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Effect of shock on the magnetic properties of pyrrhotite, the Martian crust, and meteorites

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[1] We performed planar shock recovery experiments on natural pyrrhotite at pressures up to 6.9 GPa. We find that high-field isothermal remanent magnetization in pyrrhotite is demagnetized up to 90% by shock due to preferential removal of low coercivity components of magnetization. Contrary to static experiments, we do not observe complete demagnetization. Post shock permanent changes in magnetic properties include increasing saturation isothermal remanent magnetization, bulk coercivity and low-temperature memory, and changes in squareness of hysteresis. These changes are consistent with an increase in the volume fraction of single domain grains. The lack of magnetic anomalies over large Martian impact basins is not expected to be solely due to shock demagnetization of the crust. We find that pyrrhotite-bearing rocks and meteorites can retain records of Martian magnetic fields even if shocked to pressures approaching 7 GPa. However, some paleointensity techniques may underestimate this field. **Citation:** Louzada, K. L., S. T. Stewart, and B. P. Weiss (2007), Effect of shock on the magnetic properties of pyrrhotite, the Martian crust, and meteorites, *Geophys. Res. Lett.*, *34*, L05204, doi:10.1029/2006GL027685.

1. Introduction

[2] It has been suggested that vast unmagnetized regions within and around giant impact basins on Mars [*Acuña et al.*, 1999] were demagnetized due to a shock-induced phase change or magnetic transition in magnetic carriers in the crust [*Hood et al.*, 2003; *Rochette et al.*, 2003]. Models of the decay of shock pressure with distance indicate that the unmagnetized zones extend out 1.4 to 4 basin radii [*Hood et al.*, 2003; *Mohit and Arkani-Hamed*, 2004]. This corresponds to peak shock pressures of 1 to 3 GPa and temperatures well below the Curie point of candidate magnetic minerals.

[3] Pyrrhotite ($Fe_{1-x}S$, $x \leq 0.13$) has been identified as the major carrier of magnetic remanence in many Martian shergottite meteorites [*Lorand et al.*, 2005; *Rochette et al.*, 2005, 2001]. It is also an important accessory magnetic phase in the 4.5 Ga Martian meteorite ALH84001 [*Weiss et al.*, 2002]. In hydrostatic pressure experiments, pyrrhotite undergoes a ferrimagnetic to paramagnetic transition between 1.6 and 4.5 GPa [*Kobayashi et al.*, 1997; *Rochette et al.*, 2003; *Vaughan and Tossell*, 1973].

[4] Understanding the effects of shock waves on magnetic minerals is critical for interpreting the demagnetized zones around impact basins, constraining the identity of the major magnetic carriers in the crust, and inferring the origin of magnetization in meteorites. Here we present the first controlled shock demagnetization experiments on pyrrhotite.

2. Experimental Methods

[5] We performed planar shock recovery experiments on eleven ~3 × 1 mm discs cut from two natural pyrrhotite samples (98080 and 127037). The samples were embedded in aluminum recovery capsules as analogues to pyrrhotite in rocks. Using the 40-mm gas gun in the Harvard Shock Compression Laboratory, aluminum flyer plates impacting at velocities between 180 and 751 m/s generated pressure pulses ranging from 1.0 to 6.9 GPa (principal stress) of 1.5 to 2 μs duration. The pressure and duration of pressure experienced by the samples were determined from simulations of the experiments using the 1D WONDY [*Kipp and Lawrence*, 1982] and 2D CTH [*McGlaun et al.*, 1990] shock physics codes. Prior to shock, all samples were demagnetized in three directions by peak alternating fields (AF) of 85 or 94 mT (after which a high coercivity (HC) component with total moment between 0.012 and 0.198 Am^2 kg^{-1} remained). Subsequently, but prior to shock, ten of the samples were given an isothermal remanent magnetization in a high-field (335 or 370 mT) directed perpendicular to the plane of the disc, hereafter termed IRM_{HF}. The shock experiments were performed in the ambient laboratory field (12.7 μT antiparallel to the direction of shock and the applied magnetizing field). Magnetic remanence measurements were performed on a 2G Enterprises Superconducting Rock Magnetometer at Caltech. Low-temperature and hysteresis measurements were acquired with a Magnetic Properties Measurement System, a Vibrating Sample Magnetometer and an Alternating Gradient Field Magnetometer at MIT.

[6] Sample 98080 is an ~1 cm sized polycrystalline nodule embedded in a calcite matrix from Sudbury, Canada and sample 127037 is an ~5 × 3 × 2 cm polycrystalline sample with hexagonal habit from Chihuahua, Mexico. Fe/S ratios from microprobe analyses and powder X-ray diffraction reflections indicate that both samples consist of mixtures of ferrimagnetic monoclinic (Fe_7S_8) and antiferromagnetic hexagonal pyrrhotite, although 127037 is nearly pure monoclinic. The squareness of hysteresis (defined as the ratio of saturation remanence to saturation magnetization) of our samples ranges between 0.52–0.67 for 98080 and between 0.20–0.37 for 127037 (Figure 1a).

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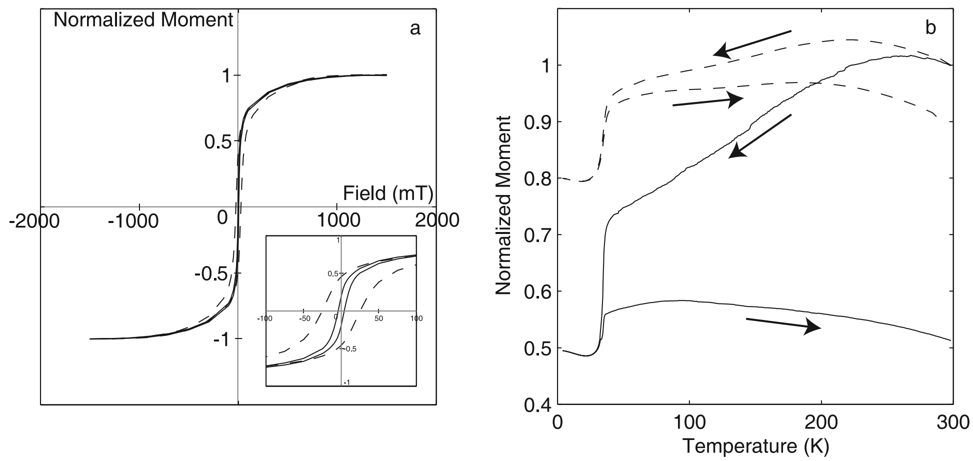


Figure 1. (a) Example of a hysteresis loop of a sample of 127037, with a detail of the region about the origin. Solid line is pre-shock and dashed line is post-shock (5.58 GPa). Paramagnetic slopes of 0.37×10^{-3} and 0.51×10^{-3} Am^2 kg^{-1} mT^{-1} have been removed from the pre- and post-shock loops respectively. (b) Example low temperature cycling (cooling followed by warming) of a sample of 127037. Solid line is pre-shock and dashed line is post-shock (5.58 GPa).

[7] Our magnetic properties measurements indicate that 98080 is predominately single domain (SD) and that 127037 contains a range of grain sizes from SD to multi-domain (MD). Cisowski *R*-ratios (the ratio of saturation remanence demagnetized to the remanent coercive force value, to the undemagnetized saturation remanence) between 0.20 and 0.43 indicate that the SD grains are interacting [*Cisowski*, 1981]. The presence of monoclinic pyrrhotite and the lack of significant quantities of super-paramagnetic grains were independently confirmed by the diagnostic 30–34 K low temperature magnetic transition [*Dekkers et al.*, 1989] in all samples (Figure 1b).

[8] In 98080, the orientations of the crystals are nearly random. However, the direction of preshock magnetization was at an angle of 14° to 40° (and not perpendicular to) the plane of the disc, indicating some intrinsic magnetic anisotropy in the sample. Discs from 127037 were cut such that an easy plane of magnetization lies in the plane of the disc and the pre-shock magnetization was directed at an angle of 6.4° ± 4.8° to the plane of the disc. The direction of shock wave propagation was perpendicular to the plane of the disc.

3. Results and Interpretations

[9] The results from our shock study on pyrrhotite (Figure 2a) demonstrate that shock demagnetization is not analogous to static pressure demagnetization. The remaining remanent magnetization (RM) after shock is reduced to 10–60% of the original magnitude (pre-shock values between 0.067 and 1.23 Am^2 kg^{-1} decrease to 0.030 to 0.746 Am^2 kg^{-1}) in a non-monotonic manner over 1.0 to 6.9 GPa for both pyrrhotite samples. Note that the post-shock magnetic moments are greater than the original HC components, indicating that shock does not efficiently remove all low coercivity components. We did not observe complete demagnetization up to 6.9 GPa. Our results do not show any demonstrative effects of the previously studied static pressure magnetic transitions [*Kobayashi et al.*, 1997; *Rochette et al.*, 2003; *Vaughan and Tossell*, 1973] or the onset of transformation to a higher density, high pressure phase between shock pressures of 2.7 and 3.8 GPa [*Ahrens*, 1979]. The total pre- and post-shock magnetic moments of the one unmagnetized sample were 0.035 and 0.032 Am^2 kg^{-1} respectively, indicating that no substantial shock remanent magnetization was acquired in the laboratory field.

[10] In our experiments, partial shock demagnetization is accompanied by rotation of the direction of the magnetic moment up to ~150° in both samples. The direction and amount of rotation do not correlate with shock pressure and are not dominated by the original HC components present in the samples. We are currently investigating the combined effects of anisotropy, interactions, and shock on the direction of the magnetic moments.

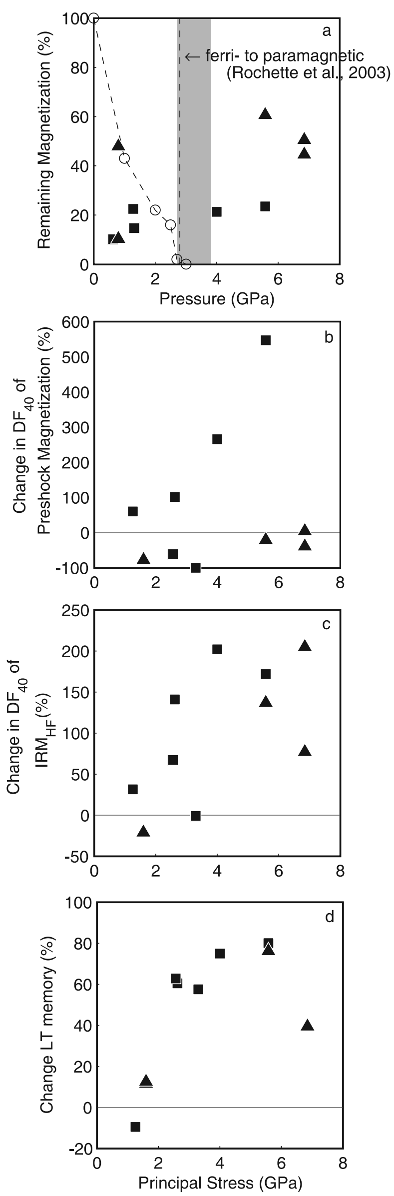
[11] The hardness of the magnetization will be represented by DF_{40}, the destructive field required to demagnetize the disc perpendicular component of the pre- and post-shock remanence by 40%. DF_{40} will be used throughout instead of the conventional median destructive field (MDF or DF_{50}) because our maximum three-axis alternating field of 94 mT was not able to demagnetize the remaining magnetization in our samples by 50%. In 98080, there is a positive correlation between the increase in DF_{40} and shock pressure (Figure 2b). DF_{40} increased substantially from a pre-shock range of 8.3 to 29.7 mT to a range of 6.7 to 80.6 mT (e.g. by up to 547%) after shock. This increase may be due to the preferential removal or demagnetization of a low-coercivity (LC) component. In 127037 this behavior is not observed, possibly because the pre-shock DF_{40} was much higher (34 ± 18 mT) indicating it already had a smaller fraction of LC magnetization.

[12] In addition to partial demagnetization, we observe irreversible changes in the magnetic properties of pyrrhotite after shock compression and release. IRM_{HF} serves as a proxy for saturation isothermal remanent magnetization (sIRM) and increased in all but two samples, up to 155%, after shock. It increases in 98080 with pressure from a range of 0.197–0.366 Am^2 kg^{-1} to a range of 0.223–0.475 Am^2 kg^{-1}. In 127037, the pre-shock IRM_{HF} is much

lower (0.018–0.086 $Am^2\ kg^{-1}$) and does not increase significantly due to shock (0.024–0.128 $Am^2\ kg^{-1}$).

[13] The DF_{40} of IRM_{HF} is a measure of the bulk coercivity of the sample. For most samples, DF_{40} of IRM_{HF} increases significantly due to shock with increasing pressure in both sample types (Figure 2c). Pre-shock DF_{40} of IRM_{HF} ranges from 8.3 to 57.4 mT; post-shock values range from 2.4 to 101.6 mT.

[14] Squareness of 127037 increased significantly with pressure for each sample by 20 to 130%, reaching post-shock ratios from 0.26 to 0.51; this indicates more SD behavior (e.g., Figure 1a). Changes in squareness for 98080 were moderately negative with pressure, presumably because the initial squareness was already near the theoretical maximum for pure SD pyrrhotite dominated by triaxial magnetocrystalline anisotropy in the easy plane (0.75–0.96). Therefore the shock itself not only has demagnetized the samples but has also irreversibly changed their rock magnetic properties as reflected by hardening of coercivity and changes in squareness.



[15] Low temperature (LT) memory (the fraction of remanence recovered when monoclinic pyrrhotite is cycled in near-zero field from room temperature through its 34 K transition) is inversely correlated with crystal size [*Dekkers et al.*, 1989]. Strong increasing trends in LT memory with pressure for both samples are observed (Figures 1b and 2d) and suggest a decrease in grain size. LT memory increases from 0.45 to 0.67 to post-shock values ranging from 0.49 to 0.93, the increase being more extreme in 98080.

[16] The *R*-ratio increases in all but one sample up to 0.34–0.40, indicating less interaction between the SD grains after shock. The field value at *R* (which approximates the remanent coercive force) increases similarly from 17.2–122.2 to 23.0–148.9 mT. This is consistent with more SD-like behavior [*Cisowski*, 1981].

[17] The aforementioned irreversible changes are evidence of an increase in SD-like behavior and are analogous to those seen in static pressure experiments up to 6 GPa [*Borradaile and Jackson*, 1993; *Gilder et al.*, 2004; *Jackson et al.*, 1993] and shock experiments up to 27 GPa [*Gattacceca et al.*, 2006; *Lamali et al.*, 2005; *Shapiro and Ivanov*, 1967; *Williamson et al.*, 1986] on magnetic minerals and rocks. A number of possible mechanisms for the observed changes and increase in SD behavior have been suggested. The break up of large, pseudo-single domain and MD grains into many smaller SD grains [*Gilder et al.*, 2004] should result in an increase in the bulk coercivity [*Jackson et al.*, 1993], saturation remanent magnetization, squareness, and LT memory [*Dekkers*, 1988].

[18] Stress hardening may also be the result of changes in the magnetostriction constants [*Gilder et al.*, 2004; *Nagata*, 1971], which would in turn increase both the SD-MD threshold radius and the saturation remanence. Defect generation, residual strain, domain nucleation and rotation, and changes in grain interactions may each contribute to the changes in magnetic properties after shock compression of

Figure 2. (a) Remaining magnetization, $\frac{RM}{IRM_{HF,pre}} \times 100$, versus pressure. Solid symbols from this work: squares – sample 98080; triangles – sample 127037; o – static pressure demagnetization experiments [*Rochette et al.*, 2003]. We assume complete loss of strength above 2.7 to 3.8 GPa [*Ahrens*, 1979] and that the shock principal stress equals the average pressure, below this region we plot the average pressure calculated from the principal stress using a Poisson's ratio of 0.13 for 98080 (isotropic) and 0.31 for 127037 (parallel to the c-plane). (b) Percentage change in peak alternating field required to demagnetize the pre-shock high field magnetization (IRM_{HF}) and post-shock remaining magnetization (RM) by 40%, $\frac{DF_{40}(RM)-DF_{40}\left(IRM_{HF,pre}\right)}{DF_{40}\left(IRM_{HF,pre}\right)} \times 100$, versus principal stress. (c) Percentage change in peak alternating field required to demagnetize the pre- and post-shock high field isothermal remanent magnetization by 40%, $\frac{DF_{40}\left(IRM_{HF,post}\right)-DF_{40}\left(IRM_{HF,pre}\right)}{DF_{40}\left(IRM_{HF,pre}\right)} \times 100$, versus principal stress. (d) Percentage change in low temperature (LT) memory, the fraction of saturation remanence at room temperature remaining after cycling below 30 K or $\frac{LTmemory_{post}-LTmemory_{pre}}{LTmemory_{pre}} \times 100$, versus principal stress.

pyrrhotite. For example, a high concentration of defects aids in domain wall nucleation, but impedes wall displacement, thereby increasing the coercivity.

[19] Because shock heating was negligible during the experiments ($\Delta T \sim 15°C$ at a principal stress of 6.9 GPa), it is unlikely that metastable hexagonal ferrimagnetic pyrrhotite [*Bennet and Graham*, 1981; *Rochette et al.*, 2005] was created. Powder X-ray diffraction measurements on samples shocked to 6.85 GPa (127037) and 5.58 GPa (98080) and the lack of new transitions in post-shock low temperature magnetic measurements indicate that no new phases were created (Figure 1b).

4. Discussion: Implications for Mars

[20] The observed differences in demagnetization behavior of pyrrhotite between shock and static experiments may be due to several effects. Unlike in static experiments, shock in pyrrhotite may produce incomplete magnetic or phase transitions [*Ahrens*, 1979; *Rochette et al.*, 2003], and there may be hysteresis in shock-induced phase transformations over the pressure range studied. A second effect is that domains may have been pinned by defects, impeding demagnetization by limiting their growth and rotation. If so, because shock waves exert deviatoric stresses, orientation effects may be more pronounced during shock experiments. *Nagata* [1970] observed that quasi-static pressure demagnetization is due to the irreversible displacement of 90° domain walls and that the effect of demagnetization is somewhat greater when the direction of applied pressure is parallel to the magnetization. Finally, unlike static experiments, the pressure loading path changes with increasing shock pressure. Hence, each sample experiences a unique pressure history, and shock and static results must be compared with caution.

[21] Static pressure measurements [*Rochette et al.*, 2003] have been used to interpret the zone of complete demagnetization of the crust surrounding impact basins on Mars [*Arkani-Hamed*, 2005a; *Hood et al.*, 2003; *Mohit and Arkani-Hamed*, 2004]. Our results imply that shock demagnetization is more complicated and that the zones of complete rock demagnetization may have been significantly overestimated. The observed demagnetization around large impact craters may be more due to processes like brecciation rather than the reduction of magnetic moment in the crust.

[22] In addition to the direct reduction in magnetic moment, predictions of the amount of remanence removed by an impact event need to account for the accumulated irreversible changes in magnetic properties (e.g., coercivity and sIRM) due to multiple shock events. *Nagata* [1971] found in laboratory experiments that repeatedly shocked basalts approach a final state of nonzero magnetization.

[23] Pyrrhotite in meteorites shocked up to even 7 GPa may retain part of its primary remanence and aid paleointensity measurements. However, many meteorites have likely been shock-demagnetized (and possibly remagnetized in surface fields and/or transient fields). Currently, the 4.0 Ga Martian paleofield is estimated to have been within an order of magnitude of the present terrestrial field [*Antretter et al.*, 2003; *Gattacceca and Rochette*, 2004; *Weiss et al.*, 2005, 2002]. Shock simultaneously reduces the original remanence by up to an order of magnitude and increases the sIRM by factors of two or more, even at shock pressures of only a few GPa. If this demagnetization were left undiagnosed, paleointensity experiments (particularly those employing total moment methods like NRM/sIRM [*Cisowski and Fuller*, 1986]) could underestimate the paleointensity of shocked rocks by an order of magnitude. Note that shock preferentially demagnetizes the low coercivity component; therefore, if the remanence in the Martian crust and meteorites is carried in higher coercivity components (e.g., in thermal or chemical remanence), then shock demagnetization will be less efficient.

[24] It has been demonstrated that the NRMs in Martian meteorites are too weak to explain the intense Martian crustal field anomalies if it is assumed that the magnetization of the crust has an intensity similar to these NRMs. But our results imply that Martian meteorites may have been shock-demagnetized by up to an order of magnitude relative to the deep, unshocked Martian crust. While we consider it unlikely that the Martian field was much stronger than has previously been assumed [*Arkani-Hamed*, 2005b], it would appear that the Martian meteorite paleointensity data are not the most compelling argument against such a strong field.

[25] Pyrrhotite is still a possible carrier phase of the magnetization in the Martian crust. However, the demagnetization behavior due to shock is more complicated than previously assumed. Partial demagnetization and changes in magnetic properties may be dominant effects in the crust and meteorites. Until the physical mechanisms that govern pressure-induced demagnetization are better understood, applying results of static or dynamic laboratory data to planetary impact events requires cautious extrapolation. Our new shock experiments are the closest analog available for understanding the effects of shock on the Martian crust and meteorites.

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