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SHOCK DEMAGNETIZATION OF PYRRHOTITE ($Fe_{1-x}S$, x≤0.13) AND IMPLICATIONS FOR THE MARTIAN CRUST AND METEORITES

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Abstract. After cessation of the dynamo on Mars, giant impact events should have demagnetized large regions of the crust. Models of the decay of shock pressure with distance indicate that the demagnetized zones are bound by peak shock pressures between 1 and 3 GPa. We performed the first planar shock recovery experiments at these pressures on natural pyrrhotite, a magnetic mineral found in Martian meteorites. Post-shock magnetic measurements show that pyrrhotite demagnetizes significantly (~85-90%) when subject to shock pressures between 1 and 4 GPa. Permanent changes to the magnetic properties of recovered samples include an increase in the saturation remanence and the mean destructive field, indicating that shocks harden the coercivity. We conclude that pyrrhotite is a candidate carrier for the magnetization in the Martian crust and that pyrrhotite in meteorites shocked to modest pressures may retain a pre-shock remanence.

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INTRODUCTION

Satellite maps of the remanent magnetic field of Mars show unmagnetized zones within and around giant impact basins, such as Hellas and Argyre [1]. The edges of the unmagnetized zones correspond with peak shock pressures of a few GPa and temperatures well below the Curie point of candidate magnetic minerals [2-4]. Hence, it is likely that vast regions of the Martian crust were demagnetized due to a shock-induced phase change or magnetic transition in the magnetic minerals.

Although pyrrhotite ($Fe_{1-x}S$, x≤0.13) is not a major magnetic carrier on Earth, it is a common phase in the Martian shergottite meteorites [5]. In hydrostatic pressure experiments, pyrrhotite undergoes a ferrimagnetic to paramagnetic transition near ~2.8 GPa, with rapid loss of magnetization above 1 GPa [6]. Previous shock experiments on magnetite-bearing igneous rocks [7-11], hematite powders [12], and pure samples of magnetite, hematite and titanohematite [4] indicate that low pressure shocks demagnetize low coercivity minerals. Previous pyrrhotite shock Hugoniot measurements did not include a magnetic study [13].

Understanding the effects of shock waves on magnetic minerals is necessary to interpret the demagnetized zones around impact basins, to constrain the identity of the major magnetic carrier phases in the crust, and to infer the origin of magnetic directions and paleointensities from meteorites. In this paper, we present preliminary results from the first shock demagnetization study of pyrrhotite.

EXPERIMENTAL PROCEDURE

We performed planar shock recovery experiments on 3×1 mm discs of natural pyrrhotite embedded 3-mm off-center in 80×24 mm aluminum recovery capsules using the 40-mm gas gun in the Harvard Shock Compression Laboratory. Planar shockwaves were generated by 34×3 mm diameter aluminum flyer plates on polycarbonate sabots. From the measured impact velocity, the peak shock pressure was inferred from both the impedance match solution and the pressure distribution in the sample from 2D simulations using the shock physics code CTH. Approximately 93% of the sample experienced a peak pressure within 0.5 GPa of the impedance match solution with the remaining fraction subject to slightly higher pressures.

The pyrrhotite samples were saturated in a 370 mT (~7400×Earth's surface) magnetic field prior to the shock and the resultant remanence was measured before and after shock. Four shock experiments were performed at room temperature in the ambient laboratory field (~0.2 mT). One experiment on a demagnetized sample confirmed no shock remanent magnetization was acquired. To assess the changes in crystallographic and magnetic properties, the shock experiments were preceded and followed by a suite of material and magnetic characterization measurements. These included magnetic isothermal and anhysteretic remanence acquisition, alternating field demagnetization, X-ray diffraction, magnetic hysteresis, and low temperature magnetism.

Pyrrhotite owes its magnetism to preferential vacancy distributions in alternating antiferromagnetically coupled Fe layers in so-called superstructures [14]. Natural pyrrhotites typically consist of mixtures of superstructures of ferrimagnetic monoclinic (Fe_7S_8) and antiferromagnetic hexagonal pyrrhotite. We analyzed a pyrrhotite nodule from Sudbury, Canada. The wasp-waistedness of its hysteresis loop [15] indicates that the sample contains both high and low coercivity fractions (coercivity is the magnetic field required to reduce the external magnetization of a magnetic substance to zero). The presence of monoclinic pyrrhotite was confirmed by the low temperature magnetic transition at 30-34 K [16] and the presence of hexagonal pyrrhotite was inferred from XRD and microprobe measurements (Fe/S=0.893). We infer that the sample is composed of crystals in sizes predominantly in the single domain range (saturation remanence to saturation magnetization ratios prior to shock of M_{rs}/M_s~0.55-0.72). The density of the pyrrhotite was 4.587 (±100) g cm^{-3}, and the longitudinal and shear wave speeds are 4399 (±87) m s^{-1} and 2873 (±37) m s^{-1} respectively.

RESULTS

Fig. 1 presents preliminary results indicating that pyrrhotite demagnetized by 85-90% when subjected to shock pressures of a few GPa. It is likely that the shocks in our experiments were elastic or near the elastic limit. Although the Hugoniot Elastic Limit of pyrrhotite is unknown, a major shock-induced phase change is observed between 2.7 and 3.8 GPa [13]. Pressure (grey symbols in Fig. 2) is inferred from principal stress (black symbols) by:

$$P=\frac{(\sigma_1+2\sigma_2)}{3}=\frac{1}{3}\left(\frac{1+\nu}{1-\nu}\right)\sigma_1 \quad (1)$$

where P is pressure, ν is the Poisson's ratio (0.32 for pyrrhotite), σ_1 is the principal stress, and the perpendicular stresses are $\sigma_2=\sigma_3$.

Two samples shocked to σ_1~2.5 GPa show good agreement with the previously published hydrostatic data (open circles). A sample shocked to σ_1~4 GPa, above the 2.8 GPa magnetic transition and just above the expected structural change, did not completely demagnetize. The phase diagram of pyrrhotite is not well known; however, troilite (FeS) undergoes a first order phase transition at 3.9 GPa [17]. The 4 GPa principal stress shock (2.7 GPa pressure) may not have reached the expected high-pressure phase. It has been suggested that a single mechanical shock of very short duration may be unable to attain the final resultant effect on the remanent magnetization [9]. Single shock pressures above 4 GPa may be needed to fully demagnetize pyrrhotite. A sample shocked twice (σ_1~1-1.5 GPa) was significantly more demagnetized than what would be expected from the hydrostatic experiments [6], indicating the efficiency of shock demagnetization from multiple impact events.

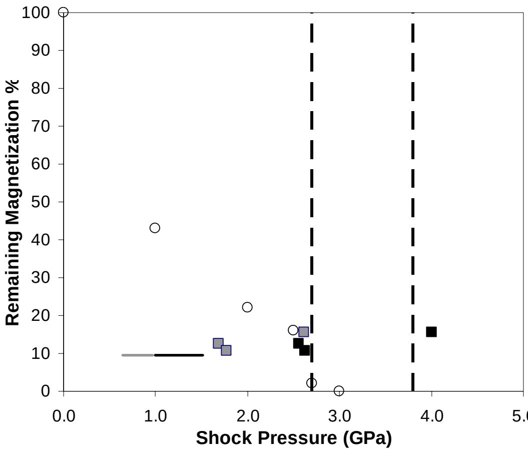

FIGURE 1. Demagnetization results of pyrrhotite: black squares – single shock principal stress; black line – double shock principal stress; grey symbols – pressure assuming elastic shock [Eq. 1]; open circles – static measurements [6]; dashed lines – phase change region in pyrrhotite from shock data [13].

Shock compression results in permanent changes to the magnetic properties of pyrrhotite. Isothermal remanent magnetization measurements demonstrate that the saturation magnetization (SIRM) of pyrrhotite increases when subject to increasing shock pressure (Fig. 2).

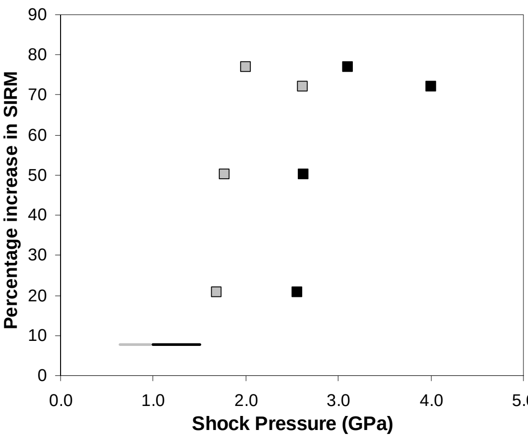

FIGURE 2. Change in saturation isothermal remanent magnetization: meaning of symbols is the same as Fig. 1.

Even more striking is the increase in the mean destructive field (MDF, the field that is required to reduce the remanence to one-half its initial value) with pressure (Fig. 3). Since the MDF is a measure of the bulk coercivity, the data show that shock treatment significantly hardens the coercivity.

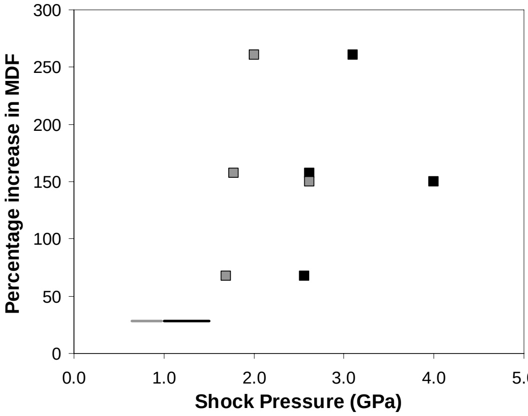

FIGURE 3. Change in mean destructive field: meaning of symbols is the same as Fig. 1.

DISCUSSION

Similar irreversible changes in magnetic properties have been observed in magnetite under hydrostatic pressures up to 6 GPa [18] and in hematite powder subjected to shocks between 8-27 GPa [12]. We have several hypotheses which could explain these changes in pyrrhotite.

The break up of large, low-coercivity, pseudo-single domain and multidomain grains into many smaller single domain grains [18] should result in an increase in the bulk coercivity and saturation magnetization [14], which is consistent with changes in MDF and SIRM. However, we would also expect to see an increasing trend in the M_{rs}/M_s with pressure [15], which is not supported by our results.

The creation of hexagonal ferrimagnetic pyrrhotite that is metastably ferrimagnetic [5], which can occur if pyrrhotite is heated above ~200ºC and then rapidly cooled, could explain the increase in saturation magnetization. However, this is unlikely as shock heating during the experiments was negligible: the temperature increase was ~10 ºC at σ_1=4 GPa.

Stress hardening may be the result of changes in the magnetostriction and magnetoelastic constants [9,18], which would increase the single domain-multidomain threshold radius and increase the saturation remanence. Defect generation, residual strain, domain nucleation, and domain rotation may each contribute to the changes in magnetic properties after shock compression of pyrrhotite.

CONCLUSIONS

Impact experiments indicate that pyrrhotite demagnetizes significantly due to shock in the pressure range inferred around Martian impact basins. After shock treatment, permanent changes in the magnetic properties of pyrrhotite include an increase in saturation remanence and coercivity.

The possible presence of pyrrhotite in the Martian crust has implications for the thickness and depth of the magnetized layers and the oxidation state of the crust. Meteorites containing pyrrhotite, that have been shocked to pressures of up to 4 GPa may retain a pre-shock remanence and may be used for paleointensity measurements of the ancient Martian field. However, the increase in saturation remanence from shock implies that typical normalization paleointensity techniques [19] may underestimate the true paleointensity.

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