THERMALLY TREATED NONTRONITE AS A MODEL FOR A COMPONENT IN THE MAGNETIC RED DUST ON THE SURFACE OF MARS. V.F. Chevrier[1], P. Gavin[1], W. Goetz[2], O. Grauby[3], M.B. Madsen[4], P.E. Mathe[5], P. Rochette[5], [1]Arkansas Center for Space and Planetary Science, MUSE 202, University of Arkansas, Fayetteville, AR 72701, USA; [2]Max-Planck-Institut fur Sonnensystemforschung, Katlenburg-Lindau, Germany; [3]CRMCN, Campus de Lumigny, Marseille, France; [4]Niels Bohr Institute, University of Copenhagen, Copenhagen, DK-2100, Denmark; [4]CEREGE, Aix-en-Provence, France. vchevrie@uark.edu.

Introduction: A thin layer of red dust covers the surface of Mars. This dust has specific chemical, spectral and magnetic properties, and various ideas about its origin and nature have been proposed [2]. Recent studies suggest alteration with very limited influence of water, due to the presence of unaltered primary phases [1-3], possibly involving long-timescale solid-gas interaction [4].

Important clues on the nature and origin of the surface layer can be obtained using iron phases, characterized through their magnetic properties. The martian dust appears to contain several magnetic phases, the strongest magnetic one being nonstoichiometric magnetite [2,5,6].

It has been previously proposed that impacted or thermally metamorphosed clays may describe the surface properties of the martian dust: the red color, the reflectance properties [7], and the magnetic phase(s) [8-10]. In fact, heating nontronite produces one or several magnetic phases with exotic behavior that has been attributed to phases like maghemite [9] or iron-rich cristobalite [10]. In this work we focus on the magnetic properties of thermally transformed nontronite [11], in light of the recent results of the MER Rovers magnetic properties experiments and Mossbauer measurements [2].

Methods: One-gram samples of nontronite from Cheney Co. WA (Ward's #49E5108) were heated in a Lindberg tube furnace, to various temperatures from ~400 to ~1100ºC and for 4 to 24 hours. Samples were heated in air as well as under a CO_2 flow to simulate the martian atmosphere. Resulting products were analyzed by conventional ways (X-ray diffraction, electron microscopy, FT-IR, see [11,12]). Here we investigate the rockmagnetic properties of the neoformed products (hysteresis properties, susceptibility versus temperature and Mossbauer properties).

Hysteresis results: The magnetic mineralogy is globally similar in both atmospheres. Transitions are mostly caused by heat (rather than chemical interaction with the atmosphere). We observe 4 different components. Up to 700ºC the signal remains paramagnetic, resulting from the presence of Fe^{3+} in the clay mineral. After heating above 1100ºC, the hysteresis curve exhibits a signal with a low saturation magnetization M_S = 0.2 Am^2 kg^{-1}, and relatively large values of remanent magnetization M_R and coercitive field H_C (Fig. 1a). Such properties indicate hematite, as confirmed by X-ray diffraction and SEM observations [11].

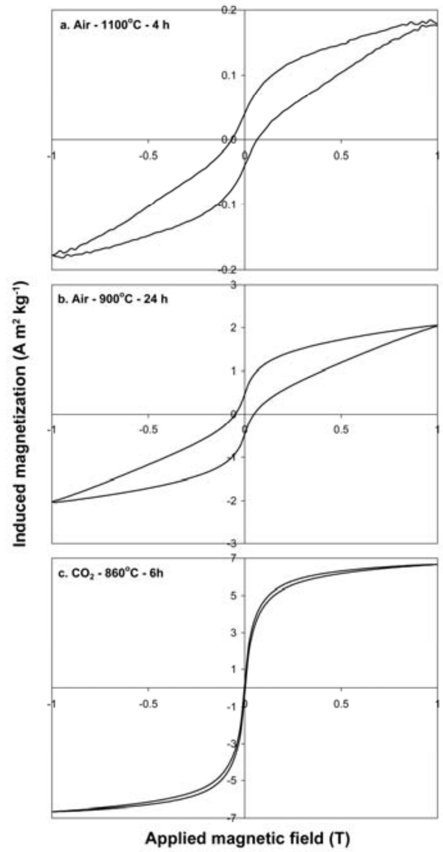

Figure 1: Hysteresis cycles of heated nontronite samples obtained using a Princeton Micrometer VSM1. Experimental conditions are indicated on each graph.

At intermediate temperatures (between 850 and 950ºC), samples show unusual properties, i.e. a high M_S = 2 Am^2 kg^{-1}, and high M_R = 0.5 Am^2 kg^{-1} (Fig. 1b). A mixture of pure hematite with pure spinel is ruled out because of the too high M_R. Non-stoechiometric magnetic phases are favored, as confirmed by thermomagnetic analysis. A spinel dominant signal is observed in one sample (860ºC in CO_2 for 6 h) with high M_S but very low M_R and H_C (Fig. 1c).

Note that the hysteresis curves shown in Fig. 1 have slightly wasp-waisted shapes indicating the coexistence of two (or more) magnetic components with strongly contrasting coercivities. This may be due to the presence of more than one magnetic mineral or to the coexistence of both multidomain and superparamagnetic particles in the sample [13].

TEM observations of the magnetic phase indicate an acicular to fibrous habitus (Fig. 2), which is strongly different from maghemite synthesized in other ways. Intereticular distances are too high for hematite and too low for goethite. Finally, chemical analysis indicate 31.5 at% Fe, 68.5 at% O, different from hematite (Fe:O = 2:3) or goethite (1:2). This indicates a probable non-stoechiometric phase in the mixture.

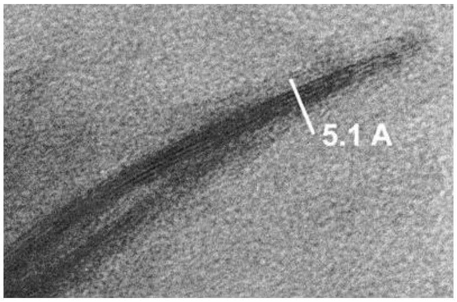

Figure 2: TEM picture of an unidentified fibrous iron oxide (sample heated at 880ºC in air for 24 hours).

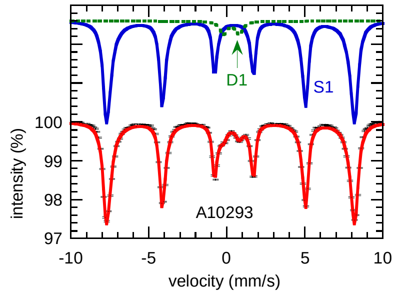

Figure 3: MB spectrum of nontronite that was heated to 1000°C / 4 h in air (cf. sample described by Fig. 1a).

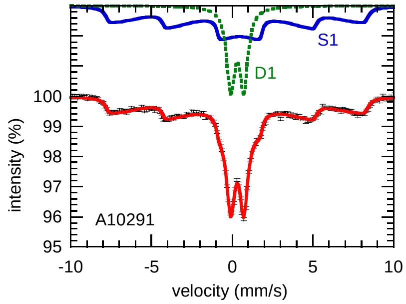

Figure 4: MB spectrum of nontronite that was heated to 900°C / 6 h in CO_2 (cf. sample described by Fig. 1c).

Mossbauer results: Mössbauer (MB) spectroscopy is used to further constrain the nature of the magnetic phases. Analysis of the spectrum shown in Fig. 3 reveals the presence of (at least) two spectral components, macroscopic, small-particle hematite and a paramagnetic or superparamagnetic ferric component (which could also be hematite). A minor component of magnetite (on the level of about 1% or a substantial component of maghemite on the level of several % cannot be excluded.

The MB spectrum in Fig. 4 consists of two components: A broad lined sextet and a ferric doublet. Parameters of the sextet are in accordance with an assignment to small particle maghemite crystals and the ferric doublet could be from a paramagnetic or superparamagnetic component that could be the same as that found in fig. 3.

The mixture of small crystallite maghemite seen in the MB spectra of Fig. 4 and the values of M_R and M_R are all consistent. Iron amounts to only a fraction of the total composition of the sample and some of this iron is seen to reside in a paramagnetic or superparamagnetic component. Moreover, maghemite may be present as ultra small particles for which surface canting and surface pinning of spins are not uncommon. Both of these effects lead to a reduction of magnetization wrt. bulk properties.

Conclusions: Heated nontronites have long been known as good chemical, magnetic and optical analogue materials for Martian soil and dust. Additionally they were once suggested as a possible pathway for the formation of these units. Given the recently discovered of clay minerals on the surface of Mars it is worthwhile to reassess their relevance for Martian surface material.

Magnetization and Mössbauer data are consistent with the presence of both macro-crystalline and a superparamagnetic (hematite ?) as well as magnetite (or maghemite) at the percent level. Both spinel and superparamagnetic hematite can have a substantial magnetization (> 1 $A{\cdot}m^2/kg$) and may well contribute to the overall magnetization observed for martian aiborne dust (~1 $A{\cdot}m^2/kg$).

References: [1] Bibring J. P. et al. (2006) *Science* 312, 400-404. [2] Goetz W. et al. (2005) *Nature* 436, 62-65. [3] Yen A. S. et al. (2005) *Nature* 436, 49-54. [4] Gooding J. L. (1978) *Icarus* 33, 483-513. [5] Gunnlaugsson H. P. (2000) *Planet. Space Sci.* 48, 1491-1504. [6] Hviid S. F. et al. (1997) *Science* 278, 1768-1770. [7] Weldon R. J. et al. (1982) *J. Geophys. Res.* 97, 10102-10114. [8] Boslough M. B. et al. (1986) *J. Geophys. Res.* 91, E207-E214. [9] Hviid S. F. et al. (1994) *hyperfine Interactions* 91, 529-533. [10] Moskowitz B. M., R. B. Hargraves (1984) *Science* 225, 1152-1154. [11] Gavin P. et al. (2007) *LPSC* XXXVIII, #2295. [12] Gavin P. et al. (2008) *LPSC* XXXIX, This meeting. [13] Dunlop D. J., Ö. Özdemir, *Rock Magnetism. Fundamentals and frontiers*. D. Edwards, Ed., Cambridge Studies in Magnetism (Cambridge University Press, Cambridge - UK, 1997).