# CHARACTERIZATION OF ADSORBED IRON IN MONTMORILLONITE BY MÖSSBAUER SPECTROSCOPY[1]

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Abstract—The Mössbauer effect of $Fe^{57}$ was used to probe and characterize iron ions adsorbed on the interlayer surfaces of montmorillonite. Measurements were performed with Fe- and Ca-saturated montmorillonites. At 210°K the intensity of the $Fe^{2+}$ line was greatly reduced, apparently due to the melting of interlayer water. Neither the structural $Fe^{2+}$ in Ca-montmorillonite nor the adsorbed $Fe^{3+}$ in Fe-montmorillonite were affected by the melting process. From the temperature dependence of the absorption intensity, the effective Debye temperature of all the iron species appears to be approximately the same ($\theta_D = 189 \pm 5°K$). This result allowed for an accurate determination of the population of $Fe^{2+}/Fe^{3+}$ in various samples.

Key Words—Debye temperature, Iron, Montmorillonite, Mössbauer spectroscopy, Water.

## INTRODUCTION

$Fe^{57}$ Mössbauer spectroscopy (Bancroft, 1973) is a well-established tool for studies of minerals in general and of clay systems in particular. It provides a nondestructive method for assessing qualitatively and quantitatively the chemical state of iron ions, their bonding symmetry, and the relative abundance of ferric and ferrous species. Most previous Mössbauer studies of clays have dealt with structural iron and with problems related to its change with oxidation-reduction reaction (e.g., Rozenson and Heller-Kallai, 1976, 1977, 1978). Malathi *et al.* (1969) also analyzed adsorbed or exchangeable iron ions in clay systems. By treating illite and montmorillite with $Fe(NO_3)_3$ solutions, they assigned an extra line with unusual (negative) isomer shift at room temperature to adsorbed $Fe^{IV}$ ion. Using both organic and inorganic ion-exchange materials, Delgass *et al.* (1969) concluded that the exchanged ferrous iron is normally trapped in a frozen water matrix. Their evidence consisted of quadrupole splitting and isomer shifts at both room and liquid $N_2$ temperatures.

The present study investigated the properties of *adsorbed* iron in contrast to structural iron by following the temperature dependence of the Mössbauer parameters. No chemical treatment of the samples was performed prior to measurements, such as in the case of Malathi *et al.* (1969) thus providing a nondestructive means of characterizing exchangeable iron ions. As will be seen, the typical features of adsorbed ferric ions

are influenced by the adsorption site, namely the interlayer surface, and the neighboring water molecules. These influences are reflected in the hyperfine interaction parameters and the local lattice dynamics as revealed through the recoil-free fraction.

## MÖSSBAUER SPECTROSCOPY METHODOLOGY

In mineral systems, a Mössbauer ME spectrum can unambiguously differentiate between the $Fe^{2+}$ and $Fe^{3+}$ chemical states (Bancroft, 1973). Those states differ both in their isomer shift (i.s.) and quadrupole splitting (QS). Generally, the i.s. of $Fe^{3+}$ (Rozenson and Heller-Kallai, 1977) is approximately 0.3 mm/sec, and the QS is 0.5 mm/sec. Comparable values for $Fe^{2+}$ are 1.10 mm/sec and 2.7 mm/sec. The average widths of the $Fe^{3+}$ lines are relatively broad due to the extra sensitivity of their electric field gradients to adjacent vacancies and local bonding distortions. On the other hand, the electric field gradients of $Fe^{2+}$ are generally well defined, resulting in narrow quadrupole split lines.

The intensity of the quadrupole split doublets, as measured by the areas, A, under the absorption lines, is proportional to the site population of ferric or ferrous ions, namely:

$$A_1/A_2 = f_1(T)n_1/f_2(T)n_2, \qquad (1)$$

where f(T) is the recoil-free fraction at temperature T, and $n_1$ and $n_2$ are concentrations at sites 1 and 2. Eq. (1) is correct for "thin absorbers."

To determine the population ratios of two iron species the relative areas and the ratio between the f values must be measured. The relative areas are obtained from a computer least-squares fit of a spectrum

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Table 1. Isomer shift, quadrupole splitting, and site population of $Fe^{2+}$ and $Fe^{3+}$ in Ca- and Fe-montmorillonite.[1]

|  | Isomer shift (mm/sec) | Quadrupole splitting (mm/sec) | $Fe^{2+}/Fe^{3+}$ concentration ratio |
| --- | --- | --- | --- |
| $Fe^{2+}$-montmorillonite | 1.04 ± 0.03 | 3.12 ± 0.03 | |
| $Fe^{3+}$-montmorillonite | 0.34 ± 0.02 | 0.64 ± 0.03 | 0.12 |
| $Fe^{2+}$ in Ca-montmorillonite | 1.09 ± 0.01 | 2.76 ± 0.02 | |
| $Fe^{3+}$ in Ca-montmorillonite | 0.37 ± 0.01 | 0.61 ± 0.02 | 1.07 |

[1] The isomer shift is with respect to metallic iron at room temperature.

with proper precautions for background, effective line widths, etc. (Bancroft, 1973). The second parameter may be obtained from independent measurements of f, or indirectly, by measuring the Debye temperatures ($\theta_D$) for each site.

At temperatures where $\theta_D < T/2$, f(T) can be expressed as follows:

$$f(T) = \exp(-k^2\langle x^2\rangle) = \exp(-6RT/k_B\theta_D^2), \quad (2)$$

where k is the $\gamma$-ray wave number, $\langle x^2\rangle$ is the atomic mean-square displacement, R is the recoil energy of $Fe^{57}$, and $k_B\theta_D$ is the effective Debye thermal energy as measured by the ME in iron. Because the area A is proportional to f, the slope ln A(T) yields the value of $\theta_D$, namely:

$$d(\ln A)/dT = -6R/k_B\theta_D^2. \quad (3)$$

Because the slope is independent of background and other experimental factors, this determination is rather accurate. Thus, the value of $\theta_D$ is inserted in Eq. (2) from which f(T) can be derived.

## EXPERIMENTAL

Measurements were performed with air-dried Ca-, Mg-, and $Fe^{2+}/Fe^{3+}$-montmorillonites prepared according to a quantitative ion-exchange method for clays (Banin, 1973). The clay was of the Wyoming type, processed by CENCO and supplied as item C-1051 with a cation-exchange capacity of 80 meq/100 g. The Ca-montmorillonite was further treated to achieve a partial reduction of the structural ferric ions ($Fe^{3+}$(s)). This was accomplished by mixing hydrazine hydrate with NaOH in a nitrogen atmosphere at 100°C. The Ca-montmorillonite was exposed to the hydrazine fumes for about 1 hr, long enough to permit a partial reduction of the $Fe^{3+}$(s). The clay was freeze-dried, equilibrated with air, and used in the air-dried state (15–18% $H_2O$).

The absorbers consisted of powder samples thoroughly mixed to avoid orientation. A typical absorber thickness was of 3 mg/cm$^2$ natural iron. This was considered a "thin" absorber, i.e., no saturation effect in the intensity was expected down to 80°K.

The Mössbauer spectrometer consisted of a home-made driver and electronics, driven in the constant acceleration mode in conjunction with a 400-multichannel analyzer. Data were accumulated up to 2–3 × 10$^6$ counts/channel and analyzed by computer with conventional least-squares fit programs to yield (1) areas under absorption peaks, (2) isomer shifts, and (3) quadrupole splittings. A commercial flow crystal with temperature stabilizer was used covering a temperature range of 80–300°K. A $Co^{57}$(Rh) source was used and maintained at room temperature. The relevant results of the hyperfine interaction and site population of the iron ions are presented in Table 1. In the present report all isomer shifts are quoted with respect to an iron metal reference.

## RESULTS AND DISCUSSION

Figure 1 shows the spectra of the partially reduced Ca-montmorillonite and Fe-montmorillonite at 300°K and 80°K, respectively. Figure 1a shows two quadrupole split doublets corresponding to ferric and ferrous structural ions in the Ca-montmorillonite. They are characterized by different QS and i.s. values. Figure 1b depicts the Fe-montmorillonite spectrum at room temperature where only the $Fe^{3+}$ absorption lines are revealed. The same spectrum was observed for the Mg- and nonreduced Ca-montmorillonite at all temperatures. In general, all of these samples showed relatively broad-line $Fe^{3+}$ spectra ($\Gamma \sim 0.57$ mm/sec), suggesting several sites of, or vacancies surrounding the ferric ion. In disagreement with the results of Malathi *et al.* (1969), extra lines which could be assigned to the adsorbed iron in oxidation states higher than $Fe^{3+}$ were not observed. The spectrum of this same sample at 80°K is shown in Figure 1c. The additional, large QS doublet in Figure 1c (80°K) can be assigned to adsorbed $Fe^{2+}$.

The temperature dependence of the area under the absorption doublets corresponding to the $Fe^{2+}$ and $Fe^{3+}$ in Fe-montmorillonite is shown in Figure 2. As can be seen, the intensity of the $Fe^{2+}$ underwent an abrupt transition at 210°K and was undetectable above 250°K. This feature characterizes adsorbed $Fe^{2+}$ because it was not observed with $Fe^{3+}$ (structural and adsorbed) nor with structural $Fe^{2+}$ (in reduced Ca-montmorillonite).

The transition at 210°K is inferred due to the onset of local large vibrational amplitudes of near-neighbor water molecules. This change took place in the same temperature range as the exothermic peak observed by Anderson and Tice (1971). They interpreted this peak to result from the freezing of the molecular water layers on the clay surface. Also, the absence of $Fe^{2+}$ (a) lines at room temperatures was noticed by Delgass *et al.*, (1969) in water-saturated ion-exchange materials (Linde zeolite Y and Dowex 50 resin); however, they did not report an abrupt transition at lower temperatures, and interpreted their results as arising from $Fe^{2+}$
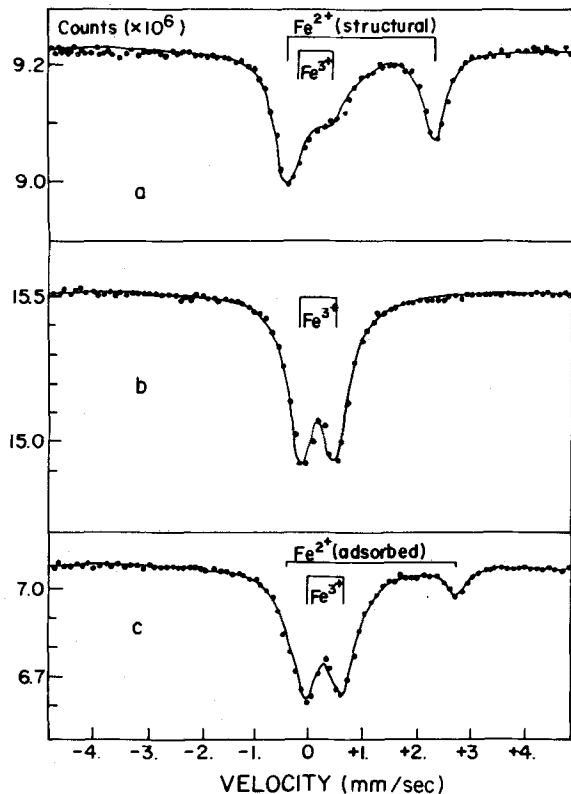
Figure 1. (a) Absorption spectrum of partially reduced Ca-montmorillonite at room temperature. (b) Absorption spectrum of $Fe^{2+}/Fe^{3+}$-montmorillonite at room temperature. (c) Absorption spectrum of $Fe^{2+}/Fe^{3+}$-montmorillonite at 80°K.
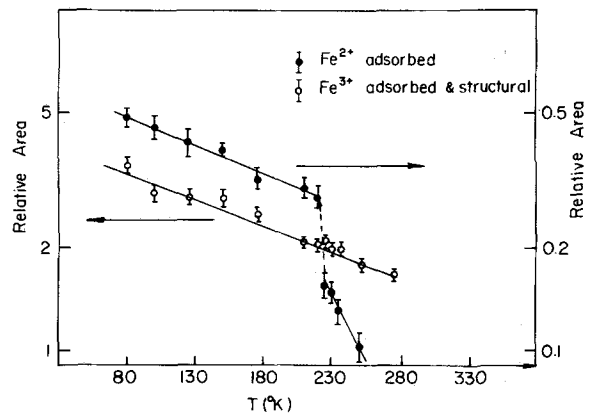


Figure 2. Temperature dependence of the area under the absorption line of structural and adsorbed $Fe^{3+}$ and adsorbed $Fe^{2+}$ in Fe-montmorillonite.

trapped in a frozen water matrix. This interpretation was supported by the resemblance of the i.s. (1.65 mm/sec) to that reported for iron ions in ice (Dezsi *et al.*, 1965). The present value for the i.s. (1.04 mm/sec) is much less than that of $Fe^{2+}$ solutes in ice. Because the i.s. is a measure of the nature of a chemical bond near the iron nucleus, the adsorbed $Fe^{2+}$ in the studied clays can not be fully surrounded by water molecules. Further evidence for this conclusion was derived from the low temperature (T < 210°K) dependence of the area, A, of the absorption line.

A striking observation is that the slope of ln A(T) for all the iron species in both Ca- and Fe-montmorillonite is approximately the same. Within the statistical error, a value of $\theta_D$ = 189 ± 5°K was deduced. Because the Debye temperature reflects the phonon spectrum as sensed by the Mössbauer nucleus it may be concluded that the nearest neighbors of the ferric and ferrous ions (structural and adsorbed) are similar.

Because such an abrupt transition was not observed with $Fe^{2+}(s)$ in the reduced Ca-montmorillonite (see Figure 3), it is concluded that in Fe-montmorillonite *all* of the $Fe^{2+}$ is in adsorbed state ($Fe^{2+}(a)$). The abrupt

transition in the recoil-free fraction at 210°K is typical of $Fe^{2+}(a)$; therefore it can be used to characterize adsorbed $Fe^{2+}$.

With temperatures as high as 350°K, no abrupt transition was observed in the intensity of the ferric ion lines. If $Fe^{3+}(a)$ cations were in sites similar to $Fe^{2+}(a)$, namely as partially solvated free ions, a break should have been detected in the ln A(T) vs. $Fe^{3+}$ plot at T = 210°K, the temperature at which part of the interlayer water started to melt. This observation may be explained as follows: $Fe^{3+}(a)$ tends to hydrolyze and polymerize on the clay's surface (e.g., Gerstel and Banin, 1980) forming hydroxyferric aggregates. The ferric ion in this state of polymerization is insensitive to water solvation. Thus, the water melting at 210°K will not induce local soft modes that ultimately reduce the recoil-free fraction. This explanation is supported by the fact that the i.s. and QS of $Fe^{3+}(s)$ are indistinguishable,
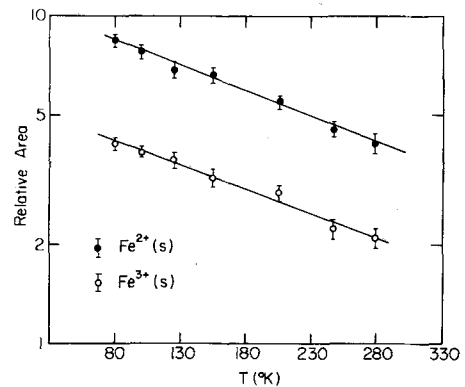


Figure 3. Temperature dependence of the area under the absorption line of structural $Fe^{3+}$ and $Fe^{2+}$ in Ca-montmorillonite.

because in both cases, the $Fe^{3+}$ will have similar nearest-neighbor atoms.

As stated above, the Debye temperature ($\theta_D$) as measured by Mössbauer spectroscopy, reflects the local phonon distribution of the Mössbauer nucleus. The similarity of $\theta_D$ for $Fe^{2+}(a)$ to that of the structural iron may be due to the fact that $Fe^{2+}(a)$ may be forced by water microcrystals into hexagonal holes on the dry surfaces. This environment, partially composed of oxygen atoms, resembles on the atomic scale that found in the structural sites.

An important result related to equality of the f factors for all iron ions at low temperatures is the possibility of determining site populations of $Fe^{2+}/Fe^{3+}$. This is accomplished in the case of thin absorbers simply by measuring the ratio of the absorption area (see Eq. (1)). In Table 1, the last column presents the results of two samples used in this experiment.

In summary, this study has shown that only adsorbed $Fe^{2+}$ is affected by the interlayer water molecules which dramatically reduces the Mössbauer absorption intensity at T > 210°K. Both this phenomenon and the identical values of the recoil-free fraction of the ferric and ferrous iron, adsorbed and structural, allows application of the Mössbauer effect to determine nondestructively the site population of iron ions in montmorillonites and possibly in other clays.

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**Резюме**—Эффект Мессбауэра был исследован для анализа и характеризации ионов железа, адсорбированных на межслойных поверхностях монтмориллонита. Измерялись Fe- и Са-насыщенные монтмориллониты. При температуре 210°K интенсивность показания $Fe^{2+}$ значительно уменьшалась, что, вероятно, было вызвано таянием межслойной воды. Процесс таяния не оказывал влияния ни на структурный $Fe^{2+}$ в Са-монтмориллоните, ни на адсорбированный $Fe^{3+}$ в Fe-монтмориллоните. Зависимость интенсивности адсорбции от температуры указывает на то, что эффективная температура Дебая для всех ферритовых монтмориллонитов является приблизительно одинаковой ($\theta_D = 189° \pm 5°K$). Этот результат позволил точно определить распределение $Fe^{2+}/Fe^{3+}$ в различных образцах. [Е.С.]

**Resümee**—Der Mössbauer-Effekt bei $Fe^{57}$ wurde verwendet, um Eisenionen, die an die Zwischenschichtoberflächen von Montmorillonit adsorbiert sind, festzustellen und zu charakterisieren. Die Messungen wurden mit Fe- und Ca-gesättigten Montmorilloniten durchgeführt. Bei 210°K war die Intensität des $Fe^{2+}$-Reflexes stark reduziert, wahrscheinlich wegen des Schmelzens des Zwischenschichtwassers. Weder das $Fe^{2+}$ in der Struktur des Ca-Montmorillonites noch das adsorbierte $Fe^{3+}$ im Fe-Montmorillonit wurde durch den Schmelzprozeß beeinflußt. Aus der Temperaturabhängigkeit der Adsorptionsintensität geht hervor, daß die wirksame Debye-Temperatur für alle Eisenarten etwa die gleiche zu sein scheint ($\theta_D = 189° \pm 5°K$). Dieses Ergebnis ermöglichte eine genaue Bestimmung der $Fe^{2+}/Fe^{3+}$-Verteilung in den verschiedenen Proben. [U.W.]

**Résumé**—L'effet de Mössbauer sur $Fe^{57}$ a été utilisé pour prober et caractériser les ions de fer adsorbés sur les surfaces interfeuillets de montmorillonite. Les mesures ont été faites avec des montmorillonites saturées de Fe et d'autres saturées de Ca. A 210°K, l'intensité de la réaction de $Fe^{2+}$ était très réduite, apparemment à cause de la fonte de l'eau interfeuillet. Ni $Fe^{2+}$ structural dans la montmorillonite-Ca, ni $Fe^{3+}$ adsorbé dans la montmorillonite-Fe n'ont été affectés par le procédé de fonte. A partir de la dépendance de l'intensité d'adsorption sur la température, la température effective Debye de toutes les espèces de fer semblait être approximativement la même ($\theta_D = 189° \pm 5°K$). Ce résultat a permis une détermination exacte de la population de $Fe^{2+}/Fe^{3+}$ dans des échantillons variés. [D.J.]