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High pressure magnetic transition in pyrrhotite and impact demagnetization on Mars

P. Rochette
CEREGE, University of Aix Marseille 3, Aix en Provence, France

G. Fillion and R. Ballou
Louis Néel Laboratory, CNRS, Grenoble, France

F. Brunet
Ecole Normale Supérieure, Paris, France

B. Ouladdiaf
Laue-Langevin Institute, Grenoble, France

L. Hood
Lunar and Planetory Laboratory, University of Arizona, Tucson, USA

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[1] Using neutron diffraction under pressure at room temperature, we observed that pyrrhotite undergoes a ferrimagnetic to paramagnetic transition at about 2.8 GPa. Complete demagnetization of remanence at the same pressure is confirmed in an independent experiment. Such a process provides a quantitative explanation of the magnetic structure of the Martian Southern Hemisphere assuming that pyrrhotite is the major magnetic mineral and that our static experiments can be extrapolated to dynamic pressure conditions. Indeed, the 3 GPa isobaric line during the two large impacts of Argyre and Hellas separates the magnetized and unmagnetized zones. We also infer a reinterpretation of Martian meteorites paleomagnetic signal. *INDEX TERMS:* 1540 Geomagnetism and Paleomagnetism: Rock and mineral magnetism; 3924 Mineral Physics: High-pressure behavior; 3954 Mineral Physics: X ray, neutron, and electron spectroscopy and diffraction; 5420 Planetology: Solid Surface Planets: Impact phenomena (includes cratering); 5440 Planetology: Solid Surface Planets: Magnetic fields and magnetism. **Citation:** Rochette, P., G. Fillion, R. Ballou, F. Brunet, B. Oulladiaf, and L. Hood, High pressure magnetic transition in pyrrhotite and impact demagnetization on Mars, *Geophys. Res. Lett.*, *30*(13), 1683, doi:10.1029/2003GL017359, 2003.

1. Introduction

[2] Pyrrhotite [*Bertaut*, 1953] is a common ferrimagnetic mineral in terrestrial rocks [*Rochette et al.*, 1990] and has been identified as the major remanence carrier in Martian SNC (Shergotty-Nakhla-Chassigny type) meteorites [*Rochette et al.*, 2001]. A ferrimagnetic to paramagnetic transition under pressure has been suggested by Mössbauer spectroscopy [*Vaughan and Tossell*, 1973]. Such a transition theoretically implies that rocks shocked over the transition pressure should be demagnetized during an impact [*Rochette et al.*, 2001], which may explain the observed correlation between impact craters and low magnetization of the Martian crust [*Hood et al.*, 2003, *Nimmo and Gilmore*, 2001] as well as raising alternative interpretations of the paleomagnetic signal of SNCs [*Collinson*, 1997; *Kirschvink et al.*, 1997; *Weiss et al.*, 2000, 2002; *Rochette et al.*, 2001; *Antretter et al.*, 2003]. We performed a neutron diffraction experiment under pressure to confirm and implement the preliminary Möss-bauer data [*Vaughan and Tossell*, 1975; *Kobayashi et al.*, 1997], and a remanence versus hydrostatic pressure experiment to check the demagnetization hypothesis and bring quantitative constraints. Indeed, precise estimates of both the transition pressure and the demagnetization curve are critical to model the attenuation of magnetic anomalies versus distance from large Martian basins such as Argyre and Hellas [*Hood et al.*, 2003]. Here we show that full demagnetization of remanence occurs at the magnetic transition pressure of 2.8 GPa.

2. Neutron Diffraction Experiment

[3] Monoclinic pyrrhotite crystallizes in the C2/c space group and exhibits ferrimagnetism with a spontaneous magnetization M_s of 18 Am^2/kg at ambient temperature, a Curie temperature T_c of 325°C and a strong easy-plane magnetocrystalline anisotropy. Its crystal structure was interpreted concomitantly with its magnetic behavior as due to an ordering of iron vacancies in an hexagonal substructure (HS) that leads to an alternating stacking of partially and fully filled iron layers coupled antiferromagnetically to each other [*Bertaut*, 1953]. The neutron diffraction experiment was performed at the ILL High Flux Reactor on the powder two-axis multidetector diffractometers D1B and D20 (http://www.ill.fr/pages/science/IGroups/dif_1.html), with incoming beam wavelength of 2.52 Å (D1B) and 2.41 Å (D20). The sample was a natural monoclinic pyrrhotite termed TTE, in the form of a powder with grain size about 200 μm. Well characterized [*Dekkers*, 1988], this TTE pyrrhotite was previously investigated by magnetostatic measurements [*Dekkers*, 1988; *Rochette et al.*, 1990] and neutron diffraction on D1B, at room pressure and low temperature [*Fillion et al.*, 1992]. Clamped cells were used

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to apply the pressure on the unheated sample. These are loaded to the desired pressure in a controlled press and then clamped using a locking nut before being transferred into the neutron beam. A pressure up to about 2GPa could be applied on the sample during the D1B measurements while a maximum of about 3GPa could be reached during the D20 measurements. A small amount of NaCl was added to the sample for absolute calibration of the pressure [*Skelton et al.*, 1984]. Deuterated ethanol was used as a pressure transmitting media to insure a homogeneous pressure.

[4] The collected neutron patterns displayed large scattering from the pressure cell which partially hid the scattering from the sample, except for some low angle Bragg peaks, among which the ferrimagnetic (001) peak and a peak indexed as (100) in the HS (Figure 1). An independent run of the TTE powder in a furnace on D1B confirms that the (001) peak does fully disappear at the Curie temperature T_c of 325°C, in agreement with a previous investigation [*Sidhu et al.*, 1959]. On the contrary, the (100) peak appeared to be almost independent of temperature and therefore of vacancy and magnetic orders. Using this peak to normalize the intensities of the other peaks, the magnetic contributions are given in absolute scales. Figure 2 shows that the normalized intensity of the (001) ferrimagnetic peak decreases with pressure and vanishes in between 2.6 GPa and 3.1 GPa. A nuclear contribution to the intensity of this peak associated with the vacancy ordering exists, but is of the order of the experimental noise (Figure 2).

3. Pressure Demagnetization of Remanence

[5] An experiment relying on remanence measurements after pressure release was designed for the remanent magnetization versus pressure experiment, since no instrument was available for such measurements under pressure up to 3 GPa with sufficient accuracy. This requires a massive sample, with a sufficiently stable remanence that the signal is not affected by spurious demagnetization due to manipulations and viscous decay in between the remanence measurements performed before and after pressure application. This implies fine-grained monoclinic pyrrhotite dispersed within a solid non-magnetic matrix. Moreover, this matrix has to minimize local pressure gradients. We used mm-sized fragments of a polycrystalline massive hexagonal pyrrhotite from Ducktown mine [*Carpenter*, 1974] with minor fine impurities of monoclinic pyrrhotite. The hexagonal phase has been identified by X rays diffraction spectra and thermomagnetic experiments. The hexagonal pyrrhotite is antiferromagnetic (thus not contributing to remanence) but is likely to have the same mechanical properties as monoclinic pyrrhotite and thus be an optimal transmitting media. Figure 3 shows the hysteresis loop of a fragment used in the experiment. The remanent coercivity (H_{cr}) of 305 mT, with $H_{cr}/H_c = 1.97$ and $M_{rs}/M_s = 0.54$, indicates a nearly single domain state of the monoclinic pyrrhotite inclusions, with particularly high stability (note that the 1 T field used is not saturating). Wasp-waistedness of the curve suggests significant contribution by non SD grains. M_s corresponds to an amount of monoclinic pyrrhotite of only 0.3%. Remanence measurements were performed using a 2G DC SQUID cryogenic magnetometer in CEREGE (Aix en Provence) with a noise level of 10^{-11} Am^2.

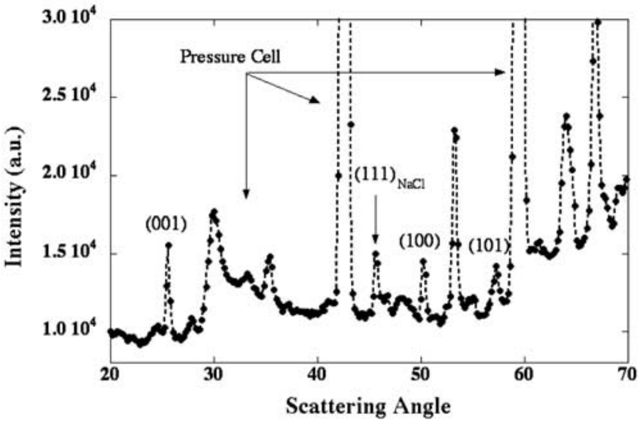

Figure 1. Neutron scattering pattern (neutron counts in arbitrary unit versus 2θ angle in degree) collected on D20 from TTE pyrrhotite powder at room pressure and temperature. The Bragg scatterings from the sample (two magnetic (001) and (101), and one structural (100)) from NaCl (labelled $(111)_{NaCl}$) and from the pressure cell (all the other peaks) are identified.

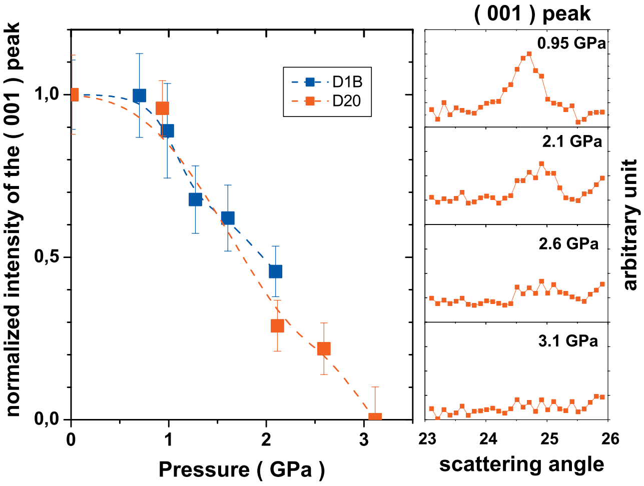

Figure 2. Neutron scattering pattern versus pressure. (Left part) Pressure dependence of the integrated intensity of the ferrimagnetic (001) Bragg peak normalized with respect to the mostly nuclear (100) Bragg peak. These are further all divided by the value at ambient pressure. Error bar corresponds to 2 sigma in neutron counting statistics. (Right part) Evolution with increasing pressure of the ferrimagnetic (001) Bragg peak as measured on D20.

[6] The mm-size rounded pyrrhotite samples are first saturated in a 3 T pulsed field and their imparted M_{rs} is measured. Fragments of 34 to 64 mg with M_{rs} comprised between 1.9 and 3.8 10^{-6} Am^2 have been cold-pressed from 1 to 3 GPa in an end-loaded piston cylinder press at the ENS (Paris). Silver chloride powder was used as solid pressure-medium since it displays a very low internal friction coefficient at high-pressure [*Hall*, 1961]. This ensures that a quasi-hydrostatic pressure is exerted on the sample. Pressure was raised by 1 GPa steps (ca. 1 bar.s^{-1}). Between each step, hydraulic valves are closed in order to let the hydraulic oil and sample pressures equilibrate for around 6 to 12 hours. Once nominal oil-pressure is reached and after overnight pressure stabilization, nominal oil-pressure is raised again up to the

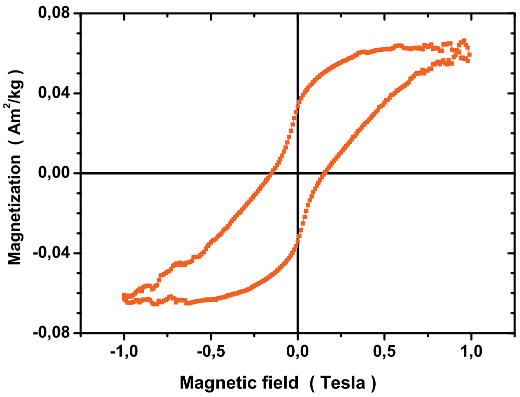

Figure 3. Hysteresis loop on a 50 mg Ducktown pyrrhotite fragment used in demagnetization experiment. Magnetization, obtained with the Micromag VSM in CEREGE, is corrected from a high field slope of 2.56 10^{-7} m^3/kg (linear fit of the descending branch in between 0.7 and 1T).

nominal value and then slowly decreased down to ambient pressure at an average rate of ca. 0.2 bar.s^{-1}. Pressure calibration was performed by monitoring the Bismuth-I/Bismuth-II transition at 2.56 GPa by in-situ impedance measurements. Although various NaCl parts of the pressure cell are fractured upon decompression, the AgCl cylinder, which enclosed the pyrrhotite fragment, remains compact and free of cracks. A visual inspection of the pyrrhotite fragments showed no significant shape change and loss of coherence, indicating that irreversible deformation or microfracturation can only be marginal. This indicates that the sample demagnetization cannot be due to the randomization of the orientations of the monoclinic pyrrhotite crystals.

[7] The pressure demagnetization curve shown in Figure 4 is based on five piston-cylinder experiments performed between 1 and 3 GPa at room temperature. A regular decrease is observed, with a sharper transition to full demagnetization just above 2.75 GPa, corresponding to the magnetic phase transition. The quite different shapes of Figure 2 and 4 are easily accounted for by the fact that the neutron peak area is proportional to the square of M_s, thus not likely to be proportional to M_{rs}. Negligible remanence is observed at 3 GPa, indicating that the remanence acquired when releasing the pressure within the uncontrolled but weak ambient field is as expected negligible with respect to the saturation remanence. A further check is brought by alternating field (AF) demagnetization of residual M_{rs}. No secondary component is seen in low AF field. The relative decrease of remanence up to the maximum AF field of 140 mT on the sample pressed at 1 GPa is only 21%. Compared to a 26% decrease on the unpressed sample, this indicates that the softer part of M_{rs} is only faintly preferentially demagnetized at intermediate pressure.

4. Discussion

[8] Our two experiments clearly confirm the ferrimagnetic to paramagnetic transition of monoclinic pyrrhotite at high pressure. However, they both concur that the transition pressure is about 2.8 GPa which is at odds with the previous Mössbauer experiments: the ferrimagnetic sextets are identified at 0.5 and 3.9 GPa, while only a paramagnetic doublet is reported at 1.6 and 5.1 GPa in the *Vaughan and Tossell* [1973] and *Kobayashi et al.* [1997] experiments, respectively (no insight into pressure calibration was given in both case). A higher than 2.5 GPa transition pressure is more in agreement with the scarce data on pyrrhotite's structural phase diagram [*Ahrens*, 1979] indicating a density change in the range 2.7–3.8 GPa, according to shock wave experiments. More data is available on troilite (FeS), with a well-documented structural transition in the range 3–3.5 GPa [*Fey et al.*, 1995; *Kusaba et al.*, 1998]. In fact the *Kobayashi et al.* [1997] spectrum at 3.9 GPa is said to exhibit a very small sextet. If this pressure value is discarded, the first value below with a clear ferrimagnetism is at 2.5 GPa, in agreement with our data.

[9] Our results have major implications on the natural remanent magnetization (NRM) of pyrrhotite-bearing rocks submitted to high pressures below their Curie point (which can occur in case of impact). In the following we will assume that the transition pressure and demagnetization behavior obtained in our static experiments can be directly extrapolated to shock waves conditions. This assumption is grounded on the fact that peak pressures during large shocks are maintained on a time scale [1 to 100 ms, see *Melosh*, 1989] much larger than the characteristic time of spin processes (collapse, exchange coupling, etc.) which is less than 10^{-8} s according to neutron experiments. A first consequence is that the paleomagnetic signal of Martian pyrrhotite-bearing meteorites, such as shergottites [*Rochette et al.*, 2001] and ALH84001 [according to *Kirschvink et al.*, 1997], postdates shock. Indeed, shock pressures much above 3 GPa have been evidenced in these rocks [*Langerhorst and Poirier*, 2000; *Chen and El Goresy*, 2000]. Therefore lack of strong NRM intensity in SNC meteorites [apart from ALH84001: *Weiss et al.*, 2002] cannot be used to constrain the lack of a Martian dynamo at the formation age of the rock but solely at the often much younger shock age. In ALH84001 this argument together with the pre-shock formation of the "nanofossil"-bearing carbonate globules [*Greenwood and McSween*, 2001] would invalidate the " conglomerate test " used in *Kirschvink et al.* [1997] to argue for a continuous low temperature stay of this meteorite since carbonates formation [see *Rochette*, 2001 for a longer discussion of this very complex subject]. However, more recent papers [*Weiss et al.*, 2000, 2002;

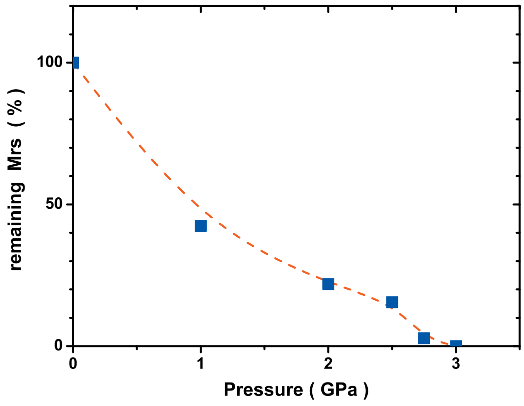

Figure 4. Pressure demagnetization of Ducktown pyrrhotite. Remaining saturation remanence (M_{rs}) of pressed fragments, normalized to initial M_{rs}, as a function of applied pressure.

Antretter et al., 2003] are more in favor of magnetite as the main carrier of ALH84001 magnetism. Nevertheless, a post-shock magnetization agrees with the high temperature origin of the carbonates globules and their shock-induced magnetite inclusions, at odds with the biogenic interpretation [*Bradley et al.*, 1998; *Barber and Scott*, 2002].

[10] Concerning impact demagnetization of a pyrrhotite-bearing Martian crust, the present contribution strongly supports our initial suggestions [*Rochette et al.*, 2001] and provides a quantitative framework for modeling magnetization attenuation versus distance to major craters [*Hood et al.*, 2003]. Indeed while obviously the crust would be fully demagnetized at 3 GPa, Figure 4 demonstrates that it is already more than half demagnetized at 1 GPa. This means nearly 4 crater radii in the case of Hellas and Argyre. The underlying assumption in impact demagnetization of a pyrrhotite-bearing Martian crust is that impact occurred after the Martian dynamo shutdown, thus imparting negligible NRM during pressure release and associated reappearance of ferrimagnetism. However, this NRM acquisition mechanism is likely to be much less effective than the primary thermoremanent magnetization (TRM). Therefore, relative impact demagnetization is also expected if dynamo was still active in case of minor thermal effects. However, in such a scenario one should observe a strong remagnetization in the impact basin (where the crust has been impact-heated above Curie point) surrounded by a demagnetized ring. This does not correspond to the observed situation on Mars. We acknowledge that a full quantitative treatment of martian crust impact demagnetization would require the knowledge of the effect of in situ temperature range (200–600 K, i.e. surface to Curie temperatures) and domain state on the demagnetization curve of Figure 4. The problem of impact heating is minor as it is estimated to be less than 10–20 K for a shock pressure less than 5 GPa [*Stöffler et al.*, 1991]. Further experiments are needed to estimate the temperature dependence of the transition pressure, likely to increase with temperature. Deep rocks may thus need a larger pressure to be demagnetized, but as their remanence is also likely less stable (due to increased grain size and viscous effects) these second order features may compensate each others. Finally the progressive collapse of pyrrhotite ferrimagnetism at high pressure would also provide an explanation for the anomalously low paleointensity found in pyrrhotite bearing metamorphic rocks whose TRM have been acquired at a pressure of about 0.3 GPa [*Rochette et al.*, 1992; *Crouzet et al.*, 2001].

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P. Rochette, CEREGE, University of Aix Marseille 3, Aix en Provence, France. (rochette@cerege.fr)

G. Fillion and R. Ballou, Louis Néel Laboratory, CNRS, Grenoble, France.

F. Brunet, Ecole Normale Supérieure, Paris, France.

B. Ouladdiaf, Laue-Langevin Institute, Grenoble, France.

L. Hood, Lunar and Planetory Laboratory, University of Arizona, Tucson, USA.