OXIDATION STATES IN MIL03346 NAKHLITE FROM EXPERIMENTS REPRODUCING PHENOCRYST-MELT EQUILIBRIA AS A FUNCTION OF fO<sub>2</sub> AND T at 40-150 MPa: M.J. Rutherford<sup>1</sup>, and Julia E. Hammer<sup>2</sup>, <sup>1</sup>Department of Geological Science, Brown University, Providence RI 02912 (malcolm\_Rutherford@brown.edu), <sup>2</sup> Department of Geology and Geophysics, University of Hawaii, Honolulu, HI.

**Abstract:** Experiments on chips of MIL03346 have reversibly duplicated crystal-melt equilibria for melts formed from both the groundmass and melt inclusions. Experiments were at 40-160 MPa at temperatures of 1080 to 1140°C at log fo<sub>2</sub>'s corresponding to QFM, QFM-1 and QFM-2 buffers. Results indicate that the interstitial melt in equilibrium with the core olivine (Fo<sub>43</sub>) and Ca-Pyx (En<sub>38</sub>Wo<sub>41</sub>Fs<sub>21</sub>) is an Fe-rich, Al-poor (~9.0wt%) basalt. The phenocryst core compositions are reproduced at 1125°C at QFM-2, but not at QFM-1, and magnetite crystallizes in place of olivine at QFM.

Introduction: The SNC meteorites are an important source of information about the petrological and volcanological history of Mars. Although most of the SNC meteorites have been extensively studied (1) in attempts to determine as much as possible about their age, origin, and petrogenetic history, many unanswered questions remain. [a] Under what conditions of pressure and oxidation state did the different samples crystallize, [b] What are the parent melts for the different SNC samples, and can they be related by differentiation processes. [c] Can we identify evidence of volatile abundance and determine whether degassing occurred in the SNC magmas? MIL03346 has been used in an experimental and analytical study that attempts to resolve these questions as they pertain to the makhlites.

**Methods:** The natural MIL03346 sample has been studied analytically and texturally using EMPA and petrographic techniques. Approximately 1mm<sup>3</sup> chips of the sample have also been used in experiments to reproduce the phenocryst-melt equilibria in the sample. The experiments have been done at ~160 MPa using graphite powders in a sealed Pt container together with the oxidized natural sample to generate a G-CO assemblage which fixes the fO<sub>2</sub> at QFM-2 (2). Experiments at QFM and QFM-1 were done at similar pressures using crimped fayalite-saturated AuPd tubes inside sealed Pt that contained a metal-metal oxide buffer. The latter experiments contained only the volatiles present in the natural MIL03346 chips.

**Results**: The MIL03346 nakhlite, like other members of this group, consists of Ca-rich pyroxene (En<sub>38</sub>Wo<sub>41</sub>Fs<sub>21</sub> cores with thin normally-zoned rims that reach En<sub>9</sub>Fs<sub>44</sub>Wo<sub>47</sub>) and olivine phenocrysts

(Fo<sub>43.5</sub> cores with ~100 micron thick normally zoned rims) in a dark fine-grained groundmass (3,4). The groundmass (~21 v%) contains dendritic-textured Farich olivine, Fe-rich Ca-pyroxene, titanomagnetite, cristobalite, and Cl-apatite in order of decreasing abundance. Olivine phenocrysts are sparse; only one and two large (1.7mm) crystals occur in the two polished sections studied (Fig.1). Low-Ca pyroxene phenocrysts have not been identified, but a 50 micron crystal (En55Fs44Wo1) is the largest daughter crystal in an olivine-hosted melt inclusion. Where an olivine phenocryst contacts or partially grows around Cpx the zoning is absent. The important observations from the natural sample for the objectives of this project are: (a) Melt that was in equilibrium with phenocryst cores was in equilibrium with Fo<sub>43</sub> olivine, Ca-Pyx, and possibly a spinel with 11 wt% Cr<sub>2</sub>O<sub>3</sub>. A microphenocryst of this composition was trapped with melt by an olivine in MIL03346,94; (b) Strongly zoned rims on the phenocrysts show a sharp change the compositions relative to homogeneous cores, but this appears explainable by a change in crystallization conditions and rate (6).

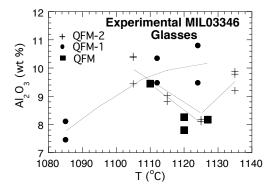
Results of experiments at QFM-2 produce a high-Fe and low-Al basaltic melt that is in equilibrium with the core Cpx at 1135 and with Fo<sub>43</sub> olivine at  $1125^{\circ}$ C (Fig. 2). At QFM conditions, the melt coexisting with Cpx crystallizes Ti-magnetite below  $1120^{\circ}$ C and olivine appears nowhere on the >1100°C liquidus. At QFM-1, the core Cpx composition of the natural sample is produced in the highest T experiment (1125°C), but magnetite is again produced before olivine and the olivine present at 1110 and 1085°C is Mg-rich (Fo<sub>55-50</sub>) compared to MIL03346 (2).

**Discussion:** The textures in the MIL03346 suggest relatively slow phenocryst growth at some depth in Mars, and the likelihood of crystal-melt segregation. Olivine phenocrysts partially enclose some of the smaller Cpx phenocrysts (Fig. 1), indicating co-crystallization of these two phases. The homogenous core compositions of the natural Olv and Cpx phenocrysts, which represent ~60-65 v% of the MIL03346, indicate that the parent magma underwent little compositional change during their formation. Thus, the olivine and Cpx cores represent a small degree of crystallization of the parent magma. MIL03346 must have formed by a process such as

crystal settling. The close correspondence between the rehomogenized groundmass composition and the melt trapped in phenocrysts at 1125°C suggests there was little or no magmatic exchange between the interstitial melt and the surroundings after the inclusion was sealed (Fig. 3). Just as the cores of the phenocrysts in this Nakhlite indicate very slow crystal growth in a large pool of melt, the rims indicate a sharp change in the cooling rate, and a relatively closed, small-volume, melt system. The thin normally-zoned rims on the Cpx, particularly the rapid increase in Al and Ti, illustrate this rapid growth. Somewhat thicker rims on olivine adjacent to groundmass compared to Cpx rims are consistent with this interpretation.

The compositions of new-growth phenocrysts produced in the experiments and the crystallization sequence with decreasing T indicates the natural assemblage formed at an fO<sub>2</sub> of QFM-2, possibly QFM-1. Using the Eu oxybarometer, (5) determines the fO<sub>2</sub> during phenocryt formation was at QFM-1. The presence of fayalitic olivine, magnetite, and cristobalite in the groundmass indicate that the fo<sub>2</sub> as crystallization was completed was at QFM. We interpret the increase in fO<sub>2</sub> from QFM-2 to QFM during crystallization as indicating the build up of Fe<sup>3+</sup> in the residual melt and the late-stage change in SiO<sub>2</sub> activity. Interestingly, a similar range of fO<sub>2</sub>'s was determined for shergottites NWA 1068/1110 using Olv-Pyx-Sp geobarometry (6,7).

**References:** (1); Longhi, J., 1991 PLSC21, 695-709; McSween H.Y. Jr. 1994, MAPS, 29,757-779 (2) Nicholis M.G. and Rutherford M.J. (2005) *LPSC XXXVI*, #1726 (3) Treiman, A.H., 2005, Chemie de Erde, 65, 203-296; (4) Day et al., 2006, MAPS, 41,581-606; (5) McCanta et al., 2004, GCA,68,1943-1952; (6) Goodrich, C.A., et al., 2003, MAPS 38, 1773-1792; (7) Herd, C.D.K., 2006, Am Min., 91,1616-1627.



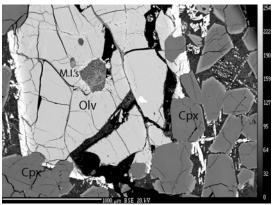
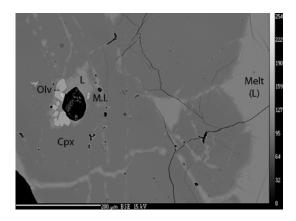


Fig. 1. (above) BSE image showing the olivine and Cpx phenocrysts in MIL03346 with fine-grained groundmass. Scale bar is 1000 um.

Fig. 2.(below) BSE image of MIL experiment at QFM-2, 1125 °C & 160 MPa. Euhedral olivine in the M.I and adjacent Cpx are identical to those in MIL03346.



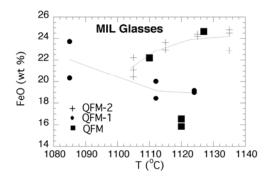


Fig. 3. (a) Plots of  $Al_2O_3$  and (b) FeO vs: temperature for MIL03346 experimental glasses. Both matrix and M.I compositions are shown for most experiments (T's), and are similar. QFM experiments contain titanomagnetitie and no olivine; QFM and QFM-2 melts coexist with CPx +Olv.