MÖSSBAUER AND REFLECTANCE SPECTROSCOPY OF IRON OXIDE MIXTURES. M. D. Dyar[1], E. Murad[2], E. C. Sklute[3], J. L. Bishop[4], and A. C. Muirhead[5], [1]Dept. of Astronomy, Mount Holyoke College, South Hadley, MA, 01075, (mdyar@mtholyoke.edu), [2]Marktredwitz, D-95615, Germany (emurad@yahoo.com), [3]Dept. of Chemistry, Penn State University, State College, PA 16802, (ecs193@psu.edu), [4]SETI Institute/NASA-ARC, Mountain View, CA, 94043, (jbishop@seti.org), [5]UCSC, Santa Cruz, CA, 95064, (amuirhea@ucsc.edu).

Introduction: The magnetic experiments on the Viking, Pathfinder, and MER missions are consistent with the presence of a few wt.% Fe_2O_3 as tiny maghemite and/or magnetite grains imbedded in dust/soil particles. It is likely that low-temperature alteration of iron oxides/oxyhydroxides (FeOx) is instrumental in influencing the current form and nature of these minerals on the martian surface. Here we use Mössbauer and reflectance spectroscopy to examine intimate mixtures of three potential martian FeOx: ferrihydrite, maghemite, and magnetite. Through this work, we aspire to better understand the detection and quantification of these minerals when they occur together in martian rocks and soils.

Samples: Mixtures were prepared for this and a companion study [1] from mixtures of finely-particulate magnetite (Mag) , two different maghemites (Mht) that were indistinguishable to the Mössbauer, a <125 µm sample (A) and a <5 µm particle size sample, and ferrihydrite (Fht), a finely-particulate Icelandic sample [2], sieved <45 µm. Proportions of different phases are given in Table 1.

Table 1. Compositions of Mineral Mixtures

Sample	Wt% of Phase in Each Mixture			
	Mag	Mht A	Mht B	Fht
JB806	50	50	0	0
JB807	50	0	50	0
JB808	0	50	0	50
JB809	0	25	0	75
JB810	50	0	0	50
JB811	25	0	0	75
JB812	0	0	50	50
JB813	0	0	25	75
JB814	20	20	20	40

Methods: Reflectance spectra were measured at Brown/RELAB after removing adsorbed surface H_2O as in other studies [2]. Mössbauer spectra were acquired at 295K (in future work, we will undertake measurements at Mars surface temperatures) and calibrated relative to the spectrum of a 25 µm Fe foil. The Mexdist program from the University of Ghent, which solves for the full Hamiltonian, was used to model the spectra. Errors on results for well-resolved components are usually ca. 0.02-0.04 mm/s for isomer shifts (δ), quadrupole splittings (Δ) and linewidths (W), ~0.1-0.3 Tesla for magnetic hyperfine fields, and 1-3% (absolute) for relative areas of the distributions. However, in heavily overlapped spectra, the errors may be considerably larger, especially those on peak areas.
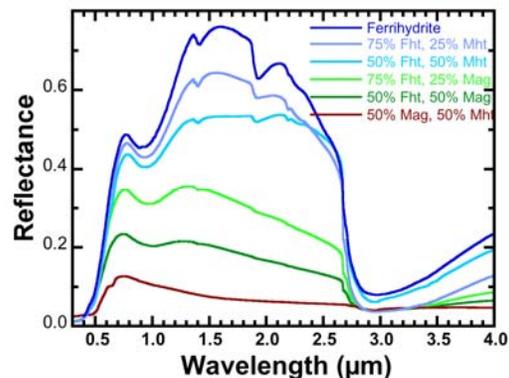

Figure 1. VNIR reflectance spectra of FeOx mixtures.

Results: *Reflectance spectroscopy.* VNIR reflectance spectra for several of the mixture samples are shown in Figure 1. These illustrate the changes in spectral slope, shifts in ~1 µm band center and reduction in hydration band (~1.43, 1.95, 2.8-3.2 µm) intensity of ferrihydrite with the admixture of other FeOx minerals.

Mössbauer spectroscopy. To interpret the Mössbauer data, it is necessary to convert from Fe atoms per unit cell to the weights used to make the original mixtures. Coincidentally, the three minerals in this study all contain roughly equivalent Fe contents (~7.5-7.8 $\times 10^{22}$ Fe atoms per g), so this correction is very small (<0.1%), an order of magnitude smaller than the errors on fitting doublet areas.

Mössbauer parameters are given in Table 2. Parameters for the pure FeOx are typical of those reported in the literature [e.g. 3,4]. Parameters of these phases in mixtures were similar, but not quite identical, to those in the pure end-member FeOx.
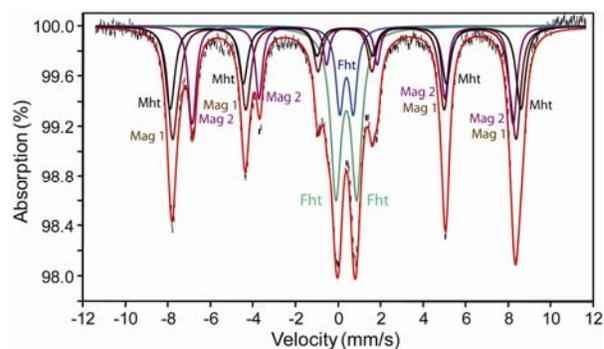
Figure 2. 295K Mössbauer spectrum of sample JB814, which is a mixture of Fht:Mag:Mht in a 40:40:20 ratio. The red line is the fit envelope, the sum of all modeled peaks.

Table 2. Mössbauer Parameters for Fe Oxide/Hydroxide Mixtures

	Sample	301	499	763	764	806	807	808	809	810	811	812	813	814
Mht	δ (mm/s)	0.33		0.33		0.30	0.38	0.32	0.34			0.32	0.33	0.35
	Δ (mm/s)	0.01		0.00		0.06	0.00	0.00	-0.01			-0.02	0.00	0.03
	B_{Hf} (Tesla)	50.3		50.1		50.6	50.8	50.9	50.0			49.9	50.0	51.3
	W (mm/s)	0.48		0.53		0.53	0.44	0.53	0.62			0.76	0.72	0.48
	Area	1.00		1.00		0.37	0.14	0.59	0.32			0.40	0.16	0.20
Mag 1	δ (mm/s)				0.28	0.27	0.28			0.26	0.26			0.29
	Δ (mm/s)				-0.03	-0.07	-0.03			-0.04	-0.05			-0.03
	B_{Hf} (Tesla)				50.0	49.1	49.9			49.0	49.0			50.3
	W (mm/s)				0.37	0.30	0.43			0.33	0.30			0.45
	Area				0.40	0.28	0.42			0.26	0.18			0.29
Mag 2	δ (mm/s)				0.68	0.70	0.68			0.70	0.70			0.69
	Δ (mm/s)				0.00	0.10	0.03			0.03	0.02			0.04
	B_{Hf} (Tesla)				46.8	46.6	46.7			46.9	46.9			46.8
	W (mm/s)				0.35	0.39	0.38			0.32	0.32			0.35
	Area				0.60	0.35	0.44			0.39	0.25			0.19
Fht 1	δ (mm/s)		0.35					0.34	0.36	0.39	0.36	0.34	0.36	0.38
	Δ (mm/s)		0.62					0.63	0.63	0.59	0.59	0.62	0.61	0.64
	W (mm/s)		0.41					0.41	0.40	0.41	0.37	0.45	0.39	0.44
	Area		0.44					0.11	0.19	0.10	0.16	0.20	0.27	0.08
Fht 2	δ (mm/s)		0.35					0.35	0.36	0.38	0.36	0.34	0.36	0.37
	Δ (mm/s)		1.01					0.93	0.96	1.00	0.97	0.95	0.98	0.98
	W (mm/s)		0.52					0.60	0.63	0.54	0.56	0.67	0.55	0.58
	Area		0.56					0.30	0.49	0.26	0.42	0.41	0.56	0.23
	χ^2	13.67	1.80	6.53	4.98	11.26	2.08	1.99	2.18	1.76	5.10	1.66	1.27	3.30

Discussion: The areas of the distributions in the mixtures do not correspond exactly to the known proportions of the mixtures. For example, sample JB809 has a ratio of 75:25 Fht:Mht, but the area ratio from Mössbauer spectroscopy is 68:32. In the samples with 50:50 by weight mixtures of mineral pairs, the ratios are 63:37, 86:14, 41:59, 36:64, and 60:40 for Mag:Mht, Mag:Mht, Fht:Mht, Fht:Mag, and Fht:Mht, respectively. JB814, which is 40:40:20 Fht:Mht:Mag by weight, is 32:20:48 by area (Figure 2).

The areas of the distributions modeled in a spectrum do not directly correspond to the amount of Fe actually present in that site, valence state, or phase; rather, the areas are a function of peak width Γ, sample saturation $G(x)$, and the Mössbauer recoil-free fraction f [2]. A correction for these factors can be made if the parameters are known for the phases of interest, but their determination is non-trivial [4]. The amount of peak overlap in these spectra is considerable (Figure 2), and this contributes greatly to errors in the areas of the distributions. It is also possible that differing grain sizes of mixture components prevented perfect mixing of the samples and thus the sample aliquots measured might be slightly different from the bulk ratios.

The errors are generally lower for magnetically ordered phases than for paramagnetic materials because of the larger spread of resonant peaks. The identification and quantification of magnetically-ordered Fe oxides will therefore in general be easier and more accurate than for paramagnetic materials (superparamagnetic Fe oxides or clay-sized phyllosilicates [6]) or clay–Fe oxide mixtures.

Conclusions: Reflectance spectroscopy of these FeOx mixtures illustrates several changes in spectral character, but is difficult to relate to abundances of the individual minerals. Mössbauer spectroscopy is very successful in identifying the Fht, Mht, and Mag components in FeOx mixtures, and it enables semi-quantitative estimation of mineral abundances for these mixtures. However, it is also difficult to accurately determine relative percentages of individual oxide phases in these complex mixtures, especially if the system contains (super)paramagnetic phases.

References: [1] Muirhead, A.C. et al. (2009) LPSC. [2] Bishop J.L. and Murad, E. (2002) in *Volcano-Ice Interactions on Earth and Mars* J. L. Smellie, M. G. Chapman, Eds. (Geological Society) pp. 357-370. [3] Dyar M.D. et al. (2006) *Ann. Revs. Earth Planet. Sci.,* 34, 83–125. [4] Murad E. and Johnston J.H. (1987) *Mossbauer Spectroscopy Applied to Inorganic Chemistry*, 2, 507-582. [5] DeGrave E. and van Alboom, A.V. (1991) *Phys. Chem. Miner.*, 18, 337-342. [6] Murad E. (2008) *Martian Phyllosilicates as Indicators of Aqueous Processes*, Abstract #7020.