NANO-SCALE INVESTIGATION OF SPINEL-ORTHOPYROXENE INTERGROWTHS IN NORTHWEST AFRICA 8159. A RECORD OF fO2 BUT AT WHAT TEMPERATURE? Paula Provencio¹, Charles, K. Shearer¹, Aaron S. Bell¹, and Paul V. Burger¹. ¹Institute of Meteoritics, Department of Earth and Planetary Science, University of New Mexico (UNM), Albuquerque, New Mexico 87131 (pprovenc@unm.edu)

Introduction: The fO2 of crystallization for martian basalts has been estimated in various studies to range from IW-1 to QFM+4 [1-3]. Studies by [1,2] observed that within the shergottite group the fO2 of crystallization is highly correlated with numerous chemical and isotopic characteristics (i.e. REE, εNd) with depleted shergottites generally crystallizing at reduced conditions and enriched shergottites crystallizing under more oxidizing conditions. In contrast to the shergottites, augite basalts such as NWA 8159 are highly depleted yet appear to be highly oxidized (e.g. QFM+4) [3]. An interesting textural attribute of NWA 8159 is that it has intergrowths of orthopyroxene and spinel adjacent to or associated with olivine rims (Fig. 1). The origin of this texture has two different interpretations that have fundamental implications for the fO2 conditions of crystallization, the nature of the martian mantle, and the interactions between mantle derived magmas and the martian crust. One interpretation is that this texture is magmatic in origin and formed by reaction A:

Olivine+Melt⇒Orthopyroxene + Spinel [4-6].

Alternatively, this texture could be formed at subsolidus conditions by reaction B:

Olivine+O2⇒Orthopyroxene+Spinel [7-9].

The relationship of temperature and fO2 between these two reactions is illustrated in Figure 2. In order to interpret these textures and their relationship to martian magmatism, we have examined these textures at the nanometer scale.

Experimental and Analytical Approach: Thin sections of the NWA 8159 were initially examined and documented using backscattered electron imaging on the JEOL JXA-8200 electron microprobe (EMP). Quantitative point analyses were conducted on olivine, pyroxene, and magnetite using the EMP. Analyses were conducted at an accelerating voltage of 15 kV, a beam current of 20 nA, and a spot size from 1-3 μm. Nanometer scale imaging and elemental analysis of the intergrowths were carried out using a FEI Quanta 3D at 30 kV, 10pA to 1nA focused ion-beam (FIB), SEM at 20kV, and energy dispersive x-ray spectroscopy (EDS). This instrument was used to cut and extract TEM thin sections, ~50nm thick, of site specific areas of the sample based on nano-textural images and elemental analysis. At 200kV, high resolution TEM (HRTEM) atomic-scale imaging, electron diffraction, energy filtered TEM, scanning TEM (STEM) and EDS mapping were done using the JEOL 2010 and JEOL 2010FX STEM at the University of New Mexico.

Results:
Mineral chemistries: Olivine ranged in composition from Fo20.40. The pyroxenes intergrown with the oxides have a range in compositions: En80.40Wo1.3. The spinel is essentially end-member magnetite.

Nano-scale textures in intergrowths and olivine host: Nano-scale measurements included HRTEM

![Figure 1. BSE images illustrating the textural relationships among olivine (OL), orthopyroxene (OPX), and magnetite (MAG). The scale bar is approximately 50 μm.](image1)

![Figure 2. Reactions in the systems MgO-FeO-Fe2O3-SiO2 and Fe-O-SiO2 plotted in temperature versus fO2. This diagram illustrates that Reaction A plots at higher temperature and fO2 than that of reaction B. Data is modified after [9,10].](image2)
imaging, electron diffraction measurements, and EDS X-ray mapping. Examples of these measurements are shown in Figures 3 and 4. Orthopyroxene intergrown with magnetite ranges from crystalline to amorphous (Figure 3). These variations in crystallinity are similar to those observations made by Bell et al. [11] for subsolidus orthopyroxene-troilite intergrowths replacing olivine in lunar lithologies. On the nanometer scale, the magnetite in the intergrowths is fairly homogeneous and does not exhibit exsolution or oxyexsolution. However, along some magnetite-orthopyroxene interfaces, there are reaction boundaries that are enriched in Ca, Al, and P (Fig. 4). With the current observations it is uncertain if these reaction boundaries represent a subsolidus event linked to reaction B or a much lower temperature reaction that is observed in the olivine [12].

**Discussion:** Many of these nano-scale features and X-ray maps are somewhat ambiguous. However, there are preliminary morphological, chemical, and mineralogical observations that are suggestive of a subsolidus origin for these intergrowths. The overall “wormy” textures exhibited by the oxides are reminiscent of the orthopyroxene-troilite, orthopyroxene-Fe-metal, and SiO$_2$-Fe-metal intergrowths that replace olivine at subsolidus conditions in many planetary materials [11]. In several of the orthopyroxenes associated with these intergrowths, the pyroxene is amorphous to nanocrystalline. This is not consistent with a magmatic origin [11]. In Figure 4 the reaction boundary between the orthopyroxene and magnetite is seemingly of a low temperature origin. Finally, the spinels in the intergrowth are end-member magnetite with no exsolution or oxyexsolution features observed at the nano-scale. Studies carried out by [13,14] suggest that for primitive martian basalts (Y98) at relatively high temperature (1100-1200°C) and oxidizing conditions (QFM to QFM+3), magmatic spinel that co-crystallizes with olivine and orthopyroxene has only a maximum of 25 mol.% magnetite component.

**Figure 3.** TEM image illustrating the textural relationship among magnetite, orthopyroxene (OPX), and olivine. Part of the OPX in the diagram is nanocrystalline to amorphous. Scale bar is 1 µm.

**Figure 4.** Elemental maps of interfaces among magnetite (M), olivine (OL) and orthopyroxene (OPX). Top two images are TEM energy filtered Si and Fe maps and illustrate the reaction boundary between orthopyroxene and magnetite. Scale bar is 50 nm. Lower four images (rotated a little to left) are high magnification STEM-EDS maps (Fe, Al, Ca, P) of the reaction boundary. See box in top left image. Scale bar is 100 nm.

**Preliminary conclusions:** Based on mineral chemistries, textures, and experiments presented by [6,13,14], our preliminary conclusions concerning the origin of these intergrowths is that they represent a subsolidus oxidation process similar to reaction B.

**References:**