MÖSSBAUER HEMATITE TEMPERATURE STUDY ON SAMPLES FROM THE MER LANDING SITES

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Introduction: Backscattering Mössbauer spectra were obtained in 10K-wide temperature windows with the two miniaturized Mössbauer spectrometers (MIMOS II) on board the two MER rovers. At Opportunity's landing site, numerous hematite-bearing samples were investigated [1]. In this study, 7 separate outcrop rocks and 10 spherule-bearing targets are considered. At Spirit's landing site, hematite-bearing rocks were encountered in the Columbia Hills [2]. Here, 6 "Pot Of Gold"-class (POG) rocks are considered. Thus, there is a large number of spectra available for a detailed, temperature-dependent study of the hematite encountered at both landing sites. Figure 1 shows typical Meridiani outcrop and spherule spectra.

The hematite Morin transition: Hematite is paramagnetic above the Curie temperature (T_C=956K). Below T_C, hematite is weakly ferromagnetic (wfm) and undergoes a phase transition to an antiferromagnetic (afm) state at the Morin temperature (T_M) [3], [4]. For well crystalline hematite, T_M=264K [5]. This temperature lies within the Martian diurnal temperature cycle, and the Morin transition has been observed in spectra from both landing sites [1, 6, 7]. Both the transition temperature T_M and transition width ΔT_M are influenced by particle size, crystallinity and cation substitution [3]. Cation substitution lowers T_M and the hyperfine field and broadens the width of the Morin transition. Especially the effect of Al-for-Fe substitution on the Morin transition has been studied (e.g., [3]). In samples with small particle sizes, weakly ferromagnetic (wfm) and antiferromagnetic (afm) phases can coexist over a range of temperatures (eg, [8]).

Data Analysis: Spectra have been obtained over the temperature range between 180K and 290K in 10K-wide temperature windows [9]. Due to limited integration time on Mars, counting statistics for single temperature windows are sometimes low. Thus, fits of individual spectra may yield unrealistic Mössbauer parameters. This problem can be overcome by fitting several spectra from one temperature window simultaneously. The data analysis was performed with the MERFit program [10] after velocity calibration with MERView [11].

For our fits, we used the model described in [1] or [2], respectively, with the exception of employing two hematite sextets. The widths of the six lines were set equal and peak area ratios of 3:2:1:1:2:3 were used. The Mössbauer doublets necessary for a fit (e.g., olivine, pyroxene, jarosite and Fe3D3 sulfate in the case of Meridiani outcrop) were constrained in the following way: both peaks were set to have equal areas and line widths, and the hyperfine parameters (δ; Δ) were constrained to the values reported in [1] or [2], respectively. For the simultaneous fits, line widths and hyperfine parameters of corresponding phases were constrained equal for all spectra in the fit; site areas were unconstrained.

Simultaneous fitting was found to be an effective method to fit many spectra in a consistent way, where repeated fits would have been necessary to arrive at a compatible set of parameter values that are consistent across all the spectra fit separately. Compared to single-spectrum fits, fewer parameters had to be constrained to fixed values, and simultaneous fitting resulted in tighter trends for the values determined for hyperfine parameters.

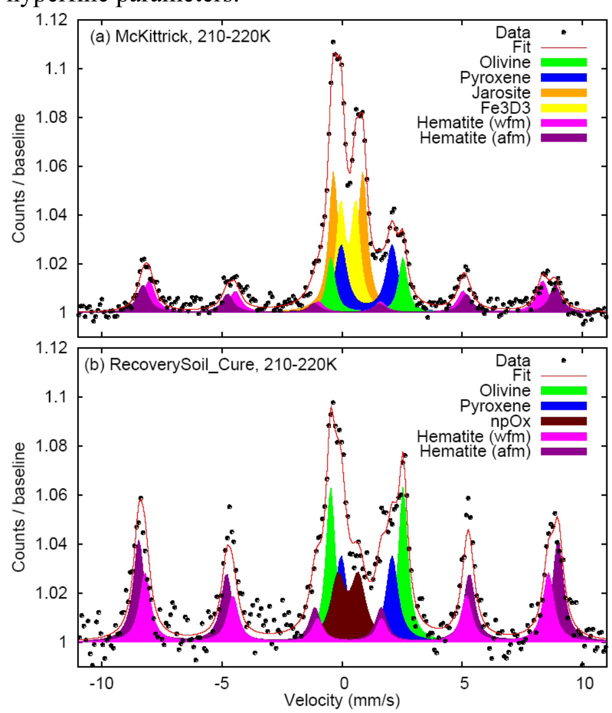

Figure 1: Spectra obtained at Meridiani Planum on outcrop rock (a) and a spherule-bearing target (b) at temperatures between 210K and 220K. Both spectra show two hematite phases.

Initial results: In the following discussion, the hematite sextet with the larger splitting will be referred to as "S1", the other as "S2". Figure 2 shows the temperature dependence of subspectral areas and hematite Mössbauer parameters. First of all, it is important to note that the two hematite phases coexist over the whole temperature range, indicated by the asymmetry in peak intensities and widths of the two outer lines (see examples in Figure 1).

The relative subspectral areas of the two phases determined in the simultaneous fit show a clear temperature dependence, two examples are shown in Figure 2a. The area of S1 is generally larger and shows a clear increase for temperatures above ~230K.

The magnetic hyperfine field (B_{hf}) of both sextets (Figure 2b) shows a decreasing trend with increasing temperature (except for S2 from POG). The magnetic hyperfine field is generally smallest for outcrop spectra, and S2 from outcrop spectra shows a striking dip centered around ~250K, possibly due to the presence of other phases.

For spherules and outcrop, the shift due to quadrupole interaction (Δ) of both sextets decreases with increasing temperature. For POG, only S2 shows a comparable trend. Generally, Δ for S1 has larger values than Δ for S2 (Figure 2c).

The temperature dependence for B_{hf} and Δ is generally rather smooth. δ shows more scatter (Figure 2d), but, as expected ([1], [2]), no temperature dependence within statistics.

The overall temperature dependence of the Mössbauer parameters is in good agreement with S1 arising from the afm state (i.e. temperatures below the Morin transition) and S2 arising from the wfm state.

Conclusions: The temperature trend of B_{hf} shows a broad Morin transition with an average value of ~240K (thus, below the value of 264K reported for well crystalline hematite [3]). A Morin temperature of ~240K would be consistent with cation substitution. However, correlations of hematite Mössbauer subspectral areas and element concentrations determined by the APXS [12] do not clearly point to any element substitutions in any of the considered samples. Apart from possible cation substitution, the observation of a broad Morin transition points to small hematite particle sizes: For particle sizes of ~50nm, a temperature width of ~40K has been observed, while the Morin transition was found to be completely suppressed for particle sizes below ~20nm [13], both consistent with the assumption that the hematite discussed here has particle sizes in a similar range.

References: [1] Morris, R.V., et al. (2006b), *JGR, 111*, E12S15. [2] Morris, R.V., et al. (2006a), *JGR, 111*, E02S13. [3] R. M. Cornell & U. Schwertmann, VCH 1996. [4] E. de Grave & R. E. Vandenberghe, Phys Chem Minerals 17 (1990). [5] N. Amin and S. Arajs, Phys. Rev. B 35 (1987). [6] Klingelhöfer, G., et al. (2004), *Science, 306*. [7] C. van Cromphaut et al, GCA 71 (2007). [8] E. Murad & J. Cashion, Kluwer Acad. Publishers (2004). [9] Klingelhöfer, G., et al. (2003) *JGR 108*, 8067. [10] Agresti D.G. & Gerakines P.A. (2009) *Hyp. Int.*, *188,113–120.* [11] Agresti D.G. et al. (2006) *Hyp. Interact.*, *170*, 67–74. [12] R. Gellert et al, manuscript in preparation. [13] R. C. Nininger & D. Schroeer, J. Phys Chem Solids 39 (1978).

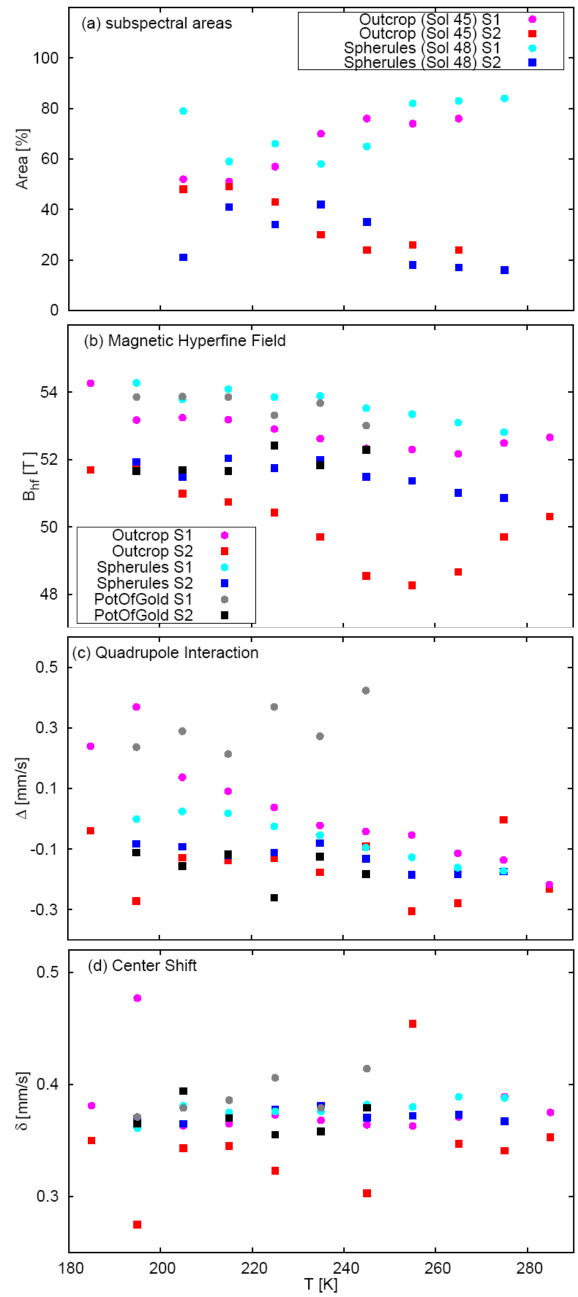

Figure 2: Temperature trends for subspectral areas (a) and hyperfine parameters (b-d).