REDUCTION AND OXIDATION OF Fe^{3+} IN DIOCTAHEDRAL SMECTITES—III.* OXIDATION OF OCTAHEDRAL IRON IN MONTMORILLONITE

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Abstract—Structural Fe^{2+} in montmorillonite is readily oxidized by contact with water, salt solutions or on mild heating. This is shown clearly by the Mössbauer spectra and is associated with a sharpening of the infrared absorption near 880 cm^{-1}. It was inferred that this band comprises the Fe^{2+}—OH—Al and Fe^{3+}—OH—Al deformations. The rate at which oxidation occurs depends on the exchangeable cations. High acidity of the interlayers is conducive to oxidation, as is contact with Cu^{2+}-containing solutions or concentrated H_2O_2 solutions.

The results show clearly that any chemical treatment of montmorillonite causes changes in the oxidation state of structural iron.

Key Words—Exchange, Iron, Oxidation, Reduction.

INTRODUCTION

The phenomenon of cation exchange of clay minerals, and in particular of montmorillonite, has been extensively studied. It is generally assumed that cation exchange affects only the composition of the interlayer space with some possible indirect effects on the clay surfaces, but that the chemical composition of the phyllosilicate layers remains unchanged. Monoionic clay samples are frequently stored in aqueous suspension and aliquots are withdrawn as required, on the assumption that no change in chemical composition occurs in the course of time. The samples are frequently dried at elevated temperatures, again presupposing that no changes occur on drying.

A preliminary Mössbauer study of a sample of montmorillonite and of the same sample after cation exchange and prolonged storage in water revealed a considerable discrepancy in the amount of divalent iron in the two specimens, suggesting that some oxidation had occurred on cation exchange and/or storage in aqueous suspension. A more detailed study was therefore undertaken of the factors affecting oxidation of structural iron in montmorillonite.

EXPERIMENTAL

A sample of montmorillonite from Wyoming having an initial chemical composition $(Si_{7.69}Al_{0.31})(Al_{3.07}$ $Fe_{0.23}^{3+}$ $Fe_{0.18}^{2+}$ $Mg_{0.51})M^{+}_{0.90}O_{20}(OH)_4$ was used throughout the study. The Fe^{2+}/Fe^{3+} ratio was derived from the Mössbauer spectra. Monoionic samples were prepared by immersing aliquots of the clay in 0.1 N solutions of the appropriate chloride for 24 hr and washing with distilled water to remove excess salt. The washing was repeated four times, 5 min each, under constant stirring (set 1). The samples were subsequently stored in aqueous suspension for 15 months (set 2). Care was

taken to preserve the clay–water ratio at 2 g/l throughout all processes including cation exchange, washing and suspension of the unreacted or cation exchanged clay in water.

Mössbauer and infrared spectra and X-ray powder diffraction patterns were obtained using air-dried specimens, unless otherwise stated. Mössbauer spectra were recorded on a 255 channel analyzer, as previously described (Rozenson and Heller-Kallai, 1976). Infrared spectra of self-supporting films and of KBr disks were taken on a Perkin–Elmer 237 spectrometer.

X-ray powder diffraction patterns were obtained using unoriented specimens with quartz as an internal standard. The d_{010} spacing was derived from the (060) reflection.

RESULTS

Mössbauer spectra

The Mössbauer spectra of dioctahedral smectites and their interpretation have been discussed previously (Rozenson and Heller-Kallai, 1976). Following the procedure outlined, the spectra were resolved into two doublets corresponding to octahedrally coordinated Fe^{3+} in M(1) and M(2) (*trans* and *cis*) sites and one doublet corresponding to octahedrally coordinated Fe^{2+} in M(1) or M(2) sites. The Fe^{2+}/Fe^{3+} ratios for the various samples are shown in Tables 1 and 2. Spectra of the samples with the highest and the lowest Fe^{2+}/Fe^{3+} ratio and the computer fitted doublets are shown in Figure 1.

The effect of adding a site populated by increasing amounts of Fe^{2+} on the 'goodness of fit' parameter χ^2 of a two-doublet spectrum was determined to establish the detection limit of Fe^{2+}. No appreciable changes in χ^2 were observed for concentrations of Fe^{2+} less than 5% of the total iron present, but at higher concentrations significant increases in χ^2 were recorded. Five percent Fe^{2+} is therefore regarded as the approximate
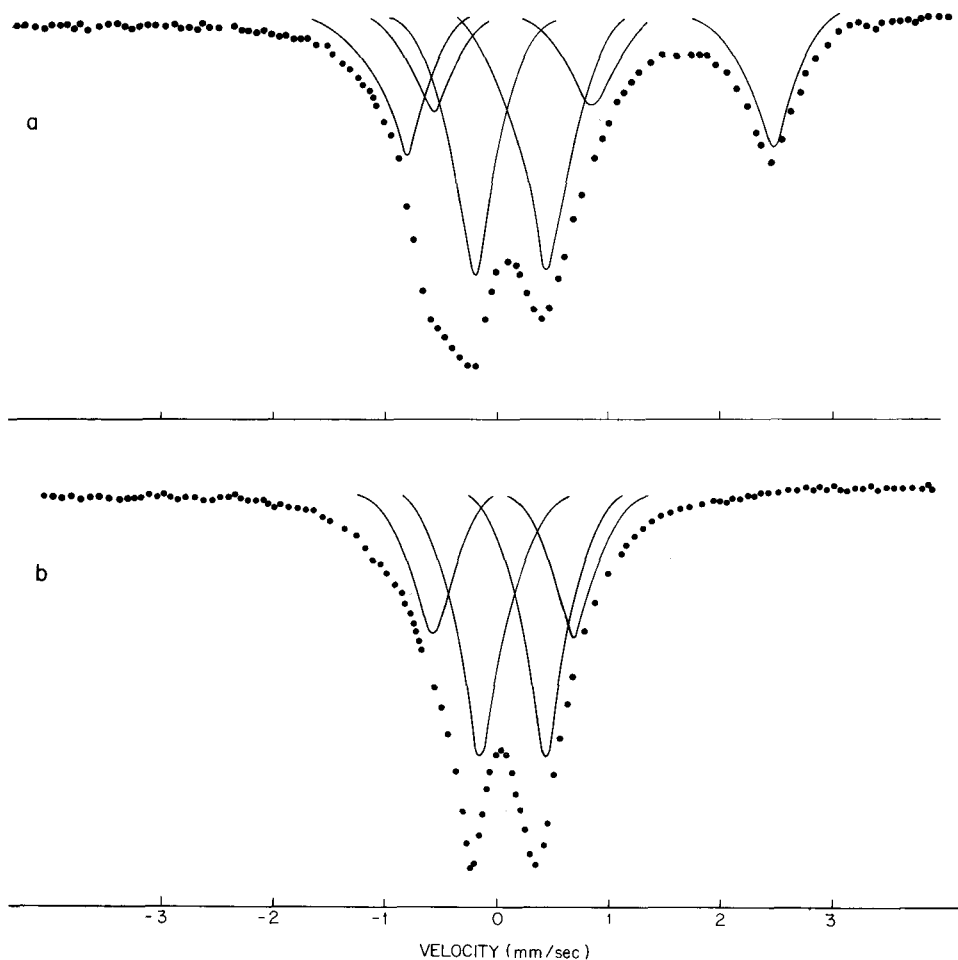

Fig. 1. Computer fitted Mössbauer spectra of (a) untreated montmorillonite, (b) Cu^{2+} exchanged montmorillonite.

detection limit of Fe^{2+} under the present experimental conditions. A small but significant difference in isomer shifts of the M(1) and M(2) sites was observed and has been discussed in the previous publication.

The quadrupole splitting (Q.S.) ranges from 1.14 ± 0.03 to 1.30 ± 0.03 and from 0.54 ± 0.02 to 0.60 ± 0.02 mm/sec for Fe^{3+} in M(1) and M(2) sites, respectively. No correlation could be established between the Q.S. of the Fe^{3+} doublets and the degree of oxidation of octahedral iron or the nature of the exchangeable cation. The relatively wide range of values of the Q.S. for different montmorillonites and the approximately linear correlation with b^{-3} has been discussed (Rozenson and Heller-Kallai, 1976). In the present study it was found that the values of Q.S. and the cell parameter b vary even for the same mineral with different interlayer cations, but the differences do not exceed the deviations of the experimental points from the straight line.

The doublets are broad, probably due to inhomogeneity of the sites either within the same octahedral layer or in different layers. The doublets corresponding to M(1) and M(2) sites overlap. Since most of the Fe^{3+} ions occupy M(2) sites, the intensity of the M(1) doublets is relatively small and the error in the calculated parameters is large. Frequently a decrease in Q.S. at the expense of increased line width or vice versa does not change the value of χ^2 significantly. Part of the scatter of the values of the Q.S. particularly for Fe^{3+} in M(1) sites, may therefore be an artifact of the interpretation of the spectra. The Q.S. of Fe^{2+} in the samples is fairly constant, ranging from 2.94 ± 0.02 to 3.02 ± 0.02 mm/ sec.

X-ray powder diffraction data

The d_{010} parameters of the variously substituted samples after 15 months' suspension in water are given in Table 2. The X-ray pattern, like the Mössbauer and infrared spectra, were recorded on air-dried samples.

It is evident from the results in Table 2 that substitution of different interlayer cations changes the d_{010} dimension of the octahedral layers, as has been previously reported (Heller et al., 1962). However, no con-

Table 1. Effect of various treatments on the oxidation of octahedral iron of Wyoming montmorillonite.

Sample treatment	Fe^{2+}/Fe^{3+}
	0.45
Washed 4 times	0.38
Suspended in water for 24 hr	0.25
Ultrasonically dispersed and suspended in water for 24 hr	0.26
Treated with 3% H_2O_2 solution for 40 min	0.30
Treated with 15% H_2O_2 solution for 3 hr	0.00
Heated 1 hr in air at 104°	0.22

Table 2. Effect of exchangeable cations on the Fe^{2+}/Fe^{3+} ratio and the b dimension of montmorillonite immersed in water.

Exchangeable cation	Fe^{2+}/Fe^{3+}		$6 \times d_{060} A^+$	
	Set 1	Set 2	Set 1	Set 2
H^+	0.13	0.11	8.97_3	8.97_3
Li^+	0.26	0.20	8.98_6	8.98_9
Na^+	0.28	0.22	8.97_4	8.97_9
K^+	0.26	0.26	8.98_6	8.98_3
Cs^+	0.40	0.28*[a]	8.99_0	8.99_8
NH_4^+	0.40*[b]	0.28	8.97_9	8.97_9
Mg^{2+}	0.39	0.19	8.97_4	8.97_8
Ca^{2+}	0.34	0.18	8.97_3	8.96_8
Ba^{2+}	0.32	0.25	8.98_0	8.98_6
Cu^{2+}	0.00	0.00	8.98_0	8.98_4
Al^{3+}	0.30	0.07	8.97_8	8.97_2

* After stirring mechanically for 24 hr: (a) 0.26 (b) 0.37.
+ d_{010} of the original sample: 8.98_0 A.

sistent correlation was observed between the fraction of octahedral iron oxidized and the d_{010} spacing. For various interlayer cations oxidation of octahedral iron was associated with a small increase or decrease in d_{010} or with no change at all. It seems that the amount of iron involved is too small to play an overriding part in the changes in dimensions of the octahedral layer, which are probably largely determined by the interlayer cations and their hydration sheaths, as shown by Low et al. (1970) and Eirish and Tret'yakova (1970). However, in none of these studies were attempts made to change either the oxidation of iron or the hydration state of the interlayer cation, keeping the other constant. Possible minor changes in b dimension due to oxidation of octahedral iron cannot therefore be definitely excluded.

Infrared spectra

Although the infrared spectra of all the samples are similar, small differences can be detected in the region of the hydroxyl deformation bands. The band at 917 cm^{-1}, assigned to Al—OH—Al vibrations, is identical in all of the samples. The band at about 850 cm^{-1}, assigned to Al—OH—Mg deformations, varies slightly both in position and in sharpness in samples saturated with different interlayer cations. This was noted previously by McBride et al. (1975) for dehydrated samples. It also seems to occur with air-dried samples, though to a lesser extent.

Greater differences were observed between the bands at about 880 cm^{-1} assigned to Al—OH—Fe deformation. This band not only differs for samples saturated with different cations, but also for samples with the same interlayer cation stored in water for various lengths of time. In general, the more oxidized the sample, the sharper the absorption in this region. Thus, Cs montmorillonite of set 1, which contained 28.5% of the octahedral iron in the ferrous state, gave rise to a broad absorption at about 880 cm^{-1} (Figure 2a). In contrast, Cu montmorillonite, with all the iron in the trivalent form, showed a relatively sharp maximum at 887 cm^{-1} (Figure 2b). Exchanging interlayer Cu by Cs, which

does not change the oxidation state of the octahedral iron, did not affect the absorption at 887 cm^{-1} (Figure 2c), indicating that the sharpening of the band is due to the absence of Fe^{2+} and not to effects exerted by the interlayer cations. The spectrum of NH_4^+ montmorillonite resembles that of Cs montmorillonite, whereas the spectra of Al and H montmorillonite of set 2, with most of the iron in the Fe^{3+} form, resemble the spectrum of Cu montmorillonite.

No differences between the spectra could be observed in the region of the OH stretching vibrations. There is considerable overlap of the various OH absorptions in this region and possible minor shifts due to a change in the valency state of small amounts of iron would not be detectable.

DISCUSSION

The effect on the oxidation state of iron of different treatments commonly employed in handling clay minerals in the laboratory is shown in Table 1. While storage of the specimen under ambient conditions did not cause oxidation of iron, at least within a period of 15 months, mere suspension in water did, indicating that oxidation is caused by dissolved oxygen. The amount of oxidation depends upon the time of contact: four brief washings with distilled water under constant stirring reduced the Fe^{2+}/Fe^{3+} ratio from 0.45 to 0.38, while suspension of the clay in water for 24 hr, under static conditions, reduced the ratio to 0.25. Dispersion by ultrasonic treatment did not affect the degree of oxidation. Care was taken to maintain the same concentration of suspension throughout all of the treatments. Brief treatment with 3% H_2O_2, such as is routinely employed for removing organic matter from soils, did not cause more oxidation than suspension in water, but more prolonged treatment or use of more concentrated H_2O_2 solution led to complete oxidation. Heating the
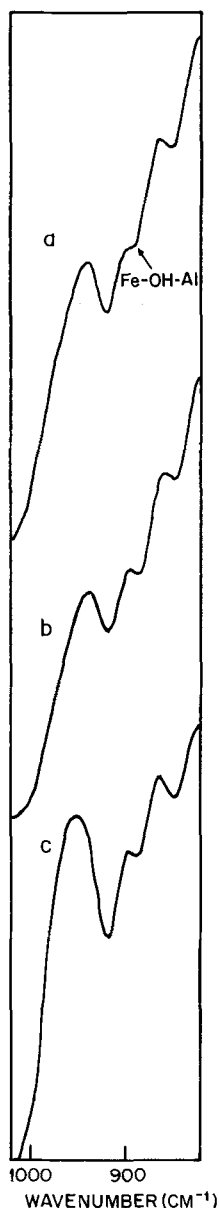
Fig. 2. Infrared spectrum of self-supporting film of (a) Cs montmorillonite, (b) Cu montmorillonite, (c) sample, (b) exchanged with Cs.

dry samples briefly at 104°C caused partial oxidation of Fe^{2+}.

Table 2 shows the effect of the exchangeable cation on the oxidation of structural iron. The samples were examined at two different stages—after 24 hr contact with 0.1 N salt solution (set 1) and after 15 months' storage of the washed samples in aqueous suspension (set 2). It is evident that the amount of oxidation of the samples in set 2 increases with increasing polarising ability of the exchangeable cations, i.e. with increasing acidity of the interlayers. The only exception is Cu montmo-

rillonite, which shows more oxidation than would have been expected on the basis of this criterion. The catalytic action of Cu on oxidation of organic matter in clay mineral interlayers has been noted previously (Heller and Yariv, 1969). It seems that copper is an effective catalyst also for the oxidation of structural iron, which proceeds to completion at an early stage of the cation exchange reaction.

The effect of surface acidity on oxidation of structural iron may be attributed to the reactions of adsorbed oxygen, which functions as a Lewis acid, accepting electrons from Fe^{2+} ions to form one or more of the species O^-, O_2^- or O_2^{2-}. They will subsequently react with interlayer protons, thus driving the reaction in the direction of further electron transfer from Fe^{2+} to adsorbed oxygen. This is similar to the mechanism proposed by Hirschler (1966) for the oxidation of organic material on alumino-silicate catalysts, which also occurs more readily at higher surface acidity. Hirschler suggested that molecular oxygen acts as a catalyst, aiding the transfer of electrons from organic material to proton acids, which trap the electrons.

The processes occurring in the early stages of the reaction are more difficult to interpret. In the presence of excess electrolyte the clay is flocculated and the state of aggregation may be expected to have some effect on the reaction. The original clay is largely Na^+ saturated. Comparison of the sample immersed in water for 24 hr with that immersed in NaCl solution (Tables 1 and 2) shows that the difference between them is small. Ultrasonic dispersion does not affect the oxidation. It thus appears that, contrary to expectation, the state of coagulation of Na montmorillonite is not decisive. In the presence of divalent and of large monovalent cations, which have a higher flocculation power, less oxidation occurs, but no direct correlation could be established between the Fe^{2+}/Fe^{3+} ratio at this stage of the reaction and the position of the cations in the lyotropic series.

In general, while some of the Fe^{2+} is oxidized rapidly, part is more resistant to oxidation. This could be attributed to the fact that the supply of oxygen is limited under the static conditions of the experiments. However, stirring the specimens for 24 hr either in the short-term or the long-term experiments did not affect the results appreciably. It thus seems that structural considerations govern the limits of oxidation.

Oxidation of octahedral iron reduces the charge on the montmorillonite layers. Charge balance can be maintained either by deprotonation of structural hydroxyl groups or by a decrease in the amount of exchangeable cations. Assuming the ideal anionic composition $O_{20}(OH)_4$, the charge per phyllosilicate layer of the natural sample is 0.98. If charge balance on complete oxidation is entirely maintained by a decrease in layer charge, this would be reduced to 0.80. A difference of 0.18 units of layer charge is thus the maximum to be expected on complete oxidation. Any chemical

method of determining CEC will itself affect the oxidation state of structural iron. Moreover, interlayer protons may contribute towards balancing the charge. No chemical method therefore could be devised for determining the CEC with sufficient accuracy to distinguish between the possible charge balance mechanisms. Infrared spectra cannot be used to differentiate between these mechanisms. Although the presence of Fe^{2+}—OH—Al vibrations can be detected in the spectra, these are expected to disappear on oxidation by either mechanism. If charge balance is maintained by deprotonation, the hydroxyl bending vibration is entirely eliminated. If oxidation occurs without deprotonation, the intensity of the Fe^{3+}—OH—Al vibrations is expected to be enhanced, but the measurements are too insensitive to permit a quantitative estimate of the absorption.

The Mössbauer spectra show no correlation between the amount of oxidation of Fe^{2+} and the quadrupole splitting. This may, perhaps, be regarded as an indication that oxidation is not associated with deprotonation, as this would be expected to distort the octahedral site, leading to increased quadrupole splitting. However, in view of the uncertainties involved, this is only a speculation.

In conclusion, it may be inferred that all chemical methods of determining CEC affect the degree of oxidation of structural iron. This may lead to a reduction in the exchange capacity or may be associated with deprotonation of some hydroxyl groups. Some of the discrepancies reported in the literature may thus be at least partly due to oxidation of structural iron. This may apply to samples with different interlayer cations tested by the same method or to the same sample tested by different methods. Similar effects may explain some of the reported hysteresis effects. Any correlation between the interlayer cations and their solvation sheaths and the structure of the phyllosilicate layers should take this factor into account.

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Резюме- Структурное Fe^{2+} в монтмориллоните было легко окислено в результате контакта с водой,соляными растворами или умеренного нагревания. Это ясно показано путем использования спектров Моссбауэра и связано с более резко выраженной инфракрасной абсорбцией вблизи 880см$^{-1}$.Было сделано заключение что эта связь обусловлена деформациями Fe^{2+} -OH-Al и Fe^{3+}-OH-Al. Скорость,с которой происходит окисление,зависит от обменных ионов.Высокая кислотность в межслойной среде ведет к окислению,также как контакт с Cu^{2+} содержащими растворами или концентрированными растворами H_2O_2.

Результаты ясно показывают,что любая химическая обработка монтмориллонита вызывает изменение в состоянии окисления структурного железа.

Kurzreferat- Strukturelles Fe(III) in Montmorillonit ist leicht oxydierbar durch Kontakt mit Wasser, Salzlösungen oder durch leichtes Erhitzen. Mössbauerspektra zeigen das deutlich und es ist verbunden mit einer Verschärfung der Infrarotabsorption bei 880 cm^{-1}. Der Schluß wurde gezogen, daß dieses Band auf die Verformungen von Fe(II)-OH-Al und Fe(III)-OH-Al zurückzuführen ist. Die Geschwindigkeit,mit der Oxydation stattfindet, hängt von den austauschbaren Kationen ab. Hohe Azidität der Zwischenschichten, sowohl wie Kontakt mit Lösungen, die Cu(II) enthalten, oder konzentrierte H_2O_2 Lösungen fördern die Oxydation.
Resultate zeigen deutlich, daß jede chemische Behandlung des Montmorilloniten, eine Veränderung in der Oxydationsstufe des strukturellen Eisens verursacht.