SPINEL UNMIXING IN MARTIAN ANALOG CRUSTAL ROCKS: IMPLICATIONS FOR THE MAGNETIZATION OF MARS. J.B. Bowles[1,2], J.E. Hammer[1], L. Tatsumi[1], and S.A. Brachfeld[3], [1]Dept. of Geology and Geophysics, University of Hawaii, 1680 East-West Rd., Honolulu, HI 96822, [2]now at Institute for Rock Magnetism, University of Minnesota, 100 Union St. SE, Minneapolis, MN 55455, jbowles@umn.edu, [3]Dept. of Earth and Environmental Studies, Montclair State University, Montclair, New Jersey, 07043

Introduction: The strong intensity of the Martian magnetic anomalies mapped by the Mars Global Surveyor (MGS) has led to considerable interest in the magnetization of the Martian crust. The magnetization is inferred to be several orders of magnitude stronger than typical terrestrial basalt, and potential magnetic carriers must therefore be capable of acquiring a strong, stable magnetization. If the remanence is of primary igneous origin, a plausible source candidate is single-domain (titano-)magnetite.

Prior work in the current study concentrated on evaluating cooling rate, oxygen fugacity, and bulk composition as variables controlling oxide mineralogy, composition, grain size, and magnetic characteristics [1-3]. Key findings include the observation that rapid cooling under moderately oxidizing (QFM) conditions can lead to fine-grained, stable single-domain titanomagnetite. However, as cooling rate decreases, oxide grain size increases, approaching or reaching a multidomain state. This larger grain size can impact both the intensity and the long-term stabiliby of magnetization.

While this earlier work produced materials analogous to rapidly-cooled extrusive basalts, the present study aims to more closely reproduce a magnetic mineralogy that might be generated in slowly-cooled intrusive Martian crust. We examine subsolidus processes at elevated temperature to understand the fate of igneous Fe-Ti oxides when allowed sufficient time for compositional unmixing (exsolution) to occur. The resulting subdivision of the large grains into an Fe-rich phase and an Fe-poor phase could decrease the effective magnetic grain size [4], possibly leading to a stronger and more stable remanence [5,6]. The processes may also serve to increase the Curie temperature [4], leading to a thicker possible magnetic source layer.

Subsolvus exsolution of spinel-structured minerals occurs in response to lattice strain incurred during cooling and results in two spinel-structured (cubic) phases. This is in contrast to oxyexsolution, which is frequently observed in terrestrial basalts and is the reaction of titanomagnetite with oxygen to form domains of Ti-rich rhombohedral-structured oxide. It is also distinct from the exsolution of rhombehedral hemo-ilmenite that has been proposed as a possible source for the Martian magnetic anomalies [e.g. 7-8].

Methods: Two basic starting compositions [3] are used for the sample synthesis. The first is Fe-rich and Al-poor (Fe/Al = 1.5) and is patterned after the SNC basaltic meteorites [9]. The second (Fe/Al = 0.4) more closely resembles a terrestrial basalt [10]. Samples were contained in Pt capsules, heated to just above the

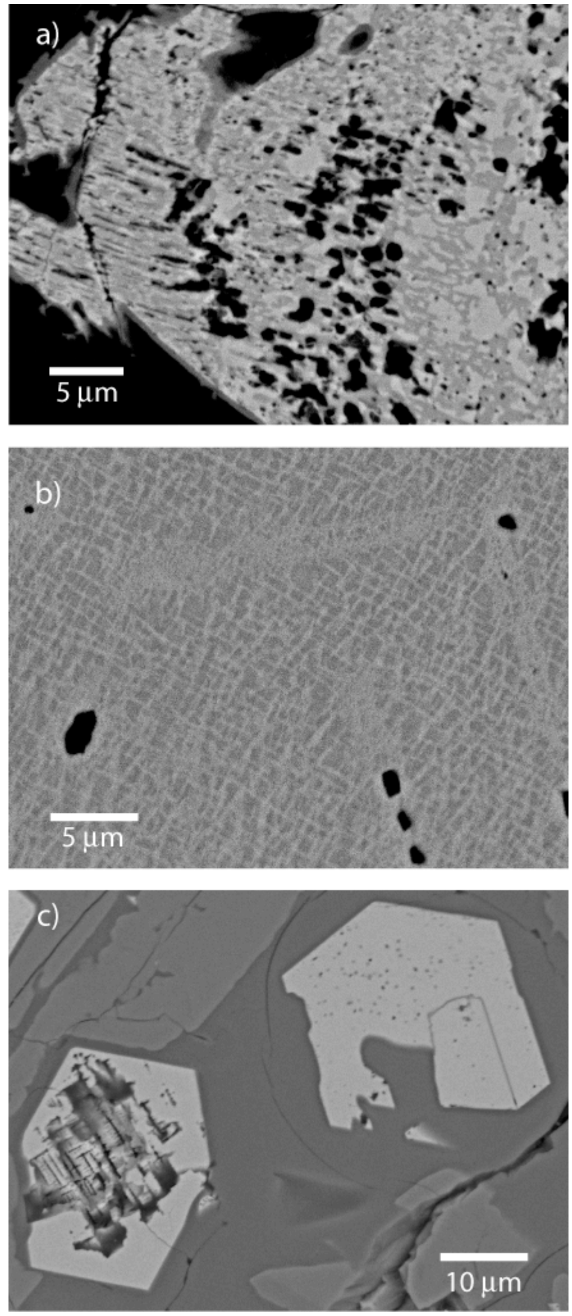

Figure 1. Backscatter images of post-anneled samples. **a)** Meteorite-type (Fe-rich) sample annealed at 710°C. Oxide grain shows both mottled compositional variations and discontinuous, wormy grain dissolution. **b)** Terrestrial-type sample annealed at 710°C. Oxide grain displays two sets of lamellae at ~90° to each other, interpreted to represent true spinel exsolution. **c)** Terrestrial-type sample showing grains with advanced (left) and incipient (right) dissolution.

liquidus, and cooled at 4°/hr to ~1070°C at the QFM buffer, and then quenched. The resulting samples with coarse-grained oxides were then sealed in Ag capsules, and the capsules were in turn sealed in evacuated Si tubes, along with ~0.5 g Fe^o powder as an oxygen getter. Samples were placed in a furnace at either 600, 630, 650 or 710°C and were left to anneal for 8-10 weeks.

Splits of each sample were used for petrographic and magnetic analysis. Preliminary compositional information was obtained using EDS spectra. Magnetic hysteresis (magnetization vs. field strength) and first order reversal curves (FORC) were measured on all pre- and post-annealed samples. In addition, a 2.5 T field was applied at both 20 K and measured on warming, and at 300 K and measured on cooling.

Results and Discussion: The oxide grains in the pre-annealed material of both bulk compositions are Mg-, Al-, and Cr-bearing titanomagnetites. A small proportion of the grains show evidence for a coarse intergrowth of an Fe- and Ti-rich phase with a separate Mg- and Al-rich phase. As the Mn content across both phases is small and nearly uniform, we tentatively infer that both are spinel-structured, as Mn strongly partitions into rhombohedral oxide phases. All samples initially display multi-domain-type magnetic hysteresis behavior, consistent with the observed coarse oxides.

Compared to pre-annealed samples, samples annealed at 650 and 710°C display dramatic differences in composition, structure and magnetic properties. Samples of both bulk compositions display oxide grains with a mottled appearance (Fig. 1a). The mottled areas are compositionally distinct from the two phases present in the starting material; the light-toned mottled areas are richer in Fe and poorer in Ti and Al than the dark-toned mottled areas. Assuming both are spinel-structured, EDS compositional analysis suggests the light-toned phase is enriched in a magnetite (Fe_3O_4) component, while the dark-toned phase is enriched in ulvöspinel (Fe_2TiO_4) and hercynite ($FeAl_2O_4$).

The terrestrial-type samples also display some oxide grains with thready, lineated, lamellae (Fig. 1b). Lamellae are lighter in tone than the matrix and are spaced fairly consistently at ~0.5 μm. (Fig. 1b). They can occur as more than one set, with second set ~90° from the first, subdividing the matrix into rectilinear regions. This pattern is consistent with spinel (cubic) exsolution structures observed by [11] in the magnetite-spinel ($MgAl_2O_4$) system. Due to their small size, constraints on the compositions of the lamellae are not yet available. However, the angular relationships among lamellae suggest they represent true exsolution from initially homogeneous spinel-structured oxides.

In addition to the oxide compositional variations within the annealed samples, many oxide grains also show evidence for corrosion or dissolution (Figs. 1a and 1c). Defined as porosity not present in the unannealed starting material, the dissolution can appear as a negative dendritic crystal within a euhedral grain (Fig. 1c), or as discontinuous blebs or wormy holes (Fig. 1a). Accounting for up to 40% of area of exposed grains, the porosity appears weakly to strongly controlled by crystallography. The corroded grains are also usually (but not always) mottled and/or or contain lamellae. The source of corrosion is still under investigation, but may result from unintended reduction of the samples by the presence of the oxygen getter.

Magnetically, the annealed samples display a dramatic increase in coercivity and saturation remanent magnetization, consistent with a reduction in effective magnetic grain size from multi-domain to single-domain or pseudo-single-domain size. While the source of the change in domain state is rendered ambiguous by the corrosion textures in the samples which could also serve to decrease effective grain size, the magnitude of the change is similar to that observed by [12] in exsolution from the magnetite-spinel solid solution. An accompanying increase in saturation magnetization is also consistent with unmixing of the homogeneous titanomagnetite to create an Fe-rich phase. Results of the FORC experiments show evidence for significant magnetic interactions, as observed by [5] and inferred by [12] for microstructions resulting from exsolution.

Conclusions: Sub-solidus annealing of basaltic Martian analogs produces: 1) an Fe-rich phase and a Ti- and Mg-rich phase in place of homogoneous Mg- and Al- bearing titanomagnetites. We infer this has resulted from spinel exsolution at temperatures ≥100°C higher than expected in pure titanomagnetite (~600°C) [13]; 2) a reduction in effective magnetic grain size from multi-domain to near-single-domain size; 3) an increase of 30-75% in saturation remanent magnetization and in saturation magnetization by up to a factor of 10; 4) considerably increased magnetic interactions.

Although the oxide grain dissolution that accompanies exsolution bears further investigation and precludes firmly linking the magnetic effects soley to exsolution at this time, we tentatively suggest that compositional unmixing of spinel oxides in the Martian crust may play a critical role in producing a strong, stable magnetization.

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