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Magnetic characterization of reduction in Mount Fuji basaltic tree-mold

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Abstract. A Mount Fuji basaltic tree-mold presents the mineralogical record associated with a large oxygen fugacity gradient during the cooling of the basalt. Magnetic exchange anisotropy is postulated to be characteristic of cation excess in some spinel titanomagnetites. The exchange anisotropy is characterized by loop shifting along the field and magnetization axes when cooled in a magnetic field, large coercivity increase, and magnetic viscosity which has discrete activation fields and logarithmic to linear decay characteristics. The cryogenic loop characteristics attributable to exchange anisotropy are not found in the tree-mold where iron and ilmenite are the main phases. The coupling has been created in the laboratory with ordinary basalt artificially reduced in Hydrogen gas. The coupling is not found in spinel oxidation non-stoichiometry. These results imply that we are able to identify the presence of spinels that have equilibrated in the low oxygen fugacity range of the spinel stability field where cation excess is characteristic.

Introduction

Spinels are widespread in lunar samples, some meteorites, and throughout the earth's crust and upper mantle and are important to the estimation of the oxidation state of the materials that contain them (Arculus,1985). In a study of the magnetic properties of magnetite-chromite solid solution series spinels synthesized at 1300C, Wasilewski et.al. (1975) noted peculiar magnetic hysteresis behavior when certain compositions were measured at liquid nitrogen temperatures. The compositions were those synthesized in relatively low oxygen fugacities yet were verified to be single phase spinels by X-ray diffraction. The same peculiar hysteresis phenomena were observed in Fe_2TiO_4-$FeCr_2O_4$ spinels and in this paper we verify the effects in the Fe_3O_4-Fe_2TiO_4 spinels. The hysteresis loops were shifted along the magnetization and the field axes in response to field cooling, the coercivity increased dramatically, and the observation of loop viscosity all appear consistent with magnetic exchange anisotropy (Meiklejohn and Bean,1957). The width of the spinel stability field is a measure of the range of oxygen fugacity over which single phase spinels can exist. Consequently the tree-mold that we describe in this paper is viewed as a test bed for the natural cation excess titanomagnetite spinels. The exchange anisotropy mechanism requires the cryogenic temperature coupling of dissimilar spin states existing in intimate contact. Antiferromagnetic wustite-like regions in the spinel host can satisfy the structural requirement at the microscopic level in the cation excess spinels which are considered to exist in the tree-mold. Consequently, in lunar samples, meteorites, and mantle spinels which have equilibrated in reducing conditions, we may have a rapid, simple, and non-destructive method to refine the oxidation state of single phase spinels.

Materials and methodology

Tree-mold basaltic samples were collected at an elevation of 1690 m above the sea level along the toll road on the northern slope of Mt Fuji (Kanehira and Shimazaki, 1971). Tsuya (1968) designated the basalt as the Oniwa-Okuniwa second lava flow. Several of the tree-molds,ranging in size from 0.3 – 0.8 m in diameter were examined in detail in Kanehira and Shimazaki (1971) and the results are summarized below.

Native iron occurs as spheroidal grains in thin layers about one cm in thickness in the basalt surrounding the tree-molds. Native iron was characterized by optical microscopy, electron microprobe and x-ray diffraction. The native iron-bearing basalt grades into normal basalt over a distance of up to 5 cm. A series of distinct mineralogical changes, most apparent in the opaque mineral assemblage, was observed in the transition from the ordinary basalt to the native iron-bearing basalt. Kanehira and Shimazaki (1971) divided these into four zones. Photomicrographs of representative magnetic minerals in these zones are shown in the paper by Kanehira and Shimazaki (1971). Zone 1 is the host basalt and contains blocky grains of titanomagnetite. In this zone they have determined that the x= 0.56 titanomagnetite steeply changes to x= 0.73 titanomagnetite over a 2 cm distance. Zone 2 contains titanomagnetite in which calculates to almost pure ulvospinel in association with ilmenite laths. Zone 3 contains ilmenite and zone 4 contains ilmenite plus native iron. The occurrence of native iron at the contact with the tree-mold and the successive reduction of the groundmass of the basalt towards the tree-mold prompted Kanehira and Shimazaki (1971) to conclude that the native iron was formed in situ by reduction of the host basalt.

We obtained one of the basaltic tree-mold samples from Professor K. Kanehira of Chiba University, Japan. The sample was cut with a Buehler ISOMET saw into sets of 8 subspecimens a few mm on a side such that their orientation relative to each other remained constant. These samples are referred to as P1-P8, with P1 at the tree-basalt contact and P8 about 5 cm from the contact.

Magnetic hysteresis loops were measured at 300 K and 77 K for the entire reduction sequence P1 to P8. Hysteresis properties were measured at 300 K and 77 K for a synthetic titanomagnetite (TM60 originally obtained from Dr. K. Kobayashi). Then the sample was oxidized by heating it in air at 673 K and the magnetic hysteresis properties remeasured. We reduced a sample of a Columbia River basalt (#556) containing a typical basaltic titanomagnetite with a Curie point near 473 K. This basalt was collected by Drs M.D. Fuller and H.Ito while both were at the University of Pittsburgh. The sample was reduced by heating small chips of the basalt for 2 hours in standard cold seal apparatus at 673 K in a 3.5 MPa (= 5000 psi) hydrogen

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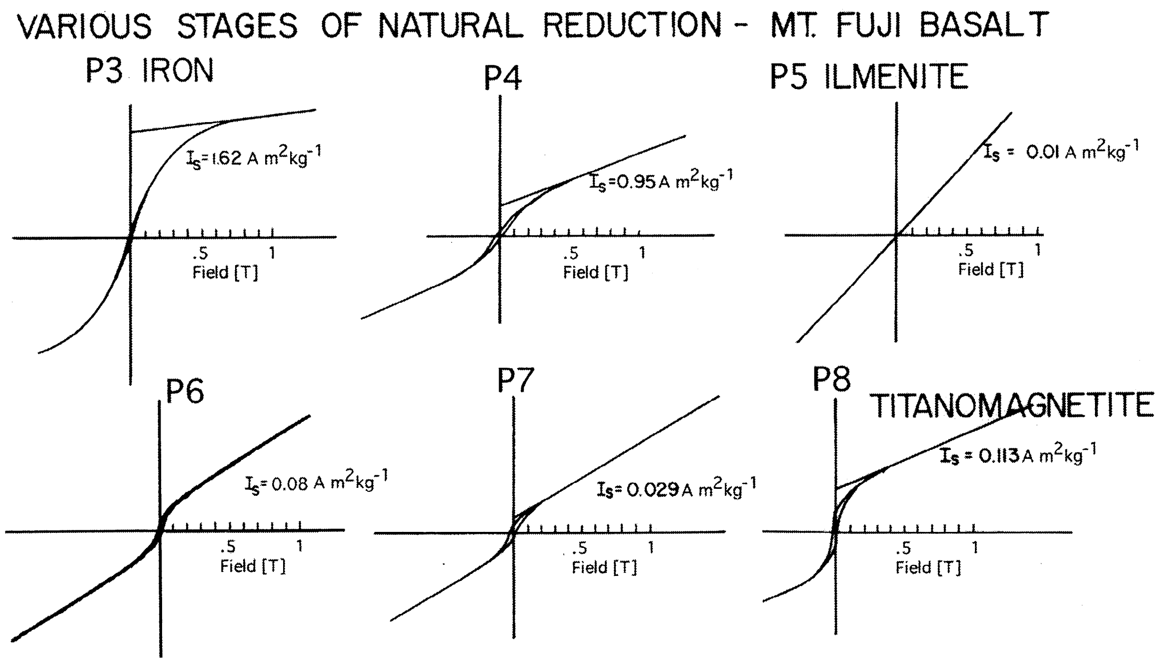

Figure 1. Representative hysteresis loops for subsamples of the tree-mold reduction profile (P3 is near the tree contact and P8 is the background basalt)

atmosphere. This work was done by Dr. Gerry Weidner. Magnetic hysteresis loops were then determined at 300 K and 77 K.

Experimental results

The progressive reduction of the Mt. Fuji basalt can be followed in the characteristic shapes of the 300 K magnetic hysteresis loops measured on the tree-mold samples (Figure 1). The P3 loop is characteristic of iron, P5 of ilmenite and P6, P7, and P8 of titanomagnetite. Iron has a large saturation magnetization and requires a field of ~0.7 T to reach the linear high field portion of the hysteresis loop. The iron grains in the tree-mold samples are globular in shape and thereby exhibit a smooth transition towards saturation instead of the ramp shaped loop expected for a multidomain iron sphere (Dickinson and Wasilewski 2000). Ilmenite is a pure antiferromagnetic oxide with a Curie temperature of 40 K (e. g. Hunt et al., 1995) and produces a paramagnetic hysteresis loop which is straight line through the origin. The tree-mold sample (P5) is dominated by ilmenite, but has a small ferromagnetic component (NRM>0) which has not been identified. The blocky titanomagnetite grains (P8) saturate between 0.2 and 0.3 T and exhibit characteristic basaltic sample loop shapes. P6 and P7 appear to have a larger x value consequently saturation is achieved in lower fields and the saturation magnetization is reduced.

The magnetic components in these samples acquired paleofield directions while the tree-mold was immobile and cooled in the geomagnetic field. All mutually oriented subsamples had NRM vectors in the same direction. NRM and SIRM data (acquired in a 1 T field) are given in Table 1. The REM value is the ratio of NRM to SIRM and is an indication of the ease of acquiring remanent magnetization (Wasilewski and Dickinson, 2000). The iron-bearing samples have REM values of 0.0030 (P1), 0.0049 (P2), 0.0027 (P3), and 0.0279 (P4). The ilmenite-bearing sample (P5) has a REM of 0.019 and the titanomagnetite-bearing samples have REM values ranging from 0.024 to 0.030 (P6, P7, P8). Since all the samples acquired

Table 1.

Sample	weight [g]	NRM [10^{-4} Am^{2}kg^{-1}]	SIRM [10^{-4} Am^{2}kg^{-1}]	REM =NRM/SIRM
P1	0.1737	2.46	812.3	0.0030
P2	0.1855	3.76	762.3	0.0049
P2	0.1717	2.1	774.02	0.0027
P4	0.1409	7.08	253.6	0.0279
P5	0.1610	0.26	13.68	0.0189
P6	0.2179	1.19	39,42	0.0300
P7	0.2348	2.32	56.98	0.0275
P8	0.3626	7.22	303.9	0.0238

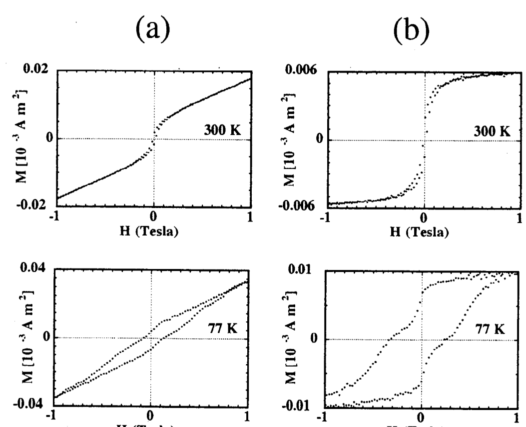

Figure 2. Magnetic hysteresis loop characterization, of subsample P7, at 300K and 77K identifying the basis for the exchange anisotropy in cation excess spinels. (a) Complete magnetic hysteresis loops. (b) Loops with paramagnetic component subtracted.

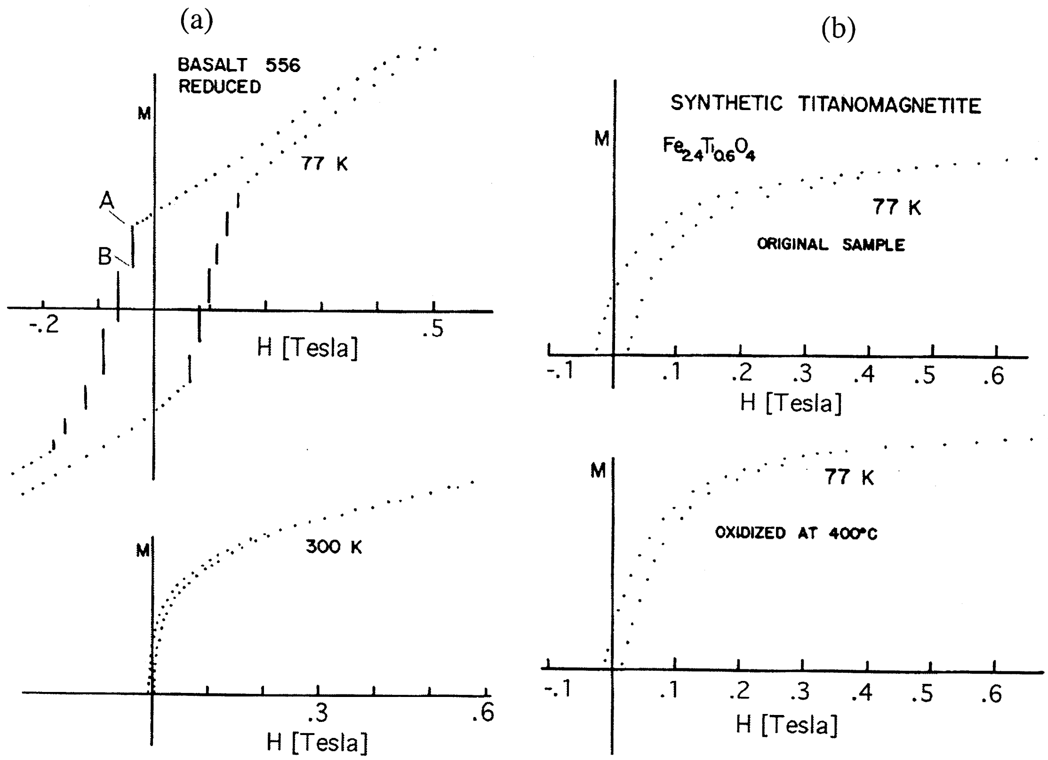

Figure 3. (a) Magnetic hysteresis behavior of the reduced Columbia river basalt shown both at 77 K and 300 K. The hysteresis loop viscosity indicated by points A and B is explained in the text. (b) Magnetic hysteresis in synthetic titanomagnetite at 77 K both before and after oxidation.

remanent magnetization under the same conditions, these data suggest the iron-bearing samples (except P4 which may represent a transition from the iron bearing zone towards the ilmenite bearing zone) acquired thermal remanence magnetization less efficiently than samples without iron.

Shown in Figure 2 are magnetic hysteresis loops measured at 300 and 77 K for the P7 tree-mold sample. P7 and P6 were the only samples from the tree-mold profile that changed hysteresis behavior drastically when measured at 77K, In Figure 2a the P7 loops are shown as measured. In Figure 2b the loops are shown at 300K and 77K with the paramagnetic feature removed in order to emphasize the ferromagnetic aspect of the loops. Because the tree-mold structure represent a natural profile of increasing oxygen activity we suspected that samples P6 and P7 were possibly similar to the FeCr spinels that were synthesized at low fO_2's (Wasilewski et al. 1975). This supposition was based on the idea that the phenomena required cation excess in spinel phases. The magnetic hysteresis loops were constructed by cooling in a 2.0 T field and then decreasing the field to zero (point by point measurements). The field was reversed and then increased in the opposite sense until a field was reached (see point A in Figure 3a for illustration) where the magnetization decayed until point B (in Figure 3a) was reached. Great care was taken to ensure that the phenomena was not associated with recorder or amplifier time constants since we had never previously observed this effect. The vertical lines on the 77 K loops (Figure 3a and b) are here identified as magnetic hysteresis loop viscosity corresponding to the anomalous magnetic hysteresis loop behavior which includes as well a large increase in the hysteresis and coercivity. We repeated this procedure with sample P7 and observed similar viscous decay (Figure 4a) as in Wasilewski et al. (1975). We noticed that the onset of viscous behavior did not start until the high coercivity component of the wasped loop (Figure 4a) was reached. The viscous nature of the loop was characterized by the time dependent measurements of magnetization at specific fields and generally showed logarithmic decay on a time scale of 1-2 minutes (see Figure 4b).

We ran additional experiments to determine if the peculiar cryogenic temperature signature is directly related to reduction. A sample of Columbia River basalt (#556) containing typical basaltic titanomagnetite with a Curie point near 473 K was reduced by running small chips for 2 hours in standard cold seal apparatus at 673 K in a 3.5 MPa hydrogen atmosphere. Before the reduction, Columbia River basalt #556, showed normal hysteresis behavior (not shown). However, after reduction the magnetic hysteresis loop measured at 77 K shows the peculiar behavior. similar to that observed in the tree- mold sample (Figure 3a) and in the FeCr spinels (Wasilewski et.al.,1975). The artificial spinel and tree-mold sample work implicates spinels that are "reduced" None of the synthetic titanomagnetites showed peculiar magnetic hysteresis when they were oxidized (Figure 3b lower loop). Examination of numerous terrestrial samples containing magnetite and titanomagnetite, as well as samples of synthetic titanomagnetite show only normal magnetic hysteresis at cryogenic temperatures as represented in Figure 3b.

Discussion

Terrestrial basalts generally crystallize near the fayalite-magntite-quartz (FMQ) buffer (Frost and Lindsley, 1991; Haggerty and Tompkins, 1983; Carmichael and Nicholls, 1967). The mineral assemblages observed in the tree-mold samples are indicative of oxygen fugacities from approximately FMQ to below IW (iron-wustite buffer). Therefore, we could expect the tree-mold spinels to contain cation excess rather than cation deficiency (Flood and Hill, 1957). At the breakdown curve of magnetite to wustite, magnetite will show a slight cation excess (Dieckmann`and Schmalzreid 1977a,b and also Ghiorso and Sack 1991). Togawa et al (1996) describe cation excess magnetite as a metastable phase inn the transformation of magnetite to alpha

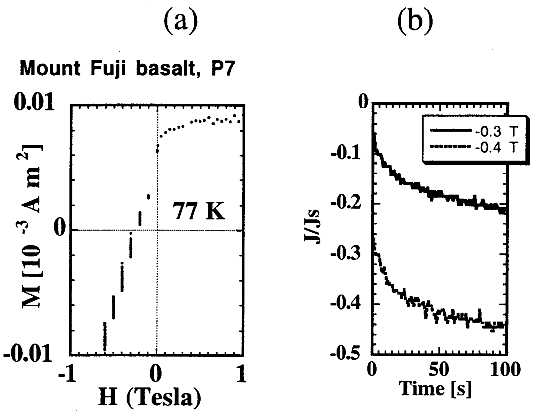

Figure 4. (a) Viscous magnetic behavior of the P7 tree-mold sample (see the text for an explanation). The paramagnetic slope of the loop has been removed. (b) Example of the logarithmic time dependent viscous behavior of the tree-mold sample P7 when reverse field of –0.3 and –0.4T was applied.

iron. A lattice constant of 0.8407 nm, substantially higher than that of stoichiometric magnetite (0.8396 nm) has been identified. The cation excess could be configured as wustite-like antiferromagnetic regions within the spinel host (Meiklejohn, 1962). Conditions for magnetic exchange anisotropy can exist when an antiferromagnetic lattice couples to a cubic ferrimagnetic lattice. Wustite (FeO) is an obvious antiferromagnetic mineral with a Neel point of about 198 K.

The Fe_3O_4-Fe_2TiO_4 solid solution series and the Fe_3O_4-$FeCr_2O_4$ and Fe_2TiO_4-$FeCr_2O_4$ solid solutions exhibit anomalous magnetic hysteresis (Wasilewski et al., 1975 and this paper). As indicated in Dieckmann and Schmalzreid, (1971 a and b) a single phase spinel can exist with cation excess. Therefore, the degree of cation excess must translate to microscopic regions that order so as to exhibit antiferromagnetic structure. The magnetic viscosity may be a clue to the structural state, and may persist over a limited range of fO_2. Magnetic exchange anisotropy requires interface coupling of antiferromagnetic and ferri- or ferromagnetic spin systems, taking place at the Neel transition temperature of the antiferromagnetic phase. In the preliminary studies that we describe here we note that the coupling takes place in samples that show magnetic hysteresis which is normal and constricted at room temperature and in addition in samples that show a minor ferromagnetic and large paramagnetic components at room temperature. Consequently the picture is quite complicated. We are in the process of sorting through the details so that we might generalize. The structural details of the antiferromagnetic phase are unknown as is the effective size of the antiferromagnetic regions. We also do not know the cation excess concentration which might be the important factor in determining the size and therefore the interfacial structure of the antiferromagnetic regions. We are presently in the process of arranging for TEM and Mossbauer analyses in order to confirm the identification of the nanoscale features in the spinels. In addition we will measure the temperature dependence (Down to 4K) of the field cooling hysteresis properties to accurately define the coupling temperature.

Conclusions

Natural and laboratory reduced basaltic rocks exhibit peculiar magnetic hysteresis loops, when measured at 77K, identified mainly by: response to field cooling, magnetic viscosity which has discrete activation fields and logarithmic to linear decay characteristics, asymmetry of the hysteresis loop along the magnetization and the field axes,and significant increase in magnetic coercivity. These results characterize exchange anisotropy which requires the cryogenic temperature coupling of dissimilar magnetic spin states. These data were acquired in the same way as the data reported by Wasilewski et.al. (1975).

We verified that oxidation induced non-stoichiometry does not result in the peculiar magnetic hysteresis behavior. We then verified that an otherwise normal basalt could be made to exhibit the peculiar hysteresis behavior by subjecting the basalt to a reducing Hydrogen gas environment. Crucial to the appearance of the peculiar magnetic hysteresis is the presence of an apparently reduced spinel phase. Therefore the results suggest a cation excess, which could be interpreted as wustite-like irregularities in the spinel host. The magnetic hysteresis results suggest an exchange anisotropy model with the cryogenic temperature coupling of dissimilar magnetic spin states in intimate contact.

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