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Contribution of multidomain titanomagnetite to the intensity and stability of Mars crustal magnetic anomalies

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Abstract Two basalts with compositions relevant to the crusts of Mars and Earth were synthesized at igneous temperatures and held at 650°C for 21 to 257 days under quartz-fayalite-magnetite fO₂ buffer conditions. The run products are germane to slowly cooled igneous intrusions, which might be a significant volumetric fraction of the Martian crust and carriers of magnetic anomalies in the Southern Highlands. Both basalts acquired intense thermoremanent magnetizations and intense but easily demagnetized anhysteretic remanent magnetizations carried by homogeneous multidomain titanomagnetite. Hypothetical intrusions on Mars composed of these materials would be capable of acquiring intense remanences sufficient to generate the observed anomalies. However, the remanence would be easily demagnetized by impact events after the cessation of the Mars geodynamo. Coercivity enhancement by pressure or formation of single domain regions via exsolution within the multidomain grains is necessary for long-term retention of a remanence carried exclusively by multidomain titanomagnetite grains.

1. Introduction

The high intensity of the Martian magnetic anomalies mapped by the Mars Global Surveyor (MGS) mission has led to considerable interest in the magnetization of the Martian crust, including the remanence acquisition process, composition of the magnetic recording assemblage, and subsequent modification of the remanence by impacts, volcanism, and near surface processes [Acuña et al., 1999, 2001; Connerney et al., 1999; Hood et al., 2003; Mohit and Arkani-Hamed, 2004; Shahnas and Arkani-Hamed, 2007]. The magnetic anomalies are more intense (up to 250 nT at ~400 km altitude as per Lillis et al. [2008]) than the largest terrestrial anomaly. The magnetic field on Mars likely exhibited a range of intensities comparable to the terrestrial magnetic field [Antretter et al., 2003; Weiss et al., 2008]. Therefore, a very efficient and robust carrier of remanent magnetization must be present in the Martian crust to acquire and retain intense anomalies after exposure to shock and thermal demagnetization processes associated with impact events.

A previous set of investigations into the magnetic recording assemblage on Mars used synthetic basalts as analogs of Mars’ crustal material [Hammer, 2006; Brachfeld and Hammer, 2006; Bowles et al., 2009]. These studies explored the effects of chemical composition, oxygen fugacity (fO₂), and cooling history on the bulk mineralogy, mineral textures, magnetic mineralogy, magnetic domain state, and remanence carrying properties of the run products. These studies found that samples synthesized under moderately oxidizing conditions, within one log₁₀ unit of the quartz-fayalite-magnetite (QFM) reference buffer, acquired intense thermoremanent magnetizations (TRM) even in relatively weak applied fields. Moderately oxidizing conditions, such as those that exist in the terrestrial crust, must have existed on early Mars in order to produce basalts capable of generating the observed crustal anomalies. Further, synthesis at QFM conditions coupled with fast cooling rates (3–231°C/h, relevant to rapidly cooled extrusive rocks) optimized TRM acquisition, with samples possessing stable-single-domain grains and TRM intensities exceeding 25 A/m [Brachfeld and Hammer, 2006; Bowles et al., 2009].

Estimates of the thickness of the magnetized layer on Mars range from 35 to 100 km [Nimmo and Gilmore, 2001; Arkani-Hamed, 2003, 2005; Voorhies, 2008]. Some portion of the magnetized layer likely consists of subsurface intrusions as suggested by: (1) cumulate textures observed in SNC meteorites; (2) Mars Orbiter...
Magnetometer (VSM) model 3900-04 at Montclair State University, NJ. Hysteresis loops were measured in a
alternating field (AF) demagnetization data were used to calculate the median destructive

difficulties in interpreting thermal histories of Martian rocks. The presence of petrographic evidence of exsolution of iron oxide phases can be observed in Martian basaltic rocks, 
and described in [Bowles et al., 2009]. "M-type" basalt is patterned after the composition of Mars basaltic meteorite Chassigny A [Johnson et al., 1991]. The T-type composition is similar to Medicine Lake Highland basalt 82-66 [Sisson and Grove, 1993], a high alumina basalt that is consistent with thermal emission spectrometer constraints on the composition of Mars' surface [Hamilton et al., 2001].

The M-type composition is poor in Al and rich in Fe (Fe/Al = 1.4), reflecting the composition of basaltic liquid in equilibrium with Martian meteorite phase assemblages. The T-type composition is rich in Al and poor in Fe (Fe/Al = 0.3) (Table S1). Other differences include silica content (the T-type composition is silica undersaturated, whereas the M-type composition is quartz-normative), normative Fe-Ti oxide speciation (T-type contains double the normative ilmenite and ~40% of the normative magnetite of M-type), and calcium content (giving rise to differences in normative pyroxene and feldspar contents) (Table S1). Although the terrestrial T-type composition is unlikely to represent a majority of the Martian crust [McSween et al., 2009], it is included to provide a counterpart to the Fe-rich, Al-poor M-type basalts associated primarily with meteorite samples and to allow evaluation of the major-element control on magnetic and mineralogical variations in the Mars crust.

Batches of each composition were cooled from >1200°C to 1070°C at 4°C/h, held at 1070°C for 100 h in a Fe-soaked 5 mL platinum crucible, and then quenched to form the starting materials for a lower-temperature "anneal" step. During the anneal step, samples were held in evacuated silica glass tubes at 650°C for periods ranging from 21 to 257 days, and then quenched. A solid assemblage of quartz + fayalite + magnetite (QFM) was included in each tube as a monitor of \( \text{FeO}_2 \) buffer conditions. The two-stage experiments effectively isolate the high-temperature and low-temperature synthesis steps, as a practical simplification of the complex thermal history typifying subsurface magma cooling. The two-stage strategy also represents the solution to furnace temperature and \( \text{FeO}_2 \) control limitations over a wide range in temperature. Six pairs of experiments, representing anneal durations of 21, 32, 48, 111, 158, and 257 days were characterized petrographically and magnetically.

Splits of the run products were made for electron microscopy and rock magnetic analyses. Electron microprobe analyses were conducted on a JEOL JXA-8500F Field Emission Hyperprobe at the University of Hawai’i at Mānoa. Low-field mass-normalized magnetic susceptibility (\( \chi_{\text{LF}} \)) was measured on an AGICO KLY-4 Kappabridge. The natural remanent magnetization (NRM) and anhysteretic remanent magnetization (ARM) were measured on a 2G-Enterprises Model 755 magnetometer at Lehigh University and on an AGICO JR6 spinner magnetometer at Montclair State University. ARM was imparted in a 100 mT peak alternating field and a 98 \( \mu \)T DC bias field. Stepwise alternating field (AF) demagnetization data were used to calculate the median destructive field (MDF) of the ARM.

Magnetic hysteresis measurements were made on a Princeton Measurements Corp. micro-Vibrating Sample Magnetometer (VSM) model 3900-04 at Montclair State University, NJ. Hysteresis loops were measured in a peak field of 1 T and field increments of 5 mT and corrected for the paramagnetic contribution to the induced magnetization. The hysteresis parameters saturation magnetization (\( M_s \)), saturation remanence (\( M_r \)), and
coercivity \( (H_C) \) were determined from the paramagnetic-corrected data. The coercivity of remanence \( (H_{cR}) \) was determined through the DC-demagnetization of a saturation isothermal remanent magnetization imparted in a 1 T field. Curie temperatures \( (T_C) \) were measured on the VSM in a flowing helium gas atmosphere. We monitored the induced magnetization in a 50 mT applied field as a function of temperature from 25 to 700°C. All rock magnetic parameters measured are reported in Table S2. In addition, low temperature magnetic measurements are shown in Figure S1.

3. Results

3.1. Mineral Assemblages and Textures

The phase assemblage in the M-type starting material (sample ID MAm-51) in order of decreasing abundance is clinopyroxene, glass, plagioclase, and Mg- and Al-bearing titanomagnetite (Figure 1). The glass in this sample results from quenching the starting material at 1070°C while the melt was still above the solidus...
Clinopyroxene crystals are subhedral, elongated, and blocky with a slight but complex zoning (Figure 1a). Plagioclase occurs as euhedral tabular crystals. Titanomagnetite crystals are euhedral, equant, and ~30–80 μm in diameter (Figure 1a), well within the multidomain size region, and much larger than those produced in the rapidly cooled samples of the same composition [Bowles et al., 2009]. We also observed rounded and equant titanomagnetite grains 5–10 μm in diameter (in the pseudo-single-domain field for titanomagnetite) that occur in clusters. In contrast to their rapidly cooled counterparts, there are no oxides smaller than approximately 5 μm visible in the electron microscopy images.

The annealed samples (MAm-E09-E16) using this starting material have the same phase assemblage as the starting material. Backscatter electron images reveal no discernable bulk mineralogical differences with anneal time (Figure 1). However, we observe that the concentrations of MgO and TiO₂ in the titanomagnetite decrease 2–4% with increasing anneal time, and we observe an increasing devitrification in the glass with increasing anneal time [Petrochilos, 2010] (Table S3).

The phase assemblage in the T-type starting material (MB2-48) in order of decreasing abundance is plagioclase, clinopyroxene, glass (solidus estimated at 895°C; Ghiorso and Sack [1995]), Mg-, Al-, and Cr-bearing titanomagnetite, olivine, and ilmenite. Plagioclase occurs as faceted, highly elongated hopper crystals (Figure 1b). Clinopyroxene crystals in this sample are faceted subhedral with a slight but complex zoning evident as concentric Z-contrast in BSE imaging (Figure 1). Olivine crystals are anhedral. Titanomagnetite crystals are euhedral, equant, and generally 5–10 μm in diameter. The T-type titanomagnetites have more Ti, Mg, and Cr than their M-type counterparts. Ilmenite crystals are euhedral and elongated, approximately 5 μm wide and 30 μm in length (Figure 1b).

The time-dependent annealed samples (MB2-E09–E16) using the T-type starting material have

![Figure 2](https://example.com/figure2.png)

**Figure 2.** (a) Low field magnetic susceptibility ($\chi_{LF}$), (b) natural remanent magnetization (NRM), and (c) anhysteretic remanent magnetization (ARM) as a function of anneal time. Vertical lines show the range of values observed in individual sample chips. Solid and open symbols are the calculated weighted average (by mass) for M-type and T-type samples, respectively. Vertical lines labeled B09 show the range of values for rapidly cooled (6–231 °C/h) basalts described in Bowles et al. [2009].

(est. ~950°C according to the MELTS model; Ghiorso and Sack [1995]).
grains without zoning. This is the only sample in which such grains are observed, which we interpret as arising from heterogeneity in the starting material or the statistical improbability of encountering sparse grains in a random section plane.

### 3.2. Magnetic Properties

Three to five chips with masses of a few milligrams to several tens of milligrams were measured from each run product. The chips are heterogeneous, likely due to gravitational settling of crystals within the 5 mL platinum crucibles, resulting in differing amounts of Fe-oxides within each chip. Maximum and minimum values for each parameter are shown in Figure 2. A weighted average value (by mass) was calculated for all chips from each run and reported in Table S2. Susceptibility values range from $7 \times 10^{-6}$ m$^3$/kg for M-type samples and $0.3 \times 10^{-6}$ m$^3$/kg for T-type samples (Table S2 and Figure 2). Both M-type and T-type samples possess a strong NRM (Table S01 and Figure 2). The NRM is inferred to be a TRM acquired during quenching and air cooling after the 650°C anneal in the ambient laboratory field (approximately 35 μT). NRM values range from 7 to 107.6 mAm$^2$/kg for M-type samples, and up to 315 mAm$^2$/kg in individual chips of the pre-anneal starting material. NRM values in T-type samples range from 2.1 to 28.1 mAm$^2$/kg. ARM values range from 0.6 to 60.6 mAm$^2$/kg in M-type samples and up to 149 mAm$^2$/kg in the pre-anneal starting material. MAm-E12 and MB2-E12 both have high NRM intensities relative to the other annealed samples (Table S2), as well as high values of susceptibility and saturation magnetization. ARM values range from 0.5 to 5.5 mAm$^2$/kg in T-type samples, and up to 14 mAm$^2$/kg in individual chips of the pre-anneal starting material (Figure 2 and Table S2).

Following NRM measurements, the samples were demagnetized in a 100 mT peak alternating field in three perpendicular directions prior to imparting ARM. After imparting ARM, the samples were stepwise...
AF demagnetized in peak fields of 0 to 100 mT. M-type samples (Figure 3a) were easily AF demagnetized. In the M-type samples <10% of the remanence remained after the first demagnetization step at 10 mT. Samples annealed for 111 to 257 days had slightly harder AF demagnetization spectra, with 40–50% of remanence remaining after the 10 mT demagnetization step. Similarly, T-type samples annealed for 111 to 257 days had approximately 34–55% of the remanence remaining after the 10 mT demagnetization step (Figure 3b). Hysteresis parameters for M-type samples plot within the multidomain region of a Day Plot [Day et al., 1977]. T-type samples plot in the lower right corner of the pseudo-single domain (PSD) region (Figures 3c and 3d).

M-type samples have Curie temperatures (Tc) that range from 285 to 410°C (Figures 4a–4c). The heating and cooling curves are generally reversible for anneal times <111 days. Samples annealed for ≥111 days were more susceptible to alteration during heating. T-type samples have Curie temperatures between 130 and 215°C [Bowles et al., 2009 and Figures 4d–4f]. T-type samples additionally display a subtle, continuous decrease in MS between 500 and 700°C (Figure 4e inset), suggestive of hematite, which may be present as nano-scale intergrowths with ilmenite. Heating and cooling curves for the T-type samples are not reversible, and the cooling curves are stronger than the heating curves.

4. Discussion

The NRM and ARM values recorded by the slow-cooled samples are comparable to, and even exceed, the TRM induced in rapidly cooled synthetic basalts of the same chemical composition [Bowles et al., 2009]. We observed no systematic relationship between NRM and ARM intensity and anneal period. However, the annealed samples generally have lower intensities of NRM and ARM than their starting materials. Annealing removes defects and dislocations from materials, which serve as pinning points for domain walls in multidomain iron oxides and contribute to remanence acquisition and retention. The annealing process may have reduced the efficiency of remanence acquisition and retention in these multidomain oxides, as suggested by the soft ARM AF demagnetization spectra of the annealed samples (Figure 3).

Both M-type and T-type samples with anneal periods longer than 111 days have slightly harder AF demagnetization spectra (Figure 3) and elevated NRM/ARM ratios (Table S3). Both M-type and T-type samples contain devitrification textures within the glass, with the amount of glass devitrification increasing with anneal time (Figure 1). We speculate that stable-single-domain (SSD) iron oxides below the resolution of the electron microprobe are forming during devitrification, leading to more PSD-like hysteresis loops, enhanced TRM acquisition, and harder AF demagnetization spectra in our annealed samples, which has also been observed in natural and synthetic basaltic glasses [Burgess et al., 2010;
Bowles et al., 2011]. The high amount of glass in these samples is a function of quenching the pre-anneal starting materials. We do not expect these conditions to occur in nature, where slowly cooled intrusions should be holocrystalline. However, the growth of SSD oxides during devitrification is relevant to basaltic glasses at the Martian surface. The effect of this phenomenon on the amplitude of crustal anomalies depends on the timing of both dynamo cessation and oxide growth. Basalts would carry a TRM if devitrification and growth of SSD oxides occurred while the basalt temperature was above the blocking temperature ($T_B$) of the magnetic mineral assemblage, a chemical remanent magnetization (CRM) if the devitrification occurred below $T_B$ but in the presence of a dynamo field, or a combination of both depending on the relative timing of cooling and oxide growth.

The Curie temperatures of the annealed M-type samples are comparable to those observed in their rapidly cooled counterparts of the same composition [Bowles et al., 2009]. The T-type samples reported here have lower Curie temperatures than their rapidly cooled counterparts. Curie temperatures in both M-type and T-type annealed samples increase slightly as a function of anneal duration. This is consistent with EMPA data that show oxides becoming very slightly more iron-rich at longer anneal times. For our purposes, $T_C$ is used to predict the depth to the Curie isotherm rather than as a diagnostic material property. For linear geothermal gradients of 5–20°C/km, the depth to the Curie isotherm is approximately 15 to 80 km for an M-type layer, and 7 to 45 km for a T-type layer.

Using simple geometric models of a uniformly magnetized prism [Nimmo, 2000; Brachfeld and Hammer, 2006] the high-intensity NRM values recorded by the M-type annealed samples (20–312 A/m using a density of 2900 kg/m$^3$ for conversion to volume-normalized units) are more than sufficient to generate the observed anomalies at satellite altitude within the layer thickness constrained by the M-type Curie temperatures. The majority of T-type annealed samples have volume-normalized remanences of 6–18 A/m, which is insufficient to generate the observed anomalies at satellite altitude in a layer thickness constrained by T-type Curie temperatures. The exception is sample MB2-E12, which has an NRM intensity of 81.4 A/m. MB2-E12 and MAm-E12 (anneal time 111 d) have NRM/ARM ratios of 28 and 14, respectively, much higher than the samples with shorter anneal durations. These samples likely contain the greatest abundance of single domain grains formed during devitrification, which reinforces the importance of domain state and oxide concentration for acquiring and retaining crustal anomalies.

Although the M-type annealed samples carry an intense NRM, the soft coercivity spectra of these samples make it unlikely that a TRM or CRM carried by this material would be retained over geologic time. Iron oxides and iron sulfides experience shock-demagnetization beginning at pressures of less than 1 to 2 GPa, with continued loss of remanence with increasing pressure [e.g., Hargraves and Perkins, 1969; Nagata, 1971; Cisowski and Fuller, 1978; Rochette et al., 2003; Louzada et al., 2007, 2011; Bezaevo et al., 2007, 2010]. Bezaevo et al. [2010] observed that a pressure of 1.24 GPa was sufficient to remove 84% of an induced isothermal remanent magnetization, with low coercivity samples more easily demagnetized than high-coercivity samples. The lack of crustal anomalies within and around the Hellas, Isidis, Utopia, and Argyre impact basins on Mars suggests that the original NRM carried by the Mars crust has been extensively modified by impact events [Acuña et al., 1999; Hood et al., 2003]. The cumulative effect of impacts on Mars may have demagnetized the upper 5–10 km of the crust after the dynamo field switched off [Arkani-Hamed, 2003; Louzada et al., 2007, 2011; Lillis et al., 2010], reducing the thickness of the magnetized layer.

An M-type intrusion containing exclusively multidomain grains and residing within 10 km of the planet’s surface would be largely demagnetized, given its soft coercivity spectra. Intrusions that are deeper than the penetration depth of the 1–2 GPa shock pressure contours but above the Curie isotherm may still contribute to the Mars crustal anomalies via several mechanisms. Gilder and Le Goff [2008] demonstrated that saturation isothermal remanent magnetization (SIRM) and coercivity of remanence (as measured via $H_{CR}$ and the median destructive field) increase in multidomain Ti-rich titanomagnetite ($x > 0.2$) as a function of pressure. They further observed that the Curie temperature is also elevated at high pressure [Samara and Giardini, 1969; Schult, 1970], and the combination of these enhancements may preserve an NRM carried by multidomain titanomagnetite in a planet’s crust. In addition, if the multidomain oxides undergo exsolution during natural timescales for cooling, then the resulting increase in coercivity would make the basalts more resistant to shock demagnetization, and they may still contribute substantially to the crustal anomalies [Robinson et al., 2002; McEnroe et al., 2004].
4. Discussion

M-type and T-type basalts studied here are dominated by multidomain titanomagnetite. The basalts display $\chi_{LF}$, NRM, and ARM intensities comparable to or exceeding those of their rapidly cooled counterparts. The annealed samples have lower NRM and ARM intensities than their pre-anneal starting materials, which may result from the removal of defects and dislocations during annealing. The M-type composition is capable of generating intense magnetic anomalies at satellite altitude; the T-type composition in general is not, although one T-type sample with elevated $\chi_{LF}$ and $M_s$ also has a very strong NRM. However, the ARM in the annealed samples is easily AF demagnetized, though slightly harder in samples annealed for 111 to 257 days. This hardening of the coercivity spectra is attributed to sub-micron iron oxides forming in glass during devitrification.

Our results have implications for the long-term stability of crustal anomalies carried by multidomain titanomagnetite assemblages. The low coercivity of both compositions suggests that these materials, if located near the Martian surface, would be shock demagnetized during impact events. Retention of the remanent magnetization carried by multidomain titanomagnetite is only possible at greater depths where high pressure enhances coercivity in Ti-rich titanomagnetites. Alternately, exsolution of multidomain grains during cooling over natural timescales could also enhance coercivity and resistance to shock demagnetization.

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