

EFFECT OF Mn SUBSTITUTION ON THE SPECTRAL PROPERTIES OF GOETHITES AND HEMATITES; R. K. Vempati, R. V. Morris (NASA-JSC, Houston, TX 77058) and H. V. Lauer (LESC, Houston, TX 77058).

INTRODUCTION: Recent studies have suggested that Mn-substituted goethites and hematites are formed in terrestrial environments [1], and the same may be the case on Mars. Because the various oxidation states of Mn have crystal-field transitions in the visible region, Mn substitution in Fe oxides is likely to result changes in their reflectivity spectra relative to unsubstituted endmembers. The objective of this study was to obtain spectral data of Mn-substituted goethites and hematites in order to determine whether there is evidence in Martian spectral data for Mn substitution in these oxides. In addition to reflectivity data, x-ray diffraction (XRD), Mossbauer, magnetic, thermogravimetric analysis (TGA), and atomic absorption spectroscopy (AAS) data were obtained to characterize the oxides.

SAMPLE PREPARATION: Mn-substituted goethites, ranging from 0 to 0.15 (Mn/(Mn+Fe)) mole fraction, were synthesized by mixing FeCl_3 and MnCl_2 in the presence of 7 M NaOH. The samples were incubated for 1 h, and the excess of the salt was removed by washing the oxide thrice with deionized water. The samples were incubated at 70°C for 24 h in a 0.3 M NaOH solution. The oxides were washed salt free by dialysis and freeze dried. Mn-hematites were obtained by heating corresponding Mn-goethites at 500°C for 24 h. The Mn and Fe contents were determined by AAS.

RESULTS AND DISCUSSION: The color of unsubstituted goethite was yellow, and changed through yellowish green to olive green with increasing Mn content. Unsubstituted hematite was dark red, and changed through tan to brown with increasing Mn content.

The XRD analysis for Mn goethites indicated that the 'a' cell dimension decreased (Fig. 1), the 'b' cell dimension increased, and no significant relationship in 'c' unit dimension was observed with increasing Mn content. The shift in the 'a' and 'b' unit cell dimensions are consistent with incorporation of Mn into the goethite structure. The TGA analysis in He gas, showed that the Mn-goethites dehydroxylated to Mn-hematites at ~250°C; no variation with Mn content was observed. The composition of the loosely bound water ($-\text{H}_2\text{O}$) and the structural and strongly bound water ($+\text{H}_2\text{O}$) measured by coulometry was ~11%, which is within error of the stoichiometric value. There were no changes in the hexagonal 'a' or 'c' unit cell dimensions for Mn-hematites. However, Mossbauer spectroscopic studies suggested that Mn was incorporated into the hematite structure (see below). The Mossbauer spectra at room temperature of Mn-goethites and -hematites showed no significant variation in isomer shift (IS) and quadrupole splitting (QS) with Mn-content. However, the hyperfine splitting (B) decreased from 38.4 T for unsubstituted goethite to 31 T for the goethite with 0.15 mole fraction Mn (Fig. 2), presumably because Mn substitution lowers the Neel temperature of goethite, which

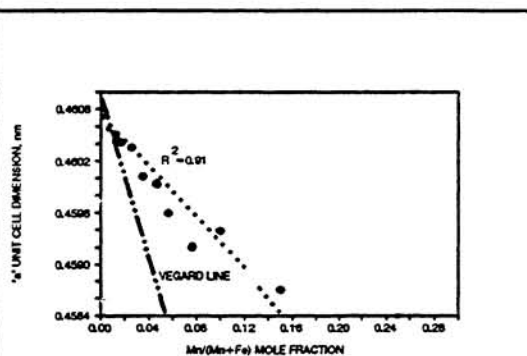


Fig. 1. 'a' unit cell dimension as a function of Mn content in goethites

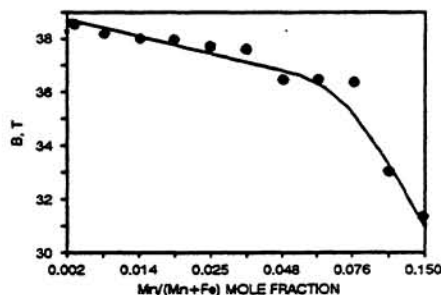


FIG. 2. Variation of B (T) at 299K with Mn content in goethite

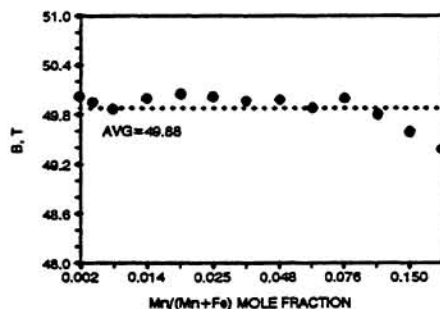


Fig. 3. B (T) of Mn goethites at 11 K

is $\sim 393\text{K}$ [2]. The decrease in B values with increase in Mn-goethites further supports the presence of Mn in goethite structure. At 11K no significant change in B values were observed because the temperature of sample analysis was below the Neel temperature.

For Mn-hematites no significant relation was observed between B and Mn-content at room temperature and 10K because the samples are much below the Curie temperature for unsubstituted hematite (Fig. 3), which is $\sim 955\text{K}$ [2]. At 11K a discontinuity of $\sim 0.7\text{ T}$ in B occurred at ~ 0.016 Mn mole fraction. This is the Morin transition (T_M) which occurs at $\sim 253\text{K}$ in pure, well-crystallized hematite [3]. The lowering of T_M is evidence that the Mn is incorporated in the hematite structure. None of the above instrumental analyses indicated the presence of secondary Fe or Mn phases in the Mn-goethites or -hematites.

The diffuse reflectivity spectra in the visible and near-IR for Mn-goethites and -hematites are shown in Figure 5 and 6, respectively. For Mn goethites with >0.074 and Mn hematites with >0.016 mole fraction, the ${}^4T_{1g}$ band position was not well defined (Fig. 5). For samples whose ${}^4T_{1g}$ band positions were resolved, no relationship between its position and Mn content was observed for either oxide. For both ferric oxides, there is a pronounced decrease in reflectivity in the region 600-700 nm, which implies the presence of an absorption in this area [4], which has been attributed to the hematite ${}^4T_{2g}$ band. Because there is also evidence for the hematite ${}^4T_{1g}$ band ($\sim 870\text{ nm}$), this is a reasonable interpretation. However, our data indicate that the presence of Mn in Martian ferric oxides cannot be excluded.

REFERENCES: [1] Thiry, M., and J. Sornin. (1983) Petrologie d'une sequence d'alteration de carbonate de fer: *Sci. Geol. Mem.* 73:195-205; [2] Murad, E. (1988) Properties and behavior of iron oxides as determined by Mossbauer spectroscopy. p.309-345. In: J W. Stucki, B. A. Goodman and U. Schwertmann (eds.). *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht; [3] Morin, R. J. (1950) Magnetic susceptibility of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ with added titanium. *Phys. Rev.*, 78:819-820; [4] Bell, J. F. III., T. B. McCord, and P. D. Owensby (1990). Observational evidence of crystalline iron oxides on Mars. *J. Geophys. Res.*, 95:14447-14462.

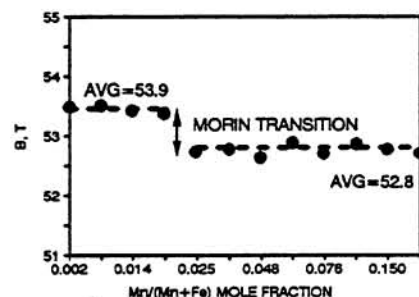


Fig. 4. B of Mn hematites at 11 K

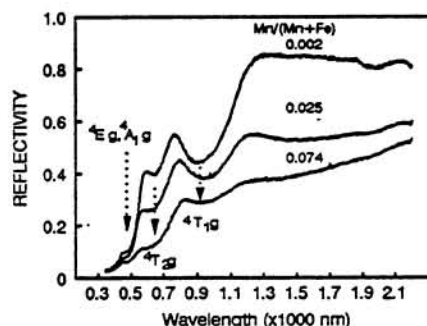


Fig. 5. Diffuse reflectivity of Mn-goethites

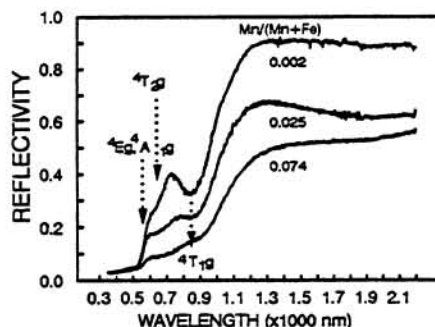


Fig. 6. Diffuse reflectivity of Mn-hematites