

# MÖSSBAUER SPECTROSCOPIC IDENTIFICATION OF IRON OXIDES IN NONTRONITE FROM HOHEN HAGEN, FEDERAL REPUBLIC OF GERMANY

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**Abstract**—Iron impurities in the Hohen Hagen nontronite (NG-1) were identified as maghemite and goethite. The phase identified as maghemite was magnetically ordered at both room temperature and 87 K, with hyperfine magnetic fields of 48.6 and 50.7 tesla, respectively. Due to the magnetic properties of this phase, it was easily separated from aqueous dispersions of the clay using a hand magnet. X-ray powder diffraction analysis revealed maghemite, quartz, and phyllosilicate in the magnetically separated phase. The impurity identified as goethite remained in the non-magnetic <2- $\mu\text{m}$  fraction of the clay, displayed magnetic order only at 87 K (47.44 tesla hyperfine field), and accounted for about 8% of the total area of the Mössbauer spectrum.

**Key Words**—Goethite, Iron, Maghemite, Magnetic properties, Mössbauer spectroscopy, Nontronite.

## INTRODUCTION

Much clay mineral research relies heavily on so-called standard or reference clay minerals. A common supposition is that such standards are relatively uniform or homogeneous, particularly after particle-size fractionation. With naturally occurring clay minerals, however, caution is advised in making such assumptions. Murad (1987) examined in detail the Mössbauer spectra of three nontronites at 298 and 77 K and found goethite in all samples, accounting for about 3 to 13% of the total areas of the spectra.

Recently, we attempted to fractionate a sample of Hohen Hagen nontronite (NG-1) obtained from the Source Clay Minerals Repository of The Clay Minerals Society. While dispersing the crude material in distilled, deionized water by vigorous stirring, the magnetic stirring bar became coated with a black material, which was thus presumed to be magnetic. Previous studies involving the NG-1 nontronite (Schneiderhöhn, 1965; Malla and Douglas, 1987) made no mention of other phases, such as iron oxides. A Mössbauer spectroscopic study was therefore undertaken to identify and characterize non-smectitic iron phases associated with this nontronite. The results of that study are reported herein.

## MATERIALS AND METHODS

The materials used in this study were two fractions of the Hohen Hagen nontronite (NG-1 from the Source Clay Minerals Repository of The Clay Minerals So-

ciety), namely, a magnetically separable fraction and the <2- $\mu\text{m}$  portion of the remaining non-magnetic fraction. The magnetic fraction was removed from the bulk sample by passing a hand magnet through an aqueous dispersion of the sample several times. The clay remaining in suspension was then saturated with  $\text{Na}^+$ , dialyzed, and freeze-dried. The magnetic separation technique was not necessarily designed to remove all of the admixed magnetic phases, but the Mössbauer spectrum at room temperature of the remaining <2- $\mu\text{m}$  fraction showed no sign of a magnetically ordered phase.

The particle-size fractionation procedure was unable to remove the magnetic fraction, as evidenced by a significant amount of magnetic material found in a <2- $\mu\text{m}$  fraction of the same nontronite fractionated without prior magnetic separation.

Mössbauer spectra were recorded in 1024 channels of a Ranger Scientific MS-900 spectrometer. A  $^{57}\text{Co}$  in Rh source of nominal strength 25 mCi was used in a sinusoidal mode with a krypton-methane proportional counter as a  $\gamma$ -ray detector. Velocity calibration was carried out with a high purity 6- $\mu\text{m}$  Fe foil, with the midpoint of the hyperfine Fe spectrum defining zero velocity. The sample temperatures were maintained at either 87 K by cooling the sample in a bath-type cryostat or at 296 K, while the source temperature was constant at room temperature. Between 5.5 million and 7.0 million counts/channel were accumulated for each spectrum. The magnetic fraction was prepared as a powder; the clay was prepared as an oriented film. The clay film was oriented with the  $c^*$ -axis about 54.7° relative to the direction of the  $\gamma$ -ray in order to minimize orientation effects on the relative intensities of the doublet components (Ericsson and Wäppling, 1976).

Mirror halves of the spectra were folded and fitted to a sum of doublets having Lorentzian peak shapes

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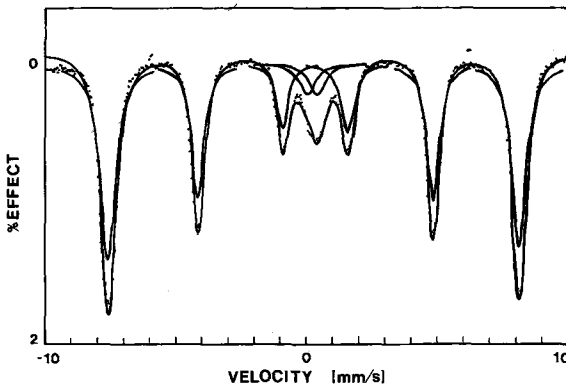


Figure 1. Mössbauer spectrum of the magnetically separated fraction of NG-1 nontronite at room temperature in the velocity range  $\pm 10$  mm/s.

using a  $\chi^2$  minimization procedure. The peaks of each doublet were constrained to have equal widths. The areas were unconstrained because the simultaneous constraint of both widths and areas caused unreasonable fits. The 1% and 99% confidence limits of the  $\chi^2$  value were 1.15 and 0.85 for the fits, regardless of the number of peaks. A small discrepancy was observed between the experimental background and the background obtained for the fitted peaks at the upper and lower limits of the spectrum (Figure 1). This probably was the result of the drive transducer deviating slightly from perfect sinusoidal waveform.

Isomer shift (IS), quadrupole splitting (QS), and the internal magnetic hyperfine field ( $B_{\text{hf}}$ ) Mössbauer parameters were calculated from six-line spectra using the relations:

$$\text{IS} = 0.125c \left( P_1 + P_6 - 8P_0 + \sum_{i=1}^6 P_i \right) \quad (1)$$

$$\text{QS} = 0.5c[(P_5 - P_6) - (P_1 - P_2)] \quad (2)$$

$$\begin{aligned} B_{\text{hf}} &= B_{\text{hf}}^0 (P_6 - P_1)_s / (P_6 - P_1)_0 \\ &= 3.106c(P_6 - P_1)_s \end{aligned} \quad (3)$$

and from two-line spectra using,

$$\text{IS} = 0.5c(P_1 + P_2 - 2P_0) \quad (4)$$

$$\text{QS} = c(P_2 - P_1), \quad (5)$$

where  $s$  and  $0$  subscripts refer to the sample and Fe foil, respectively;  $P_i$  is the channel number position of the respective peaks, in ascending order, in the six- or two-line spectra;  $P_0$  is the channel number of the center of the Fe foil spectrum;  $B_{\text{hf}}^0$  is the magnetic hyperfine field of Fe foil ( $=33$  tesla); and  $c$  is the factor converting channel number to mm/s, and is calculated from

$$c = (L_u - L_l)/512, \quad (6)$$

where  $L_u$  and  $L_l$  are the upper and lower limits, respectively, of the mm/s scale. In the present experiments,  $P_0$  was 254 at 296 K and 255 at 87 K.

X-ray powder diffraction (XRD) patterns of the magnetically separated phase were obtained on a Philips X-ray diffractometer using  $\text{CuK}\alpha$  radiation.

## RESULTS AND DISCUSSION

Based on Mössbauer and XRD evidence, the magnetic phase was identified as maghemite. The Mössbauer spectra of the magnetic fraction revealed magnetic hyperfine fields,  $B_{\text{hf}}$ , of 48.6 and 50.7 tesla at room temperature and 87 K, respectively (Figure 1; Table 1), which are similar to reported values of 49.4 and 52.0 tesla at the respective temperatures (Sprenkel-Segel, 1970).

The XRD pattern showed the crystalline phases in the magnetic fraction to be quartz, maghemite, and a phyllosilicate, thus confirming maghemite as the magnetic component. The association of a phyllosilicate with the magnetic phase is also confirmed by the Mössbauer spectra (Figure 1; Table 1), which show a small peak in the center of the spectrum with IS and QS consistent with the  $<2\text{-}\mu\text{m}$  fraction of the clay (Figure 2; Table 1). The phyllosilicate and quartz phases are apparently either strongly bound to or coated with the iron oxide phase.

The slightly smaller values of  $B_{\text{hf}}$  reported in Table 1 compared to published values (Sprenkel-Segel, 1970)

Table 1. Computer-fitted Mössbauer data for the magnetic and nonmagnetic fractions of NG-1 nontronite.<sup>1</sup>

Sample	Phase	Temp. (K)	IS (mm/s)	QS (mm/s)	$\Gamma$ (mm/s)	$B_{\text{hf}}$ (tesla)
Magnetic fraction	Oxide	296 <sup>2</sup>	0.329 (5)	-0.046 (5)	0.277 (7)	48.6 (5)
	Smectite		0.278 (8)	0.358 (1)	0.36 (1)	—
	Oxide	87	0.448 (6)	0.014 (3)	0.291 (9)	50.7 (2)
	Smectite		0.466 (3)	0.315 (1)	0.35 (1)	—
$<2\text{-}\mu\text{m}$ fraction	Oxide	87	0.388 (8)	0.014 (5)	0.41 (1) <sup>3</sup>	47.5 (6)
	Smectite		0.460 (7)	0.430 (4)	0.375 (9)	—

<sup>1</sup> IS = isomer shift; QS = quadrupole splitting;  $\Gamma$  = full width at half maximum;  $B_{\text{hf}}$  = effective hyperfine field. Errors on the last digit are given in parentheses.

<sup>2</sup> Parameters at room temperature are from spectra in the velocity range  $\pm 10$  mm/s; at 87 K, from  $\pm 12$  mm/s.

<sup>3</sup> Widths of the outer lines.

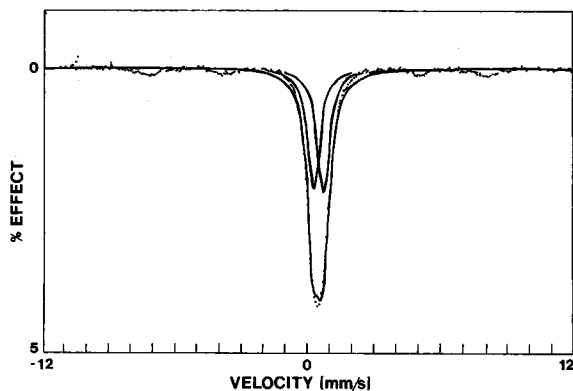


Figure 2. Mössbauer spectrum of the  $<2\text{-}\mu\text{m}$  fraction of the non-magnetic portion of NG-1 nontronite at 87 K in the velocity range  $\pm 12$  mm/s.

for maghemite suggest that this phase may be Al substituted and/or of lower crystallinity than pure maghemite (Murad, 1988).

Mössbauer spectra of the non-magnetic,  $<2\text{-}\mu\text{m}$  fraction of sample NG-1 (Figure 2; Table 1) revealed a strong central doublet with IS and QS generally consistent with Fe(III) in nontronite (Goodman *et al.*, 1976). The small peaks at  $-7.3$ ,  $-3.8$ ,  $5.1$ , and  $8$  mm/s ( $B_{\text{hf}} = 47.5$  tesla), which were observed at 87 K but which were absent from the room-temperature spectrum, are evidence for an additional iron phase in the clay, which appears to be goethite (Murad and Schwertmann, 1983; Murad, 1987). The value of  $B_{\text{hf}}$  deduced from the Mössbauer spectra reported in Figure 2 is significantly lower than for the maghemite (47.5 compared to 50.7 tesla) at the same temperature. Further, if this phase were maghemite, then a six-line pattern should have been seen at room temperature. The value of IS is also consistent with reported values for goethite (Golden *et al.*, 1979). QS, however, is much lower in magnitude and of opposite sign from goethite (0.014 compared to  $-0.26$ ), but little significance can be placed on the values of QS reported in this case because the actual positions of the small, broad peaks in Figure 2 could vary substantially from the calculated positions. This uncertainty is large compared to the magnitude of QS calculated from Equation (2). The goethite phase accounts for about 8% of the total area of the spectrum.

The presence of these non-phyllsilicate phases, goethite and maghemite, are not mentioned by Schneiderhöhn (1965), who studied the clay fraction of the

original NG-1 material. This is understandable inasmuch as those results were based on bulk chemical analysis, XRD, and microscopic examination. Ignoring these phases, however, could lead to false interpretations of the properties and behavior of the Hohen Hagen nontronite. Therefore, the identification and possible removal of iron oxides should be considered when working with this mineral.

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