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Key Points:

- NWA 7034 contains 15 wt % of iron oxides (magnetite and maghemite)
- The magnetic assemblage is partly linked to near-surface hydrothermal alteration
- NWA 7034 is an analogue source for the magnetization of the Noachian crust

Supporting Information:

- Table S1

Correspondence to:

J. Gattacceca,
gattacceca@cerege.fr

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Martian meteorites and Martian magnetic anomalies: A new perspective from NWA 7034

J. Gattacceca¹, P. Rochette¹, R. B. Scorzelli², P. Munayco², C. Agee³, Y. Quesnel¹, C. Cournède¹, and J. Geissman⁴
¹CNRS/Aix Marseille Université, CEREGE UM34, Aix-en-Provence, France, ²CBPF, Rio de Janeiro, Rio de Janeiro, Brazil,

³Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico, USA, ⁴Department of Geosciences, University of Texas at Dallas, Richardson, Texas, USA

Abstract We present the magnetic properties of the Noachian Martian breccia NWA 7034. Among the 25 unpaired Martian meteorites studied to date, NWA 7034 has a unique magnetic mineralogy. It contains about 15 wt % of iron oxides as magnetite that has experienced cation substitution and partial alteration to maghemite, with about a quarter of the oxides being pure maghemite. It also contains oxyhydroxides in the form of superparamagnetic goethite. The presence of maghemite and goethite makes NWA 7034 the most oxidized Martian meteorite. The overall magnetic assemblage is partly linked to near-surface hydrothermal alteration. The high concentration of magnetic phases with high laboratory unblocking temperatures makes NWA 7034 a plausible analogue source lithology for the strong magnetization of the Martian Noachian crust. Near-surface hydrothermal alteration can enhance the remanence of Martian rocks and account for local, high magnetic anomalies of shallow source.

1. Introduction

Significant magnetic anomalies have been documented over large parts of the Noachian crust at satellite altitude by the Mars Global Surveyor mission [Acuña *et al.*, 1999]. Current models for these anomalies require remanent magnetizations up to 15–30 A/m over a crustal thickness of 20–50 km [e.g., Langlais *et al.*, 2004, 2010]. Some studies set the magnetization over the strongest—but localized— anomalies in the 20–60 A/m range using a thick magnetized crust, but other interpretations require a thinner and even more magnetized layer [Connerney *et al.*, 2005]. Strong magnetizations in such large volumes require a global magnetic field at least during crustal cooling and rocks capable of acquiring strong remanent magnetizations. Mars likely had a dynamo in the past [Acuña *et al.*, 1999; Weiss *et al.*, 2008] that ceased functioning at about 4.1 Ga [Lillis *et al.*, 2008] or 3.6 Ga [Milbury *et al.*, 2012]. A number of exotic rocks and magnetic minerals have been proposed to account for the Martian magnetic anomalies [e.g., Kletetschka *et al.*, 2004; McEnroe *et al.*, 2004]. However, Martian rocks (available in the form of meteorites) contain only magnetite and/or pyrrhotite as magnetic minerals, usually in too small concentration to account for such strong remanence [Rochette *et al.*, 2005]. The small number of sufficiently magnetic meteorites does not represent the Noachian Martian crust, so that to date there is no satisfactory candidate rock to account for the Martian magnetic anomalies. In 2013, a new type of Martian meteorite (NWA 7034 and subsequent paired stones NWA 7475, NWA 7533, NWA 7906, NWA 7907, NWA 8114, and NWA 8171, called collectively NWA 7034 in the following) was recovered in the Sahara. Here we present the magnetic properties of this unique meteorite, a volcanic breccia of Noachian age [Agee *et al.*, 2013a; Humayun *et al.*, 2013], and discuss the implications for the understanding of Martian magnetic anomalies.

2. Samples and Methods

NWA 7034 is recognized as a Martian meteorite mostly on the basis of its chemistry and mineralogy [Agee *et al.*, 2013a]. It is a water-rich breccia containing several distinct igneous lithologies (polymict breccia). Its petrogenesis involved volcanism, impacts, and possibly hydrothermal alteration [Agee *et al.*, 2013a; Humayun *et al.*, 2013]. Ages of ~4.4 Ga have been obtained from zircons [Humayun *et al.*, 2013] and pyroxenes [Nyquist *et al.*, 2013]. Younger Rb–Sr ages [Agee *et al.*, 2013a] are now interpreted as late disturbances [Humayun *et al.*, 2013; Nyquist *et al.*, 2013]. The composition of NWA 7034 is similar to the average Martian crust [Agee *et al.*, 2013a], indicating that NWA 7034 could be representative of the Noachian crust. We studied samples obtained from NWA 7034 and NWA 7533, which represent stones from the same meteorite fall.

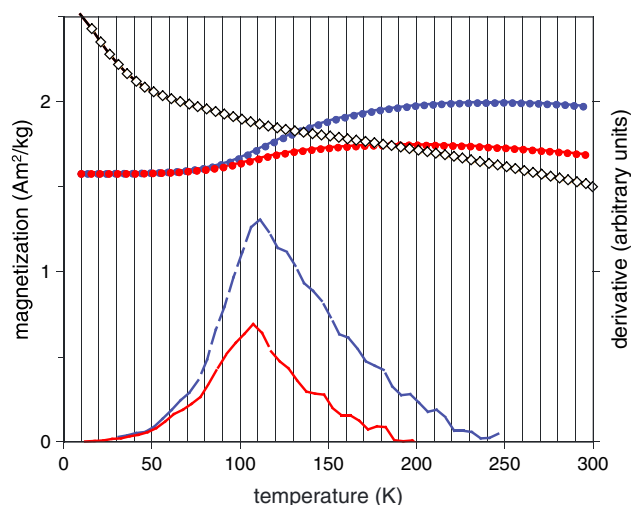


Figure 1. Low-temperature SIRM (diamonds) during warming in zero field, and room temperature SIRM (circles) and its derivative during cooling and warming in zero field (blue: cooling, red: warming) for a 101 mg sample of NWA 7034.

(anhysteretic and isothermal remanent magnetizations, susceptibility versus temperature, and hysteresis at room and high temperature). The natural remanent magnetization was also measured in CERGE and University of New Mexico. The sensitivity of all the instruments used is orders of magnitude smaller than the values measured for NWA 7034. Mössbauer spectroscopy was performed at Centro Brasileiro de Pesquisas Físicas (Rio de Janeiro) on a powdered ~100 mg sample, in transmission geometry at room and liquid helium temperature (4.2 K), using a 512 channel Halder spectrometer. The drive velocity was calibrated using a $^{57}\text{Co}/\text{Rh}$

Eighteen samples in the 5–350 mg range, totaling 1.13 g, were selected from over several millimeters away from the fusion crust (usually sand blasted). The intrinsic magnetic properties were measured at Centre Européen de Recherche et d'Enseignement de Géosciences de l'Environnement (CERGE) in Aix-en-Provence (low-field magnetic susceptibility, its anisotropy, and its variation with low and high temperatures using a MFK 1A Kappabridge instrument from Agico, hysteresis properties using a Micromag vibrating sample magnetometer, and anhysteretic and isothermal remanent magnetizations using a 2G superconducting magnetometer), Institute for Rock Magnetism in Minneapolis (low-temperature remanence using a MPMS), and the University of New Mexico and University of Texas at Dallas

matrix source and an iron foil both at room temperature. All measurements were performed at high velocity (± 12 mm/s), with an average recording time of 24 h, absorber and source at same temperature. NORMOS code was used for spectral analysis based on a least square fitting routine.

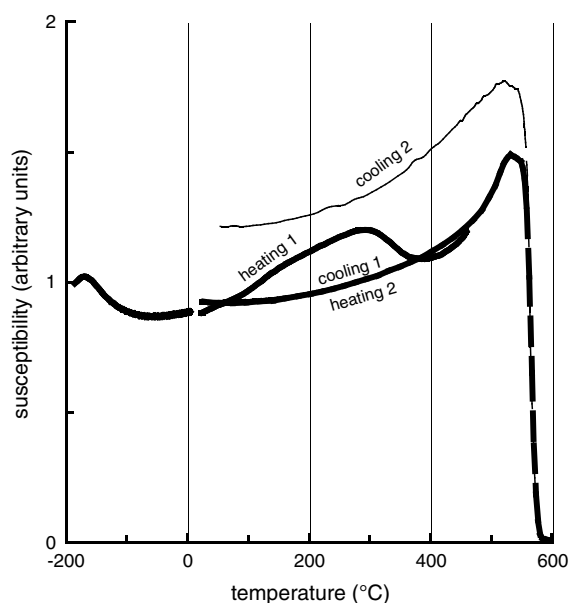


Figure 2. Low-field magnetic susceptibility versus temperature during warming (thick line) from -185°C to 600°C and subsequent cooling (thin line) for a 70 mg sample of NWA 7034. A cooling and warming cycle was performed between 450°C and 20°C to better evidence the irreversible transformation at 350°C . Note that the cooling curve for this cycle (cooling 1) is masked by the subsequent heating curve (heating 2).

3. Magnetic Mineralogy of NWA 7034

Evolution of the room temperature saturation isothermal remanent magnetization (SIRM) shows the presence of a Verwey transition at 110 K (Figure 1). This indicates the presence of magnetite with only limited cation substitution (5% maximum). The transition temperature is lower than the canonical Verwey transition at 120 K indicating that the magnetite is slightly oxidized [King and Williams, 2000]. However, saturation remanence is largely unaffected by the Verwey transition (Figure 1) indicating the dominant contribution of another magnetic mineral whose properties are independent of temperature in the low-temperature range, an observation that is confirmed by the low-temperature evolution of low-field magnetic susceptibility that shows only a very faint Verwey transition (Figure 2). The high-temperature

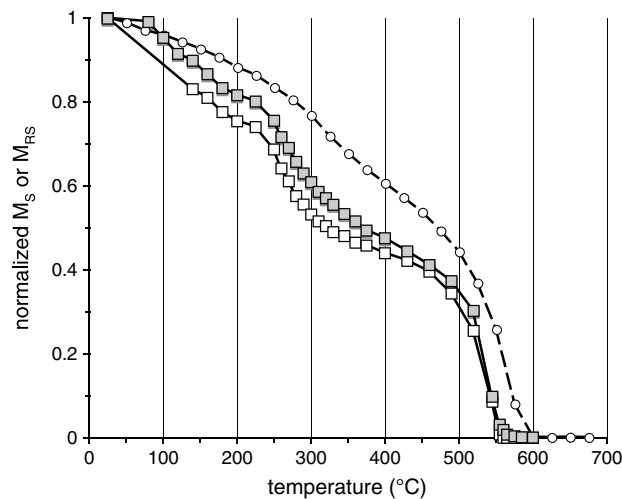


Figure 3. Thermal demagnetization of SIRM for a ~1 mg sample of NWA 7034 and NWA 7533 (boxes), and evolution of saturation magnetization (M_S) of a 22 mg sample of NWA 7034 with temperature (circles).

behavior of magnetic susceptibility (Figure 2) shows an irreversible transition at ~335°C, typical of the transformation of maghemite into hematite, and a Curie temperature at 565°C typical of magnetite with limited substitution (~1 wt % TiO_2 or ~1 wt % Cr_2O_3 computed after Hunt *et al.* [1995] and Robbins *et al.* [1971], respectively). Thermal demagnetization of SIRM also shows maximum unblocking temperatures at ~270°C and 550°C (Figure 3) in agreement with the above interpretation. The presence of maghemite is confirmed by refined X-ray diffraction spectra and electron microprobe analyses with totals significantly lower than the M_3O_4 formula.

The S_{-300} ratio (ratio of SIRM superimposed with a back-field isothermal remanent magnetization at 300 mT over SIRM) in the range -0.99 to -1.00 indicates the absence

of significant amounts of high coercivity minerals like pyrrhotite that is commonly found in other Martian meteorites [Rochette *et al.*, 2005]. Saturation magnetization (M_S) is $6.15 \text{ A m}^2/\text{kg}$ (mass-weighted average for 16 samples totaling 1.13 g), which would translate into 6.7 wt % pure magnetite. This is about half the amount of cubic iron oxides determined by X-ray diffraction (10 vol % or 15 wt % [Agee *et al.*, 2013b]), in agreement with the fact that magnetite in NWA 7034 shows a range of oxidation and substitution by Cr, Ti, and Al. The average composition for magnetite grains we analyzed with an electron microprobe is $12.2 \pm 6.9 \text{ wt } \%$ Cr_2O_3 , $3.8 \pm 2.6 \text{ wt } \%$ Al_2O_3 , $2.9 \pm 1.3 \text{ wt } \%$ TiO_2 , and $1.5 \pm 0.5 \text{ wt } \%$ MgO ($n = 10$). This range of substitution would result in Curie temperature much lower than the measured one (565°C). The substitution by 12.2 wt % Cr_2O_3 alone would result in a Curie temperature of about 370°C [Robbins *et al.*, 1971], and the substitution by Al and Ti would further lower this temperature. This discrepancy shows that the electron microprobe analyses, which focus on large grains, do not provide the elemental composition of the bulk of the magnetite grains that is made of smaller grains with lower substitution, either as individual grains or as fine-scale exsolutions in larger grains. Indeed, hysteresis parameters (Table 1) indicate that magnetite and maghemite are dominantly in the pseudo single domain size range, i.e., with a magnetic grain size of 50 to 300 nm (assuming a spherical grain shape).

Mössbauer spectra at room temperature (Figure 4) were fitted with five components (Table S1 in the supporting information): two Fe^{2+} doublets (D1 and D2) assigned to silicates, one Fe^{3+} doublet (DS) associated with small particles of goethite, and two sextets of Fe-rich spinels (A and B). Spectra analysis indicates that 55 wt % of the iron is in the Fe-rich spinels, 37 wt % is in the silicates, and 8 wt % is in goethite. This goethite is superparamagnetic at room temperature but splits magnetically at lower temperature with a

Table 1. Magnetic Properties of Martian Meteorites Studied Since [Rochette *et al.*, 2005]^a

	$\chi_0(10^{-9} \text{ m}^3/\text{kg})$	$\chi_{\text{HF}}(10^{-9} \text{ m}^3/\text{kg})$	$M_S(10^{-3} \text{ A m}^2/\text{kg})$	$M_{\text{RS}}(10^{-3} \text{ A m}^2/\text{kg})$	M_{RS}/M_S	$B_{\text{cr}}(\text{mT})$	B_{cr}/B_c	S_{-300}
NWA 7034	$27,900 \pm 600$ ($n = 5$)	632 ± 165 ($n = 5$)	5530^b	1880^b	0.34 ± 0.04 ($n = 18$)	52 ± 3 ($n = 17$)	1.54 ± 0.06 ($n = 17$)	-1.00 ± 0.00 ($n = 3$)
NWA 1950	4,776	370	187	58	0.31	75	3.26	-0.98
NWA 2737	26,600	1456	377	49	0.13	11	5.58	-0.97
NWA 5790	6,475	402	1188	297	0.25	58	1.81	-0.98
Tissint	1,140	456	163	62	0.38	78	1.67	-0.76

^a χ_0 = low-field magnetic susceptibility (measured at 200 A/m and a frequency of 976 Hz), χ_{HF} = high-field susceptibility (determined by linear fit for applied fields above 0.7 T of the hysteresis loops), M_{RS} = saturation remanent magnetization, M_S = saturation magnetization, B_{cr} = coercivity of remanence, B_c = coercivity, S_{-300} = see text.

^bMass-weighted average for 16 samples totaling 1.13 g.

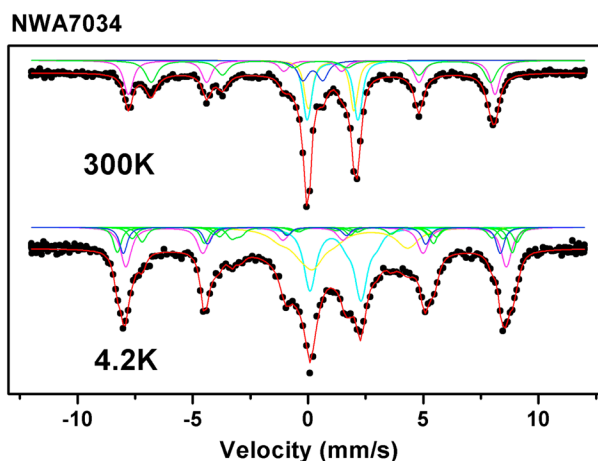


Figure 4. Mössbauer spectra at 300 K and 4.2 K for a 258 mg sample of NWA 7034. Solid circles are measured spectra, colored lines represent the fitting results (red: total spectrum, blue: goethite, pink and green: magnetite, and cyan and yellow: silicates).

blocking temperature estimated at about 25 K from the areal evolutions of the goethite doublet and sextet with temperature. The existence of a population of superparamagnetic grains is also suggested by the initial decay of the low-temperature SIRM during warming (Figure 1). It is noteworthy that maghemite was not detected with Mössbauer spectroscopy. This may be due to the small-scale heterogeneous distribution of maghemite, or to the effect of the large range of substitution and maghemitization that blur the Mössbauer signature of maghemite and lead to superimposition with that of magnetite.

All studied samples, down to a mass of 1 mg (the smallest studied sample), yield similar magnetic properties and inferred magnetic mineralogy. Thermomagnetic measurements

performed on four 30 mg samples gave exactly identical results. Similarly, hysteresis parameters are remarkably constant: the average coercivity B_c is 32.9 ± 4.3 mT for seven samples with mass in the 50–350 mg range, compared to 35.2 ± 1.6 for 10 samples with mass in the 5–20 mg range. This agrees with petrographic observations showing that oxides are present in the matrix and in all studied clasts [Santos *et al.*, 2013].

It is noteworthy that the natural remanent magnetization (NRM) of all the studied samples has been overprinted by the use of rare Earth magnets by the meteorite hunters, as evidenced by the response to progressive alternating field demagnetization, the high NRM/SIRM ratio and the persistence of REM' ratio (as defined in Gattacceca and Rochette [2004]) above 0.3 for alternating fields up to 170 mT.

4. Discussion

As the original NRM of Martian meteorites is strongly affected by impacts at the surface of Mars [Cisowski, 1986; Gattacceca and Rochette, 2004; Gattacceca *et al.*, 2013], weathering at the surface of the Earth for meteorite finds, and the widespread use of strong magnets by meteorite hunters and collectors, an indirect proxy for the in situ NRM of these rocks in the Martian crust is required. SIRM is a reliable proxy: assuming the NRM is a thermoremanent magnetization, we have $NRM/SIRM \sim B/3000$ where B is the paleofield in μT [Kletetschka *et al.*, 2003; Gattacceca and Rochette, 2004]. Using such scaling law with a paleofield of 50 μT for the Noachian [Weiss *et al.*, 2008], the required minimum crustal magnetization of 15 A/m [Langlais *et al.*, 2004] translates into a minimum SIRM of 900 A/m or 0.29 A m²/kg using a bulk density of 3100 kg/m³ (value for shergottites and nakhlites from Britt and Consolmagno [2003]). Using such approach and compiling data for 21 unpaired Martian meteorites led Rochette *et al.* [2005] to the conclusion that a very minor fraction of these meteorites had sufficient concentration of magnetic phases, either magnetite or pyrrhotite, to account for the Martian magnetic anomalies.

We revisit these conclusions, adding data for five new unpaired meteorites of special interest (Table 1): Iherzolitic shergottite NWA1950 and chassignite NWA2737, which contain a significant amount of impact-generated metallic iron nanoparticles [Van de Moortèle *et al.*, 2007]; nakhlite NWA5790 which may represent the top of the nakhlite pile [Jambon *et al.*, 2010; Mikouchi *et al.*, 2012]; the recent shergottite fall Tissint [Gattacceca *et al.*, 2013]; and NWA7034. Using this updated database, only three Martian meteorites (other than NWA 7034) satisfy the condition $SIRM > 0.29$ A m²/kg (Figure 5): Los Angeles (shergottite), MIL 03346 and NWA 5790 (nakhlites). However, Los Angeles exhibits magnetization unblocking temperatures below 150°C and impact melt characteristics that disqualify this lithology as a carrier of strong widespread magnetization in the Martian crust. MIL 03346 and NWA 5790 are interpreted as shallow, hypovolcanic rocks and as such are not representative of the Martian crust [McSweeney *et al.*, 2009]. The two meteorites with high concentration of metallic nanoparticles (NWA 1950 and 2737 [Van de Moortèle *et al.*, 2007]) have low

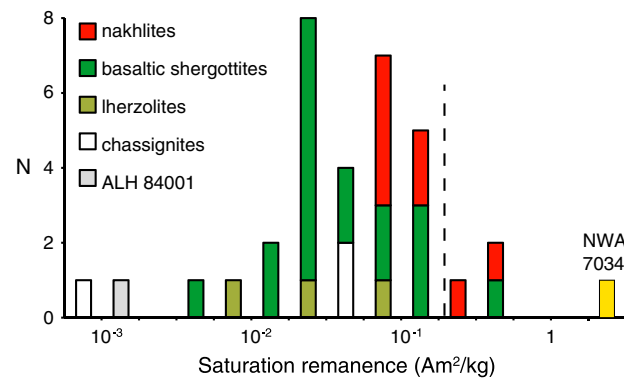


Figure 5. Frequency histogram of M_{RS} of Martian meteorites. The different lithologies are identified by color. The vertical broken line is the threshold value of $0.29 \text{ A m}^2/\text{kg}$ that is required to account for Martian magnetic anomalies (see text). The graduations of the horizontal axis follow a geometric progression with a ratio $10^{0.25}$.

SIRM despite their high magnetic susceptibility and thus are dominated by superparamagnetic particles. NWA 7034 is anomalous, with SIRM almost an order of magnitude above the threshold and above all previously studied Martian meteorites. It could acquire a NRM (thermoremanence) of $\sim 120 \text{ A/m}$ in a $50 \mu\text{T}$ field. However, part of the ferromagnetic mineral assemblage is secondary, as maghemite is not a primary igneous phase but is formed by low-temperature oxidation of magnetite and must be related to near-surface hydrothermal alteration. The secondary magnetic phases formed by this hydrothermal alteration likely acquired thermochemical remanent magnetization,

a process that can be almost as efficient as thermoremanent magnetization [McClelland, 1996], and in the case of the magnetite-maghemite transition may essentially preserve the original thermoremanent magnetization direction of magnetite [Özdemir and Dunlop, 1985]. Therefore, NWA 7034 possesses more than enough ferromagnetic minerals with high unblocking temperatures to account for a thick Martian crust with a NRM of $20\text{--}60 \text{ A/m}$, the range of magnetization usually invoked to account for Martian magnetic anomalies. This remains true even if a large fraction of the magnetic mineral assemblage was formed by hydrothermal activity after the cessation of the Martian dynamo. Moreover, NWA 7034 has chemical and mineralogical compositions that match the main crustal lithology on Mars [Agee et al., 2013a]. Furthermore, the Noachian age of NWA 7034 [Humayun et al., 2013; Nyquist et al., 2013] makes this material a plausible source candidate for the strong magnetic anomalies associated with Noachian terrains on Mars.

The low-temperature hydrothermal activity responsible for the maghemitization may also have formed part of the magnetite and may be impact related as observed in some terrestrial craters [Quesnel et al., 2013]. If this hydrothermal activity took place before the cessation of the dynamo, this may have formed a several kilometers thick layer with NRM of $\sim 120 \text{ A/m}$. Although the remanence of such a layer would have been partly demagnetized and/or modified by subsequent impact reworking of the first kilometers of the Martian crust (using crater density of Hartmann and Neukum [2001] and the pressure profiles of Pierazzo et al. [1997]), or by localized hydrothermal activity, it may explain the strongest localized intense magnetic anomalies of shallow origin. Such thin magnetic sources were not considered up to now in magnetic field anomaly modeling [Langlais et al., 2010], mainly because the data were acquired at satellite altitude (implying that the whole lithosphere/crust should contribute to this signal).

It must be noted that we do not assume that the NRM of NWA 7034 itself, if it could be measured, would necessarily be as high as 120 A/m , since it may have been demagnetized by postdynamo impacts, and/or some magnetite grains may have crystallized after the cessation of the dynamo. But the magnetic properties of this rock prove that lithologies that can account for Martian magnetic anomalies do exist on Mars.

5. Conclusions

Among the 25 unpaired Martian meteorites studied to date, NWA 7034 has a unique magnetic mineralogy. It contains about 15 wt % of iron oxides as magnetite that has experienced cation substitution and partial alteration to maghemite, with about a quarter of the oxides being pure maghemite. It also contains oxyhydroxides in the form of superparamagnetic goethite. The presence of maghemite and goethite, two purely ferric phases, makes NWA 7034 the most oxidized Martian meteorite, consistent with the presence of pyrite [Agee et al., 2013b]. We associate this mineral assemblage with near-surface low-temperature hydrothermal alteration. The same hydrothermal alteration, possibly triggered by impact, may also be responsible for the formation of part of the magnetite.

The high concentration of magnetic phases with high laboratory unblocking temperatures makes NWA 7034 a plausible analogue source lithology for the strong magnetization of the Martian Noachian crust, including high magnetic anomalies of shallow source. Such shallow sources should be considered in future modeling of the Martian magnetic field.

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Erratum

In the originally published version of this article, the third and fourth column headings contained unit errors. The units have since been corrected, and this version may be considered the authoritative version of record.