place under mildly acidic conditions ($\text{pH} = 5$), Lee et al. (2013) calculated that removal of enough olivine to form the observed thicknesses of subsequent fracture-filling veins in Nakhla could be accomplished in days to years depending on the temperature. Their calculations applied experimental laboratory-determined olivine dissolution rates directly, without accounting for the widely recognized up-to-four-orders-of-magnitude discrepancy between natural and experimentally determined silicate-mineral weathering rates (Velbel, 1993a; White and Brantley, 2003). Adjusting their estimated timescales by four orders-of-magnitude yields decades rather than days at the higher temperature extreme of their range for estimation, and tens of thousands of years rather than years at the lower temperature extreme. Using the molar volumes and retrieved dissolution rates tabulated and used by Lee et al. (2013) and the sizes of the etch-pits they show from Nakhla olivine as the parameter values in the equations of Velbel (2014b) and this paper (for site-selective etching, including adjustment for the lab/field rate discrepancy), timescales of thousands to tens of thousands of years are required to produce etch-pits of the sizes observed in Nakhla at $\text{pH} 5$. The lab/field-corrected rates and consequent dissolution timescales calculated by either approach (all-surface vs. site-selective dissolution) suggest conformity between the estimates of Lee et al. (2013) and those of this paper if common

assumptions are invoked. Furthermore, the vein-dissolution timescales estimated without lab/field correction by Lee et al. (2013) would permit the observed amount of dissolution to occur at temperatures and on timescales completely overlapping the two years of terrestrial exposure between fall and recovery of the Nakhla sample Lee et al. (2013) examined. In contrast, the lab/field-corrected dissolution timescales calculated here are unequivocally too long for etch-pits of the size observed in Nakhla to have formed during the two years of terrestrial exposure between fall and recovery, and are thus more consistent with the widely accepted pre-terrestrial origin of aqueous alteration features (including olivine etch-pits) in Nakhla. Given that independent evidence would be required to fix the pH at 5, and that recent forward modeling of nakhlite alteration successfully modeled mineral assemblages similar to the alteration products of Lafayette from model brines with circum-neutral to alkaline pHs of 6-9 (Bridges and Schwenzer, 2012), a wider range of pHs and consequent olivine dissolution rates than those invoked by Lee et al. (2013) remains plausible for the pre-terrestrial (Mars) aqueous alteration in Nakhla.

Etch-pits of the observed size on olivine would be relatively easy to form under brief episodic acidic ($\text{pH} \ll 6$) Antarctic conditions, but the terrestrial age of MIL 03346 is long enough that weathering of its olivine to the observed state by films of alkaline Antarctic water ($\text{pH} > 8$) cannot be precluded. Similar studies of olivine etching in other Antarctic achondrites with known terrestrial ages may eventually reveal combinations of pH-dependent etch-pit formation timescale estimates and measured terrestrial ages that demonstrate a tendency toward more open acidic or more closed alkaline conditions. Also, if alteration products are cogenetic with olivine etching, they may further constrain the pH of the alteration solution.

5.3.3 *Implications for olivine alteration in nakhlites and chassignites on Mars*

Nakhlites, as a group, contain olivine corrosion features and diverse alteration minerals including phyllosilicate-like phases (incl. “iddingsite”), carbonates, sulfates, and halite; some alteration phenomena are widely distributed among nakhlites and others known from only a few of the nakhlites (Velbel, 2012). The results reported here from MIL 03346,171 show that some Mars-relevant styles of olivine alteration occur in (terrestrial) cold desert environments on timescales that are short relative to the time available for possible similar processes on Mars (see also Stopar et al., 2006, Hurowitz and McLennan, 2007, and Hausrath et al., 2008a). The widespread persistence of olivine in the surface materials of Mars suggests that such alteration has not been extensive.

Mars meteorites were exhumed during impact and ejection from subsurface depths of tens of meters up to ~200 m (Fritz et al., 2005), possibly sufficient to isolate those rocks from such Mars atmospheric acidity as may have existed at the time (Newsom, 2005; Tosca and McLennan, 2006; McLennan and Grotzinger, 2008; Tosca et al., 2008; Hurowitz et al., 2010). Acid-consuming reactions with basaltic minerals (e.g., reaction 2 of Velbel, 2012) confined to igneous grain boundaries and with consequent low water-rock ratios would raise local pH beyond that in equilibrium with Mars’ atmosphere (Tosca and McLennan, 2006; Bridges and Schwenzer, 2012; see also above). Natural terrestrial spring waters of meteoric origin issuing from numerous terrestrial ultramafic bodies are universally undersaturated with respect to olivine but in most cases supersaturated with respect to clinopyroxene (Barnes et al., 1969, 1972; Neal and Shand, 2002). If similar aqueous solutions evolved from reactions between water and ultramafic rocks on Mars, then the question “why the secondary minerals are much more abundant within olivine than the volumetrically dominant augite” in nakhlites (Lee et al., 2013)

might be answered “because the solutions were undersaturated with respect to and reactive toward olivine but not to clinopyroxene.”

All alteration products in nakhlites yield radiometric ages that are (as expected) younger than nakhlites’ crystallization age of ~ 1.3 Ga (670 ± 91 Ma; Swindle et al., 2000; $<880 \pm 32$ Ma, references in Swindle and Olson, 2004; 633 ± 23 Ma, Borg and Drake, 2005). Etch-pits occur in Nakhla, the only nakhlite fall, in which the etch-pits and many (but not all) other aqueous alteration features are almost certainly pre-terrestrial (e.g., Gooding et al., 1991; Wentworth et al., 2005; Velbel, 2012; Lee et al., 2013, 2015b). MIL 03346 contains iddingsite-like material that is almost certainly pre-terrestrial (Treiman, 2005; Dyar et al., 2005; Day et al., 2006; Imae and Ikeda, 2007; Hallis and Taylor, 2011; Udry et al., 2012; Stopar et al., 2013), so MIL 03346 shares with other nakhlites a history of some pre-terrestrial aqueous alteration of olivine.

At least some olivine etching in MIL 03346,171 appears to be independent from iddingsitization and associated with proximity to the fusion crust. Evidence from MIL 03346,171 favors an origin no earlier than the fusion crust (consistent with a terrestrial-weathering origin) for etch-pits on the exterior olivine phenocryst near (within a few hundred micrometers of) the fusion crust in this Antarctic find, and no corresponding features with similar relationships to fractures and products in the exterior olivine phenocryst far (more than a few hundred micrometers) from the fusion crust, or in the interior olivine phenocrysts of this or other previously examined MIL 03346 allocations. Therefore, although other forms of aqueous alteration (esp. iddingsitization) affected MIL 03346 on Mars, MIL 03346 was likely exposed to even less *specifically olivine-corroding water after the* ($<\sim 0.6$ to 0.9 Ga) iddingsitization that occurred during its ~ 1.3 Ga history on Mars than it has been exposed to during its short residency on Earth. Furthermore, the 1.3 Ga Mars meteorite fall Chassigny (with similar

crystallization and ejection ages to the nakhlites, and therefore probably ejected from the same area as the nakhlite stack) contains sulfates and carbonates but lacks olivine etch pits (Wentworth and Gooding, 1994; Wentworth et al., 2005; Velbel, 2012). Therefore, either the water to which these 1.3 Ga Martian clinopyroxenites and dunites were exposed on Mars (after iddingsitization) was of a composition that did not corrode olivine, or there was less specifically olivine-corroding liquid water on Mars at the source area of MIL 03346, Chassigny, and the other 1.3 Ga Mars meteorites during their post-iddingsitization interval on Mars than the amount to which MIL 03346 was exposed over the past 10-40 kyr in Pleistocene-Holocene Antarctica. The implied paucity of Amazonian near-surface liquid water is consistent with the conclusions of Lee et al. (2013, 2015b) based on evidence from Nakhla, and from the grain-size distribution of the surface material at the Phoenix Mars Lander landing site (Pike et al., 2011). Continued characterization of aqueous-alteration products in MIL 03346 (Hallis and Taylor, 2011; Hallis, 2013; Stopar et al., 2013; Kuebler, 2013), its pairs (Hallis et al., 2014), and other nakhlite finds will shed additional light on the physico-chemical nature of the terrestrial fluids that reacted with olivine and produced terrestrial-weathering products, and can thereby place limits on the properties of solutions that produced, or failed to produce, similar pre-terrestrial alteration features and assemblages in Mars meteorites before they were ejected from Mars.

6. SUMMARY AND CONCLUSIONS

Olivine in the Antarctic Mars meteorite find MIL 03346,171 corroded in a typical manner for weathering upon exposure in Antarctica. The notches and serrations observed along fractures in olivine grains are interpreted to be cross-sections through small etch-pits; their geometries are consistent with the typical conical and biconical forms for weathered olivine

(Velbel, 2009). Discrete, small etch-pits in olivine (Figures 5-8) are concentrated within a few hundred microns of the meteorite's fusion-crust surface, a relationship not previously described from this or any other nakhlite. Spatial association of these small etch-pits with the surface of the meteorite exposed to the Antarctic environment is consistent with the interpretation that etching formed by terrestrial weathering in Antarctica. If so, it also indicates that small quantities of cold water are sufficient to weather olivine in Martian igneous rocks. Maximum dimensions of the wedge-shaped cross-sections through the etch-pits near the fusion crust are $\sim 2 \mu\text{m}$.

Decade-to-multimillennial timescales are estimated here for the formation of terrestrial etch-pits of the observed size in MIL 03346,171 olivine. These timescales are consistent with wetting episodes of durations compatible with the measured terrestrial age of the meteorite. Corrosion of MIL 03346,171 olivine under extremely acidic conditions could have occurred quickly, if temporary episodic acidic conditions resulting from Antarctic volcanic emissions coincided with episodic supraglacial exposure of the meteorite at the ice surface; less acidic conditions would require longer durations of ice-surface exposure to liquid water. Alternatively, Antarctic olivine corrosion in MIL 03346 may have occurred under mildly alkaline geochemical conditions ($8 \leq \text{pH} \leq 9$), during prolonged weathering under the influence of englacial grain-boundary films of undercooled water. Higher pHs may be precluded by the meteorite's measured terrestrial age, if the maximum (four orders of magnitude) correction for the well-known lab/field silicate dissolution-rate discrepancy applies; if a smaller correction applies, higher pHs are allowed.

Mars-relevant etching of olivine occurred in a (terrestrial) cold desert environment on timescales that are short relative to the time available for possible similar processes on Mars.

MIL 03346 may have been exposed to even less specifically olivine-corroding liquid water (including brine) during the approximately half-billion to billion years after the iddingsitization of its olivine on Mars (~mid-late Amazonian) than it has been exposed to during its short (Pleistocene-Holocene) residency in Antarctica.

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FIGURE CAPTIONS

Figure 1. Arrays of submicron- to micron-scale etch-pits in naturally weathered terrestrial olivine. In this image, the largest ($>1\ \mu\text{m}$ in longest dimension) etch-pits are expressed in cross-section as wedge-shaped notches (W) along one face of the fracture (F) running from the upper middle of the frame's left edge to the middle right of the frame's bottom edge, and penetrating into olivine from fractures. Note the absence of counterpart notches across the fracture. Several *en echelon* arrays of submicron to micron-scale etch pits along dislocation arrays or subgrain boundaries (the ends of which arrays are marked D) occur in the unfractured interior of the olivine at a distance from fracture (left of and below center of frame, and right of and above center of frame). Diamond shaped (rhombohedral) cross-sections of biconical etch-pits (R) occur where symmetrical etch-pit growth proceeds from the dislocation array. BEI of polished thin section, Webster–Addie metadunite sample described in Velbel (2009); this image is a close-up image acquired from the same area as the feature shown in a lower magnification image in Velbel (2009) Figure 7a.

Figure 2. Etch-pits ranging in size from submicron to ten microns in long dimension in naturally weathered terrestrial olivine. These *en echelon* arrays of submicron to micron-scale etch-pits occur in the unfractured interior of the olivine at a distance from a fracture just beyond the left margin of the frame. As noted by Velbel (2009), these small ($<1\ \mu\text{m}$ in longest dimension) etch-pits, the largest of which are resolvably diamond-shaped in cross-section, strongly resemble in their size, shape, and distribution those formed by terrestrial weathering of terrestrial olivine along dislocations, as imaged by Eggleton (1986) and Banfield et al. (1990). As etch-pits overlap and coalesce (as shown in the secondary electron image of Velbel, 2009, his Figure 3), a

1448 mirror-image arrangement of counterpart wedges and serrations develops on the opposite
1449 interfaces of the cavity. BEI of polished thin section from slightly weathered corestone interior,
1450 Schofield Barracks (Oahu) basalt sample described in Velbel (2009); this image is a close-up
1451 image acquired from the same area as the feature shown in a lower magnification image in
1452 Velbel (2009) Figure 5.

1453
1454 Figure 3. The exterior olivine (light grey; ol) phenocryst hosts several melt inclusions (mi), has
1455 grown around unzoned augite cores (aug), and is surrounded by compositionally zoned
1456 clinopyroxene (aug) and mesostasis (mss) containing titanomagnetite (Ti-ilm). Fusion crust (fc)
1457 transects olivine, the larger melt inclusion, and alteration-product (iddingsite) veins (idd). The
1458 maximum perpendicular distance from fusion crust to the distal edge of the olivine phenocryst is
1459 approximately 600 μm . BE image of polished thin-section MIL 03346,171.

1460
1461 Figure 4. Iddingsite vein in the exterior olivine phenocryst approximately 550 μm perpendicular
1462 distance from fusion crust (see Figure 3 for context). The vein material at lower left (H) has
1463 homogenous atomic-number contrast and is visually identical to vein material in the interior
1464 olivine phenocryst of this allocation and olivines in other interior allocations of this nakhlite.
1465 Lamellar atomic-number contrast variations (L) appear toward the upper right. Note the absence
1466 of fractures crosscutting both the vein and the adjacent olivine. BE image of polished thin-
1467 section MIL 03346,171.

1468
1469 Figure 5. Iddingsite vein in the exterior olivine phenocryst approximately 250 μm perpendicular
1470 distance from fusion crust (just beyond the top of this frame; see Figure 3 for context). Vein

1471 material within approximately 300 μm of the fusion crust is vesiculated, and the solid material
1472 exhibits variegated atomic-number contrast (see also Figure 4). Note the absence of fractures
1473 crosscutting both the vein and the adjacent olivine. BE image of polished thin-section MIL
1474 03346,171.

1475

1476 Figure 6. Vesicular alteration product in exterior olivine approximately 250 μm perpendicular
1477 distance from fusion crust (just beyond the top of this frame; see Figure 5 for context). Note
1478 individual wedge-shaped notches (W) up to 2 μm in long dimension on olivine along olivine-
1479 vein interface. BE image of polished thin-section MIL 03346,171.

1480

1481 Figure 7. Vesicular alteration product in exterior olivine approximately <100 μm perpendicular
1482 distance from fusion crust (just beyond the top of this frame; see Figure 3 for context). Note
1483 individual wedge-shaped notches (W) up to 2 μm in long dimension on olivine along olivine-
1484 vein interface. BE image of polished thin-section MIL 03346,171.

1485

1486 Figure 8. Fractures with thin or no alteration product in the exterior olivine phenocryst
1487 approximately 300 μm perpendicular distance from fusion crust (just beyond the top of this
1488 frame; see Figures 3 and 5 for context). Note individual wedge-shaped notches (W) up to 2 μm
1489 in long dimension on olivine along olivine-vein interface. Counterpart notches or wedges do not
1490 occur on the opposite interfaces of the vein material. BE image of polished thin-section MIL
1491 03346,171.

1492

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8