QUANTIFYING THE TIMESCALES OF FLUID-ROCK INTERACTION ON MARS USING THE NAKHLITE METEORITES. T. Tomkinson[1], M. R. Lee[2], D. F. Mark[1], F. M. Stuart[1] and C. L. Smith[3,4] [1]Scottish Universities Environmental Research Centre, East Kilbride E75 0QF, U.K. E-mail: tim.tomkinson@glasgow.ac.uk., [2]School of Geographical and Earth Sciences, University of Glasgow, G12 8QQ, U.K. [3]Department of Mineralogy, Natural History Museum (London), Cromwell Road, London SW7 5BD, U.K. [4]ESA ESTEC, Keplerlaan 1, 200 AG Noordwijk, The Netherlands.

Introduction: The nakhlite meteorites are olivine-bearing clinopyroxenites that sample a region of Amazonian (~1.3 Ga) Martian crust. Despite their igneous origin, these rocks contain inter- and intra-granular clays, phyllosilicates, carbonates [1]. These 'secondary minerals' crystallized from water, and so can be used to reveal the longevity, length scale and compositional evolution of crustal fluids [e.g. 2, 3].

Here we have focused on understanding the nature of fluid-rock interaction by seeking evidence for dissolution of primary silicates. Etch pits have been previously recorded from the constituent olivine grains of nakhlite meteorites, but their origin is controversial. In addition to a Martian provenance that was proposed from studies of Miller Range (MIL) 03346 thin sections [4], etch pits have also been suggested to have formed by terrestrial weathering (MIL 03346 [5]) and microbial action (Nakhla [6]). Here we show that etch pits in olivine and augite grains from the Nakhla and Yamato 000749 (Y000749) meteorites formed by dissolution on Mars. We also describe the timing of dissolution relative to secondary mineralization and use the etch pits to quantify the duration of fluid-rock interaction.

Methods: This study used the freshly exposed surfaces of olivine and augite grains taken from a 1.7 g chip of Nakhla (BM1913,25) and a 0.5 g chip of Y000749,59. The grains were examined optically, then using a FEI Quanta 200 field-emission SEM for backscattered electron (BSE) imaging and energy dispersive X-ray (EDX) analyses. All SEM work was undertaken at low vacuum (45 Pa) and 15-20 kV. Foils were cut from olivine grain surfaces using a FEI Duomill dual-beam focused ion beam (FIB) instrument operated with a 30 kV Ga^+ ion beam. They were milled initially to ~2 µm thickness using a ~1 nA current before thinning to ~90 nm at ~100 pA. Images and selected area electron diffraction (SAED) patterns were acquired from these foils using a FEI T20 transmission electron microscope (TEM) operated at 200 kV.

Results and discussion: The freshly exposed surfaces of some of the Nakhla olivine grains are decorated by small rounded structures that are interpreted to be etch pits. [7]. These pits may be empty, or filled with secondary minerals, which have been previously demonstrated [1] to be pre-terrestrial (i.e. Martian) in origin. The empty pits range from diamond to bowl shape, reflecting the crystallographic orientation of the grain on which they have formed. Morphologically similar etch pits have been observed in terrestrial olivine whose shapes are also crystallographically controlled [8]. The grain in Figure 1A has an array of ~100 by 100 aligned etch pits that range from ~30 µm to sub-micron in diameter.

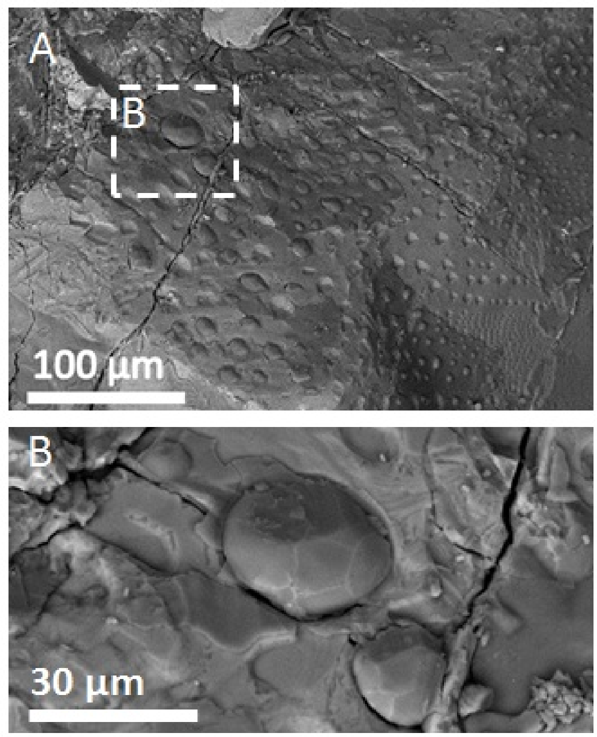

Figure 1: BSE images of a Nakhla olivine grains. [A] Overview image of a pitted grain surface. Some of the pits are empty and cut into olivine (light grey), whereas others are filled by secondary minerals (darker grey) to produce domes. [B] The boxed area in [A] showing two domed secondary mineral-filled pits.

Using the FIB technique a foil was cut from a domed feature very similar to that in the center of Figure 1B. The TEM image of this foil (Fig. 2A) shows that beneath the dome is a faceted pit in olivine. The volume between the surface of the dome and the floor of the pit is occupied by compact nanocrystalline smectite (Fig. 2A). The domes are interpreted to be secondary mineral casts of etch pits that had formed within the counterpart olivine grain that was removed during sample preparation (Fig. 2B).

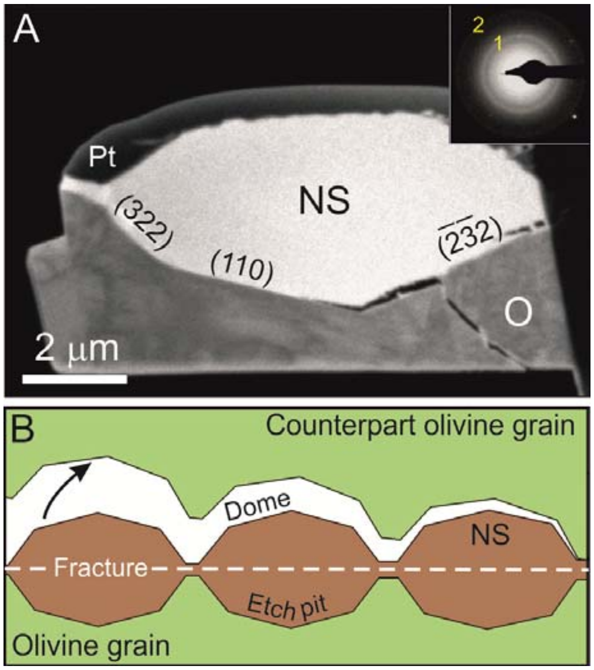

Figure 2: [A] Dark-field TEM image of a foil cut from a dome on a Nakhla olivine grain surface. The dome is composed of nanocrystalline smectite (NS), and in the olivine (O) beneath is an etch pit. The crystallographic orientations of pit walls are indicated. A SAED pattern acquired from nanocrystalline smectite (inset) has d-spacings of 0.256 nm (ring 1) and 0.157 nm (ring 2). The image was formed using part of the 0.157 nm diffraction ring. Pt is FIB-deposited platinum. [B] Diagram showing the origin of the domes. Initially, hemispherical etch pits form by dissolution of olivine on both sides of a fracture. The newly formed intracrystalline pore space is then filled by nanocrystalline smectite (NS). During sample preparation the olivine grain has separated along the upper interface between the nanocrystalline smectite-filled pits and olivine (shown by the arrow) to leave casts of the pits (i.e. the domes).

Surfaces of the Y000749 pyroxene grains also reveal elongated and faceted etch pits (Fig. 3). These pits range from 10 to 1 µm in diameter, and are lined by a thin layer of nanocrystalline smectite.

Implications: Etch pits in the Nakhla and Y000749 grains are clear evidence for dissolution of silicate minerals within the Martian crust. Timescales of etching can be estimated from pit size, and assuming a fluid pH and temperature. For example, at pH 5/100 °C a 2.5 µm deep pit in olivine could have formed in 1.8 days, whereas at pH 5/25 °C the duration of dissolution required increases to 3.1 yr. Over a range of likely conditions, dissolution timescales were therefore brief.

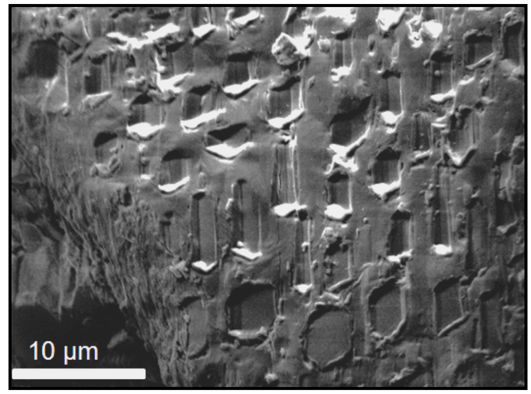

Figure 3: BSE image of etch pits in a Y000749 pyroxene grain that are lined with secondary minerals.

The intra- and inter-crystalline pores produced by dissolution were subsequently filled by secondary minerals. Although the time gap between dissolution and mineralization cannot be determined, it is likely that the cations liberated from olivine and augite contributed to precipitation of nanocrystalline smectite in a chemically near-closed system, as also proposed by [3,9,10]. Secondary minerals occur in all of the nakhlites [10], and as etch pits have now been identified in MIL 003446, Y000749 and Nakhla, it is likely that dissolution was a prerequisite for secondary mineralization. Etching served the dual purpose of enhancing porosity and permeability, thus facilitating further fluid ingress, and supplying cations. Nonetheless, liquid water was present only briefly so that the aqueous system was temporally, and spatially, limited. The etch pits we have found on rough grain surfaces would have been lost in conventional thin section manufacture, which may explain why they are rarely observed.

Acknowledgements: We thank the Natural History Museum (London) for provision of the Nakhla sample and to the Japanese Antarctic Meteorite Research Center for the chip of Yamato 000749. This work was supported by grants from the UK Science and Technology Facilities Council (ST/H002472/1 and ST/H002960/1).

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