EXSOLUTION OF IRON-TITANIUM OXIDES IN MAGNETITE IN MILLER RANGE (MIL) 03346 NAKHLITE: EVIDENCE FOR POST CRYSTALLIZATION REDUCTION IN THE NAKHLITE CUMULATE PILE.

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Introduction: MIL 03346 is one of the most mesostasis-rich nakhlites [1] and thought to have equilibrated at oxygen fugacities near the fayalite-magnetite-quartz oxygen (FMQ) buffer ([2,3]). Studies of FeTi oxides in nakhlites have led to additional constraints on their equilibration temperatures and fO_2s [4,5,6,7]. Comparison of these results to fO_2s calculated for shergottites indicates that nakhlites are among the most oxidized samples from the martian meteorite suite [2].

The mesostasis of MIL 03346 contains skeletal titano-magnetite. Several scientists noticed several years ago (e.g. [8]) that this titanomagnetite contains very fine oxidation-driven exsolution lamellae (Figure 1). However, the lamellae are so small that they cannot be characterized by electron microprobe analysis (EMPA). Here we select several areas for focused ion beam (FIB) extraction, prepare transmission electron microscopy (TEM) foils, and identify and analyze the lamellae using TEM at the Johnson Space Center (JSC). The resulting analyses are combined with previous work on nakhlites to interpret the thermal and oxidation history of this meteorite group.

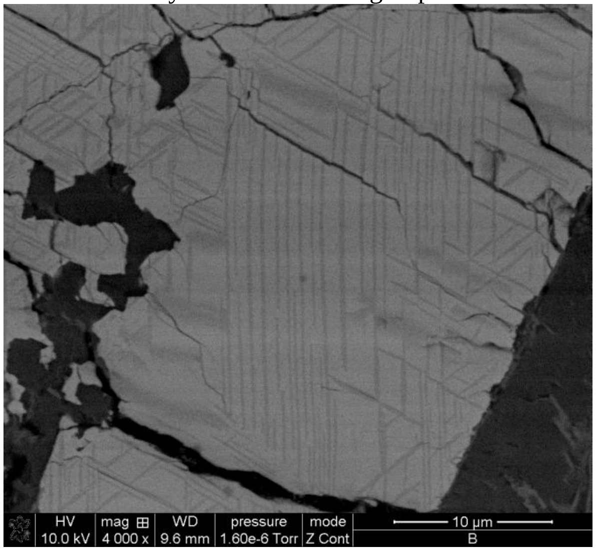

Figure 1: Backscattered electron image of titanomagnetite showing the fine oxidation-driven exsolution lamellae of ilmenite in MIL 03346 ,106.

Petrography and FIB extraction

Section 106 was approved by the Meteorite Working Group (MWG) to have FIB samples removed to do this work. Searching of the section using scanning electron microscopy allowed identification of several regions where well developed lamellae are present and in regions that have substantial depth beneath the surface. These regions were then extracted in the form of 1 x 10 x 15 um sheets using a dual focused ion-beam **(**FIB) instrument (FEI: Quanta 3D-FEG) using 30 KV Gallium ion-beam at the NASA Johnson Space Center (JSC) and then thinned further using 5 KV and 2 KV gallium ions for TEM work. We obtained imaging, diffraction and chemical data from the FIB section using the JSC JEOL 2500 field-emission STEM equipped with a Noran thin window energy-dispersive X-ray (EDX) spectrometer.

EDX data: Recalculation of the EDX data in oxide wt.% results in the following analyses of the ilmenite and host magnetite: bulk ilmenite: FeO 45.94%, MnO 1.40%, TiO_2 52.65%; bulk Titanomagnetite: FeO 35.15%, Fe_2O_3 58.06%, TiO_2 3.87%, Al_2O_3 2.92%. A small amount of MgO (0.14 wt%) is measured in the host magnetite using EMPA [2], but was below EDX detection limits for these analyses.

TEM analysis: The TEM confirms that the lamellae are typical trellis type oxidation-driven exsolution of ilmenite on (111) of the host titanomagnetite (Figure 2). From the EDX analyses, the ilmenite stoichiometry is $\sim(Fe_{0.97}Mn_{0.03})TiO_3$ – electron energy-loss spectroscopy will be used to determine Fe3+ contents. The host “bulk” titanomagneite is $(Fe_{2.76}Al_{0.13}Ti_{0.11})O_4$. There is further exsolution within the host titanomagnetite into nearly endmember magnetite $[(Fe_{2.87}Al_{0.06}Ti_{0.07})O_4]$ and more Al and Ti-rich very thin (~10 nm thick) lamellae exsolved on (100), $[(Fe_{2.41}Al_{0.33}Ti_{0.26})O_4]$ (Figure 2). The Al- and Ti-rich magnetite also occurs as a ~5-10 nm thick layer at magnetite-ilmenite interfaces.

Temperature and fO_2 calculations: The coexistence of ilmenite and magnetite allows calculation of T and fO_2 of equilibration based on the oxidation of FeO to Fe_2O_3 [9]. The most recent version of this oxythermometer, [10], is applied because it is best calibrated for long and short range cation order, and also includes the newest experimental data for the $Fe^{2+}Ti – (Fe^{3+})_2$ exchange equilibria. The resulting temperature is 340 °C and relative fO_2 is FMQ-4.0 (NNO-4.9). This relative value is much lower than typical estimates for nakhlites which are between FMQ+1 and FMQ-2. However, this temperature is quite a bit lower than many previous calculations and is indeed the lowest calculated for a nakhlite (e.g., [4-7, 14)).

Comparison to other nakhlites: Using chemical analyses of magnetite and ilmenite from nakhlites reported in the literature, we have recalculated T and fO_2 using the Ghiorso and Evans (2008) FeTi oxide geothermometer. The values of temperature and relative fO_2 are higher than those calculated for MIL 03346, but all the data define a trend with the lowest temperature FeTi pairs also being the most reduced relative to FMQ. MIL 03346 falls along the trend defined by other samples (Nakhla, Lafayette, NWA 998, Yamato 000589). Such a trend of temperature and ΔNNO is observed in terrestrial volcanic tuffs such as the Bishop Tuff and Katmai and various plutons ([10,12]), suggesting that there was reduction upon subsolidus cooling and degassing of those igneous bodies. One possibility is a reduction reaction such as $Fe_2O_3 + FeS = 1/2S_2 + 3FeO$, which occurs while S_2 is lost through cooling and degassing. This hypothesis could be tested against careful studies of the S content of nakhlite mesostasis to see if there is a trend with the temperatures and ΔFMQ (or ΔNNO) values calculated here. Although such data have not yet been obtained for MIL 03346, the nakhlites thought to have formed shallower – e.g. NWA 817 [15] – have the lowest S content [16], whereas those thought to have formed deeper – e.g. NWA 998 [15] – have the highest S content [16]. This suggests that the shallower samples lost more S and became more reduced, whereas those forming deeper stayed oxidized and retained more S during cooling.

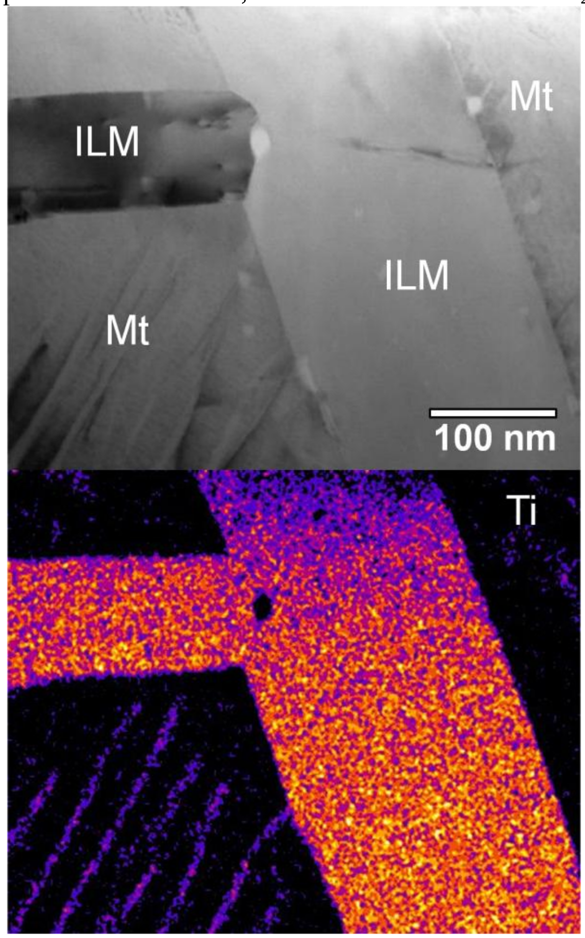

Figure 2: Transmission electron microscope image (top) of subsolidus oxidation-driven exsolution of ilmenite (ILM) in titanomagnetite (Mt). There is further set of exsolution lamellae of an Al-Ti bearing spinel from the magnetite that are apparent in the Ti map (bottom).

The exsolution of $FeAl_2O_4$ from titanomagnetite host is consistent with very low temperatures, as there is a solvus in the Fe-Al-O system at 860 °C [13].

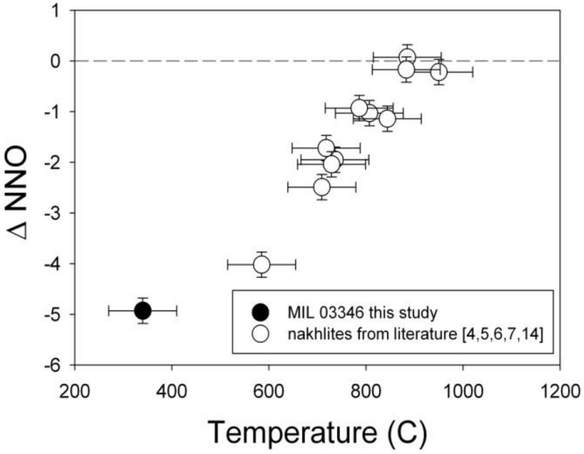

Figure 3: Temperature and fO_2 (relative to the nickel-nickel oxide NNO buffer) for the MIL 03346 nakhlite magnetite-ilmenite pairs in this study, compared to those from previous studies. All temperatures and fO_2 calculated using the Ghiorso and Evans (2008) oxybarometer. Previous studies include [4,5,6,7,14].

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