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DEHYDROXYLATION OF DIOCTAHEDRAL PHYLLOSILICATES

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Abstract—Mössbauer spectroscopy of dioctahedral phyllosilicates showed that on dehydroxylation iron which originally occupied M(2) and M(1) sites became, respectively, 5- and 6-coordinated. The 6-coordinated sites are very distorted. No migration of cations occurs in the course of heating the specimens for 1–3 hr at 600°–700°C.

By using a combination of several physicochemical methods, different successive stages of the dehydroxylation process could be distinguished: (1) migration of protons; (2) localized dehydroxylation of individual associations without significant change in the overall configuration of the octahedral sheets; and (3) loss of most of the hydroxyl groups with concomitant changes in the cell dimensions. Penetration of Li into the octahedral sheets does not affect the course of the reaction, but reduces the dehydroxylation temperature and the stability of the products.

Dehydroxylation was preceded by or associated with the oxidation of any divalent iron present. Fe^{3+} derived from Fe^{2+} was indistinguishable by Mössbauer spectroscopy from iron initially present in the trivalent form. High concentrations of Fe lower the dehydroxylation temperature and reduce the stability of the dehydroxylate to the extent that partial disintegration may precede complete dehydroxylation.

Key Words—Dehydroxylation, Iron, Montmorillonite, Mössbauer spectroscopy, Oxidation, Smectite.

INTRODUCTION

Although the dehydroxylation of dioctahedral silicates has been extensively studied, many questions about the coordination of the octahedral cations after dehydroxylation, the details of the reaction mechanism, and the fate of dehydroxylates formed in nature remain unanswered. On heating phyllosilicates four different processes may occur separately or concurrently: (1) oxidation of cations; (2) loss of water to form a dehydroxylate; (3) migration of cations to different sites; (4) disintegration of the structure.

Dehydroxylation does not necessarily occur simultaneously throughout the entire phyllosilicate structure. By using different methods of investigation, the changes occurring in various structural units may be assessed independently. Thus, Matyash *et al.* (1969), who followed the dehydroxylation of glauconite by electron spin resonance (ESR) and nuclear magnetic resonance (NMR), demonstrated that "destruction of the hydromica structure begins in the vicinity of iron ions at a temperature of 500°C, long before general destruction of the structure begins, at 850°C." It is generally known that dioctahedral 2:1 silicates give rise to well-defined dehydroxylates and that small interlayer cations may migrate into the octahedral sheets on heating. Whether heating also causes migration of cations within the octahedral sheets and which factors lead to breakdown of the structure have not been established.

Heller-Kallai (1975, 1976) showed that the course of dehydroxylation was modified when samples were heated in the presence of an alkali halide, e.g., KBr, which acts as a proton acceptor, leading to reactions of the type:

$$M^{+}_{0.90}(Si_{7.69}Al_{0.31})(Al_{3.07}Fe^{3+}_{0.36}Fe^{2+}_{0.05}Mg_{0.51})O_{20}(OH)_4 + (x + y)KBr \rightarrow M^{+}_{(0.85-y)}(Si_{7.69}Al_{0.31})(Al_{3.07}Fe^{3+}_{0.41}Mg_{0.51})O_{(20+x)}(OH)_{(4-x)}K_{(x+y)} + xHBr + yMBr$$

Her results suggested that a comparison of the changes occurring when samples were heated with or without alkali halides might throw additional light on the dehydroxylation process itself. For example, Fe^{2+} in octahedral sheets might oxidize. The effect of the oxidation of Fe^{2+} on the thermal changes of trioctahedral micas and vermiculites has been studied by many investigators, but little is known about the ease with which iron is oxidized on heating dioctahedral phyllosilicates or about the mutual effect of iron oxidation and dehydroxylation of these minerals.

A model of pyrophyllite dehydroxylate was developed by Wardle and Brindley (1972), but no detailed structure determination of a dioctahedral phyllosilicate dehydroxylate has been reported in the literature. Mössbauer studies were therefore made in the present investigation to establish some of the structural features of the dehydroxylates. Several phyllosilicates, ranging from those with low iron content (montmorillonite, muscovite, phengite) to those with high iron content (nontronite, celadonite) and having varying site occupancies, were selected for detailed analysis. Dehydroxylation at different temperatures was studied by

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comparing X-ray powder diffraction (XRD) and X-ray fluorescence (XRF) measurements with results obtained by infrared (IR) and Mössbauer spectroscopy.

EXPERIMENTAL

Materials

The identity of the following starting materials was confirmed by XRD and IR examination:

Montmorillonite: Upton, Wyoming (API Reference clay No. 25);

$M^{+}_{0.90}(Si_{7.69}Al_{0.31})(Al_{3.07}Fe_{0.41}Mg_{0.51})O_{20}(OH)_4$

(Heller-Kallai, 1975)

Beidellitic montmorillonite: Scan Raff, Sweden;

$M^{+}_{1.16}(Si_{7.46}Al_{0.54})(Al_{3.02}Fe^{3+}_{0.34}Fe^{2+}_{0.06}Mg_{0.58})O_{20}(OH)_4$

(Bystrom-Brusewitz, 1976)

This smectite has a higher tetrahedral charge than is commonly found for montmorillonite and is designated "beidellitic" to distinguish it from the Wyoming montmorillonite.

Nontronite: Grant County, Washington (CMS Source clay repository SWa-1);

$(Ca,Mg)_{0.49}(Si_{7.25}Al_{0.78})(Al_{0.85}Fe^{3+}_{2.75}Mg_{0.33}Ti_{0.25})O_{20}(OH)_4$

(Rozenson, 1975)

Muscovite: Pegmatite deposit, Israel (M 9061, Hebrew University collection);

$(K_{1.98}Na_{0.01})(Si_{6.11}Al_{1.89})(Al_{3.71}Mg_{0.10}Fe^{3+}_{0.20})O_{20}(OH)_4$

(microprobe analysis)

Celadonite: Verona, Italy (HU 3159, Hebrew University collection);

$K_{1.9}(Si_{7.1}Al_{0.9})(Mg_{0.8}Al_{0.3}Fe^{3+}_{2.3})O_{20}(OH)_4$.

Phengite: Alpine metamorphic rocks (P 1378) and metamorphic rocks from the Caledonian Mountains (77L27); separated by G. Steinitz.

Methods

Powdered samples were heated in open crucibles at the temperature indicated and cooled in air. Unless otherwise stated, all samples were heated for one hour. In addition, samples of montmorillonite and nontronite were mixed with KBr in the ratio of 1:3 and heated at various temperatures.

Mössbauer spectroscopy. The experimental details and the method of resolving spectra were described by Rozenson *et al.* (1979). Isomer shifts were measured relative to metallic iron. No theoretical limit can be placed on the number of doublets into which an observed Mössbauer spectrum may be resolved, but beyond a certain maximum the fit ceases to be significant. Three criteria were therefore used to limit the number of doublets into which the spectra were resolved: an optimally low value of χ^2, acceptable Mössbauer parameters (in particular, line widths), and reasonable agreement with known or inferred structural features.

The spectra under investigation were resolved into one or two Fe^{3+} and one or two Fe^{2+} doublets. The second doublet Fe^{3+} or Fe^{2+} was introduced only when doing so led to a significant (>200) decrease in χ^2. The additional doublet does not affect the magnitude of the isomer shifts (I.S.).

The assignment of the doublets was based on the data from ~200 samples of dioctahedral phyllosilicates obtained in this laboratory or gleaned from the literature (Rozenson, paper in preparation). In general, the doublets associated with 6-coordinated iron in phyllosilicates were assigned according to their quadrupole splitting (Q.S.). The q_{lat} contribution for both Fe^{3+} and Fe^{2+} ions depends on the configuration of the octahedral site, i.e., whether the OH groups are in *cis* [M(2)] or *trans* [M(1)] arrangement (Bancroft, 1974). Goodman (1978) suggested that the effect of trivalent ions in tetrahedral sites on the Q.S. of the doublets associated with octahedral Fe^{3+} may obscure the difference between M(1) and M(2) sites. This was not borne out by the results obtained by Rozenson, which were derived by comparison of the Mössbauer parameters with known crystal structures wherever available, by determining the temperature dependence of the Q.S. of Fe^{2+} doublets, and by theoretical calculations of the values of the Q.S. for some of the samples. A correlation was found between the magnitude of the Q.S. and the composition of the octahedral sheets.

For the purpose of assigning the doublets, dioctahedral phyllosilicates may be divided into two groups—Group A, minerals with a low iron content (Al-mica, illite, montmorillonite, beidellite) and Group B, minerals with a high iron content (nontronite, glauconite, celadonite). The ranges of the values observed (mm/sec) for the Q.S. of the various doublets are shown below:

		M(1)	M(2)
Fe^{2+}:	Group A	2.10–2.40	2.20–2.40
	Group B	1.70–2.00	2.70–3.00
Fe^{3+}:	Group A	1.00–1.25	0.50–0.70
	Group B	0.65–0.75	0.30–0.35

The doublets in the present study were assigned accordingly.

X-ray powder diffraction. The position of the 060 reflection was measured on a random powder with quartz as an internal standard to ±0.001 Å. This parameter measures changes in the overall dimensions of the sheets.

X-ray fluorescence. $\Delta 2\theta$, the difference between the position of the AlKα peak of the sample and that of aluminum metal was determined as described by Wardle and Brindley (1971) to an accuracy of 0.003°2θ. Changes in $\Delta 2\theta$ reflect changes in the environment of Al. In montmorillonite the amount of octahedral Al greatly exceeds that of tetrahedral Al and no major changes are expected in the coordination of tetrahedral Al. Observed shifts were therefore attributed entirely to changes in octahedral Al. The method was not applied to the other samples, which have a higher proportion of tetrahedral Al.

Infrared spectroscopy. The samples were examined in the form of KBr discs. In the study of smectites attention was focused on OH bending vibrations:

Montmorillonite	*Nontronite*
915 cm^{-1} Al-OH-Al	870 cm^{-1} Al-OH-Fe
880 cm^{-1} Al-OH-Fe	815 cm^{-1} Fe-OH-Fe
850 cm^{-1} Al-OH-Mg	

For muscovite and celadonite changes in the hydroxyl stretching vibrations were recorded. The bands were assigned according to Farmer (1974).

RESULTS AND INTERPRETATION

Montmorillonite (Table 1, Figures 1 and 5)

In the original sample Fe^{3+} occupies M(2) sites preferentially, and approximately one third of the total iron is Fe^{2+}. After heating to 400°C no Fe^{2+} remained, but the parameters of the Fe^{3+} doublets were not affected.

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Table 1. Mössbauer parameters of montmorillonite (M), Li-saturated montmorillonite (LiM) and beidellitic montmorillonite (B).[1]

Sample	Temperature (°C)	Fe^{3+} M(2) I.S.	Q.S.	Γ	%	Fe^{3+} M(1) I.S.	Q.S.	Γ	%	χ^2
M	25	0.37 (1)	0.57 (2)	0.48 (3)	55 (6)	0.37 (1)	1.29 (2)	0.48 (3)	20 (6)	216
		[1.14 (1)	2.95 (4)	0.46 (3)	25 (6)][2]					
M	400	0.37 (1)	0.55 (3)	0.50 (1)	45 (20)	0.37 (1)	1.26 (9)	0.78 (3)	55 (20)	220
M	500	0.34 (1)	0.58 (4)	0.68 (3)	48 (15)	0.37 (1)	1.29 (7)	0.88 (3)	52 (15)	215
M	600	0.33 (1)	1.31 (5)	0.67 (2)	70 (20)	0.38 (1)	1.80 (10)	0.74 (4)	30 (20)	238
M	700	0.34 (1)	1.24 (3)	0.44 (4)	30 (15)	0.39 (1)	1.77 (4)	0.67 (4)	70 (15)	203
M + KBr	400	0.35 (2)	0.65 (4)	0.64 (4)	80 (10)	0.35 (1)	1.80 (6)	0.64 (4)	20 (10)	219
M + KBr	500	0.36 (1)	0.95 (3)	0.50 (3)	72 (10)	0.39 (1)	1.70 (7)	0.66 (3)	28 (10)	223
M + KBr	600	0.37 (1)	1.06 (3)	0.50 (7)	25 (15)	0.38 (1)	1.65 (12)	0.90 (3)	75 (15)	216
M + KBr	700	0.36 (1)	1.31 (8)	0.72 (4)	85 (10)	0.38 (1)	2.10 (13)	0.78 (9)	15 (10)	217
LiM	400	0.36 (1)	0.55 (2)	0.55 (4)	65 (10)	0.38 (1)	1.29 (4)	0.70 (4)	35 (10)	223
LiM	500	0.35 (1)	0.59 (3)	0.68 (4)	60 (10)	0.40 (1)	1.34 (9)	0.77 (9)	40 (10)	223
LiM	600	0.35 (1)	1.31 (4)	0.66 (3)	70 (15)	0.39 (1)	1.80 (8)	0.74 (4)	30 (15)	216
LiM	700	0.36 (1)	1.27 (5)	0.57 (4)	75 (10)	0.40 (1)	1.86 (8)	0.65 (3)	25 (10)	217
LiM + KBr	400	0.36 (1)	0.67 (4)	0.70 (3)	70 (10)	0.37 (1)	1.52 (10)	0.95 (4)	30 (10)	251
LiM + KBr	500	0.37 (1)	1.15 (5)	0.70 (3)	68 (15)	0.38 (1)	1.82 (12)	0.81 (6)	32 (15)	220
LiM + KBr	600	0.35 (1)	1.21 (3)	0.77 (4)	67 (15)	0.39 (1)	2.05 (15)	0.69 (9)	33 (15)	216
LiM + KBr	700	0.35 (1)	1.12 (10)	0.76 (3)	70 (15)	0.38 (1)	2.03 (20)	0.82 (12)	30 (15)	210
B	25	0.36 (1)	0.56 (2)	0.56 (2)	74 (4)	0.36 (1)	1.35 (2)	0.56 (2)	7 (4)	199
		[1.13 (1)	2.76 (3)	0.33 (2)	19 (4)][2]					
B	600	0.38 (1)	1.29 (2)	0.56 (3)	100					212
B	700	0.38 (1)	1.36 (2)	0.60 (3)	100					216

[1] I.S. (relative to Fe metal), Q.S. and Γ in mm/sec.
[2] Fe^{2+} M(2).

No further modification of the spectra occurred up to 600°C.

No changes in d(060) or $\Delta 2\theta$ were observed below 500°C, but the Mg-OH-Al absorption at 850 cm^{-1} was considerably reduced in intensity at 400°C. At 600°C drastic changes occurred: the Fe-OH-Al (880 cm^{-1}) and Mg-OH-Al (850 cm^{-1}) absorption bands disappeared entirely, the Q.S. of Fe^{3+} in both M(1) and M(2) sites increased, and $\Delta 2\theta$ decreased; however, no appreciable change in d(060) was noted. Heating to 700°C did not affect the Q.S. of M(1) and M(2) doublets, but the Al-OH-Al absorption band (915 cm^{-1}) disappeared, $\Delta 2\theta$ decreased further, and d(060) increased from 1.495 to 1.502 Å.

Li-montmorillonite (Figure 6)

Substitution of Li in the interlayers led to partial oxidation of Fe^{2+}, as previously reported (Rozenson and Heller-Kallai, 1978), but did not affect the Mössbauer spectra of either the unheated or the heated material. The sample, however, differed from natural (largely Na-substituted) montmorillonite in several other respects: the OH bending vibrations were modified, as described by Calvet and Prost (1971), who attributed the changes to partial penetration of Li into the octahedral sheets. $\Delta 2\theta$ decreased, as for natural montmorillonite, but the final value was reached at a considerably lower temperature. Similarly d(060) increased to 1.500 Å at a lower temperature than that of montmorillonite. After heating the sample to 700°C[1], the reflection could no longer be detected. The Mössbauer spectra were not significantly affected by the presence of Li.

Montmorillonite + KBr (Figure 7)

The presence of KBr did not affect the values of the Mössbauer parameters nor of $\Delta 2\theta$ or of d(060). The infrared spectra, however, showed considerable differences. The Fe-OH-Al bending vibration was the first to be affected by heating the sample. It was appreciably weakened after heating to 400°C and disappeared at 500°C, while Al-OH-Al and Al-OH-Mg vibrations persisted at this temperature. No OH-bending vibrations were observed after heating the sample to 600°C. A drastic increase in the Q.S. of M(1) doublets occurred after heating to 400°C (in contrast to 600°C for montmorillonite without KBr), but an increase in Q.S. of M(2) doublets was observed only after the sample was heated to a much higher temperature.

Li-montmorillonite + KBr

The changes observed were very similar to those recorded for natural montmorillonite heated in the presence of KBr. Some perturbation of the infrared pattern was observed, but less than for Li-montmorillonite

[1] Ed. note: As stated in the experimental methods section (p. 356), samples described as being heated *to* a particular temperature were heated *at* that temperature for one hour, unless otherwise indicated.

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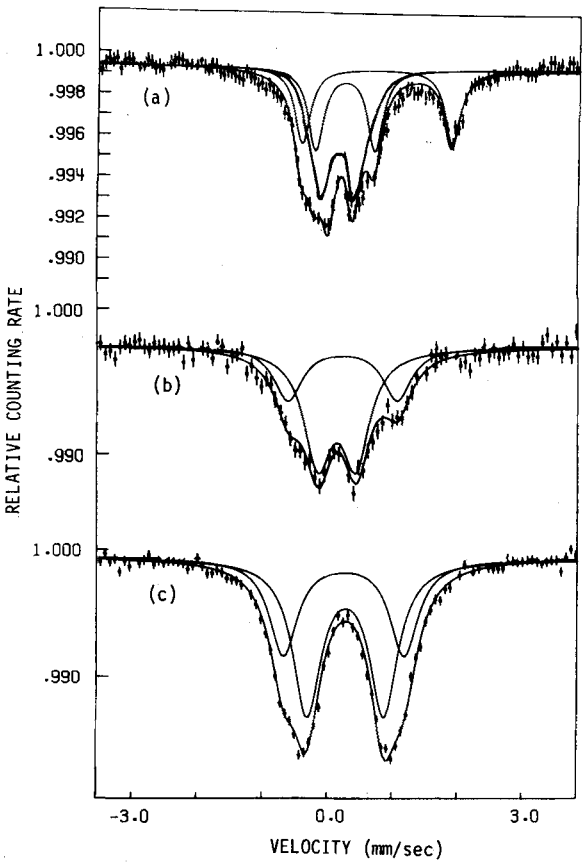


Figure 1. Mössbauer spectrum of montmorillonite: (a) original sample; (b) mixed with KBr and heated at 400°C; (c) heated at 600°C.

without KBr. It was attributed to partial penetration of Li into the octahedral sheets before interaction with KBr occurred (Heller-Kallai, 1976).

Beidellitic montmorillonite (Table 1)

The Mössbauer spectrum of the original sample could be fitted satisfactorily by one Fe^{3+} and one Fe^{2+} doublet, corresponding to Fe in M(2) sites. After heating the sample to 600°C, only one Fe^{3+} doublet with relatively large Q.S. remained.

Nontronite (Table 2, Figures 2 and 8)

The Mössbauer spectrum was resolved into two Fe^{3+} doublets, with relative intensities of ~1:2, indicating that the Fe content of all octahedral sites is equivalent, as previously discussed (Rozenson and Heller-Kallai, 1977). The spectrum remained unchanged for samples heated to 350°C, at which temperature the Q.S. of the doublets increased. The Q.S. continued to increase steadily as the samples were heated to higher temperatures. Nontronite differed from the other minerals studied in showing a gradual increase in Q.S. with increasing temperature. On heating above 600°C, the

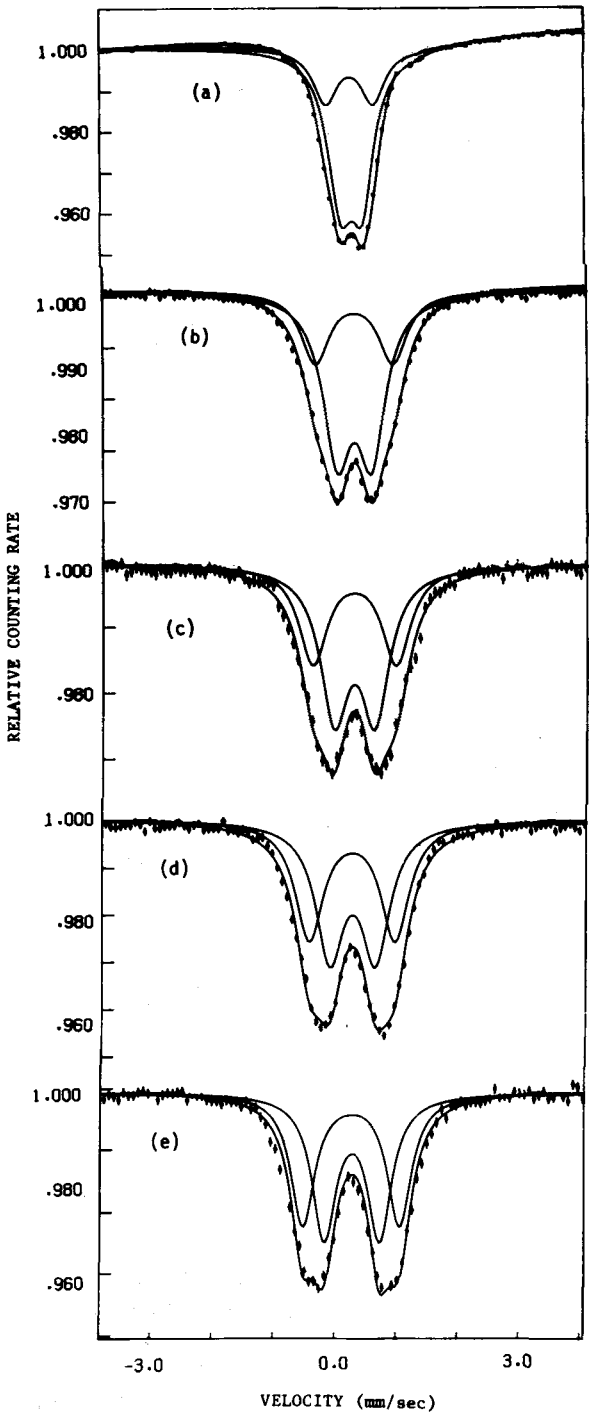


Figure 2. Mössbauer spectrum of nontronite: (a) original sample; samples heated at: (b) 400°C; (c) 450°C; (d) 500°C; (e) 600°C.

mineral disintegrated, and a six-line magnetic spectrum characteristic of hematite was obtained.

The intensity of the Fe-OH-Al absorption band was considerably reduced after the sample had been heated

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Table 2. Mössbauer parameters of nontronite.

Temp (°C)	Fe^{3+} M(2) I.S.	Q.S.	Γ	%	Fe^{3+} M(1) I.S.	Q.S.	Γ	%	χ^2
25	0.39 (1)	0.29 (2)	0.40 (2)	65 (7)	0.39 (1)	0.68 (1)	0.39 (2)	35 (7)	216
300	0.39 (1)	0.32 (2)	0.43 (2)	62 (4)	0.38 (1)	0.69 (2)	0.48 (2)	38 (4)	240
350	0.38 (1)	0.28 (2)	0.40 (2)	60 (8)	0.38 (1)	0.66 (2)	0.50 (2)	40 (8)	233
400	0.38 (1)	0.53 (3)	0.52 (3)	60 (7)	0.38 (1)	1.16 (6)	0.65 (3)	40 (7)	200
450	0.39 (1)	0.74 (2)	0.65 (4)	55 (7)	0.39 (1)	1.40 (4)	0.61 (2)	45 (7)	195
500	0.39 (1)	0.83 (3)	0.65 (2)	52 (8)	0.38 (1)	1.47 (4)	0.53 (2)	48 (8)	199
600	0.39 (1)	1.00 (2)	0.60 (3)	55 (8)	0.37 (1)	1.60 (4)	0.59 (2)	45 (8)	208

to 450°C, and d(060) decreased slightly. After heating the sample to higher temperatures, the Fe-OH-Al absorption band disappeared and d(060) decreased further. The low concentration of Al in the sample precluded accurate measurement of $\Delta 2\theta$.

Muscovite (Table 3)

The Mössbauer spectrum of muscovite resembles that of montmorillonite in showing two Fe^{3+} doublets, with a pronounced preference of Fe^{3+} for M(2) sites. After heating the sample to 500°C, no Fe^{2+} could be detected, and the Q.S. of both doublets increased. No significant changes in the Mössbauer spectra were observed on further heating to 700°C.

After heating the sample to 630°C, d(060) increased from 1.503 to 1.515 Å, but the presence of weak hydroxyl stretching bands indicated that dehydroxylation was not complete. Changes in $\Delta 2\theta$ could not be determined because of the high content of tetrahedral Al.

Celadonite (Table 4 and Figure 3)

The Mössbauer spectrum of celadonite showed one intense doublet corresponding to Fe^{3+} in M(2) sites and a weak doublet corresponding to Fe^{2+} in M(2) sites. After heating the sample to 420°C, a weak doublet appeared with a Q.S. of 1.16 mm/sec, and some of the iron persisted in the divalent form (Figure 3b). After heating the sample to 530°C, the Fe^{3+} doublet with a larger Q.S. predominated and the Fe^{2+} doublet disappeared; however, a weak Fe^{3+} doublet with the same parameters as that produced by the original mineral was still detectable (Figure 3c). In addition, a weak six-line magnetic spectrum characteristic of hematite appeared. On further heating of the specimen the inner doublet entirely disappeared and the spectrum of hematite became more intense.

After heating the sample to 530°C, IR bands at 3550 and 3520 cm^{-1}, assigned to Fe-OH-Mg and Fe-OH-Fe stretching vibrations, respectively, became broad and unresolved. A band at 3600 cm^{-1}, assigned to Mg-OH-Al vibrations, remained unchanged. The value of d(060) decreased slightly, from 1.511 to 1.509 Å.

Phengite (Table 5 and Figure 4)

Sample 77L27 showed only one doublet, corresponding to Fe^{2+} in M(2) sites. The doublet is narrow and cannot be meaningfully resolved. Heating the sample to 200° or 300°C for 5 days had no effect on the spectra. After heating the sample for 5 days at 400°C, about half of the iron was oxidized. At this stage, the spectrum could be resolved into two doublets, one with the original parameters, the other with a Q.S. of 1.20 mm/sec (Figure 4b). Aliquots heated at 700°C in air or under vacuum gave rise to a spectrum composed of only one doublet, with Q.S. 1.18–1.20 mm/sec.

Sample P 1378 showed two doublets corresponding to Fe^{3+} and Fe^{2+} in M(2) sites, respectively. The spectrum of the sample after heating to 700°C was identical with that of sample 77L27 heated to the same temperature, demonstrating that the doublet due to Fe^{3+} that was derived from Fe^{2+} became indistinguishable from that of Fe^{3+} present in the original mineral.

Table 3. Mössbauer parameters of muscovite.

Temp (°C)	Fe^{3+} M(2) I.S.	Q.S.	Γ	%	Fe^{3+} M(1) I.S.	Q.S.	Γ	%	χ^2
25	0.38 (1)	0.49 (1)	0.51 (2)	60 (3)	0.39 (1)	0.99 (1)	0.52 (2)	20 (4)	216
	[1.12 (1)	3.00 (2)	0.38 (2)	10 (2)][1]	[1.12 (1)	2.40 (1)	0.38 (2)	10 (2)][2]	
500	0.38 (1)	0.94 (2)	0.64 (2)	60 (5)	0.39 (1)	1.83 (2)	0.64 (2)	40 (5)	220
600	0.37 (1)	1.13 (2)	0.76 (2)	59 (4)	0.39 (1)	1.78 (2)	0.78 (2)	41 (4)	250
700	0.37 (1)	0.96 (1)	0.82 (2)	60 (5)	0.39 (1)	1.69 (1)	0.74 (2)	40 (5)	220

[1] Fe^{2+} M(2).
[2] Fe^{2+} M(1).

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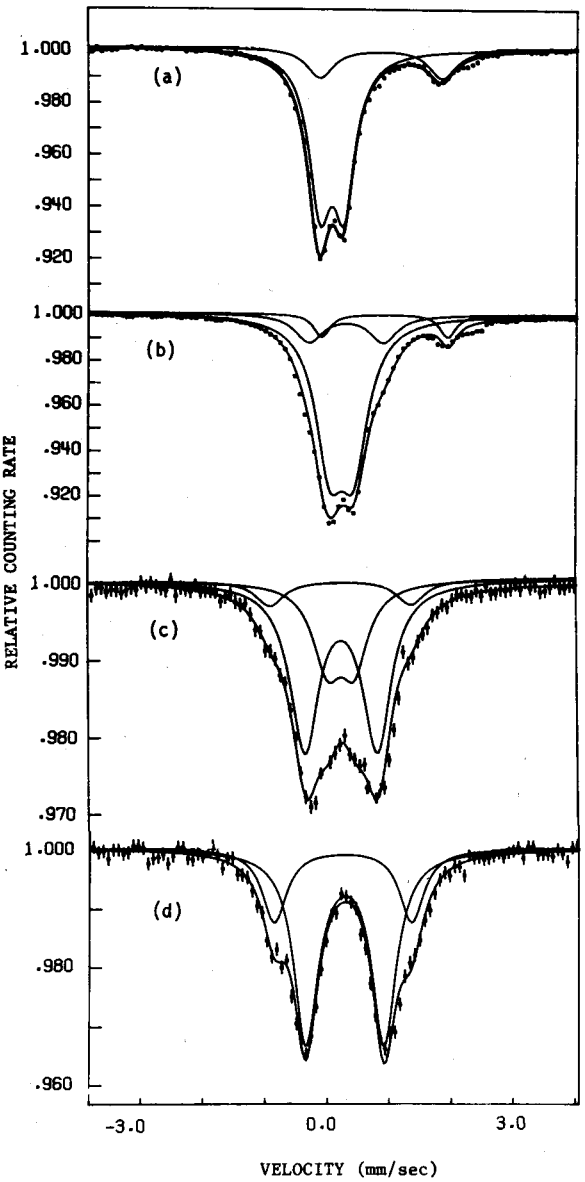


Figure 3. Mössbauer spectrum of celadonite HU 3159: (a) original sample; samples heated at: (b) 420°C; (c) 530°C; (d) 600°C.

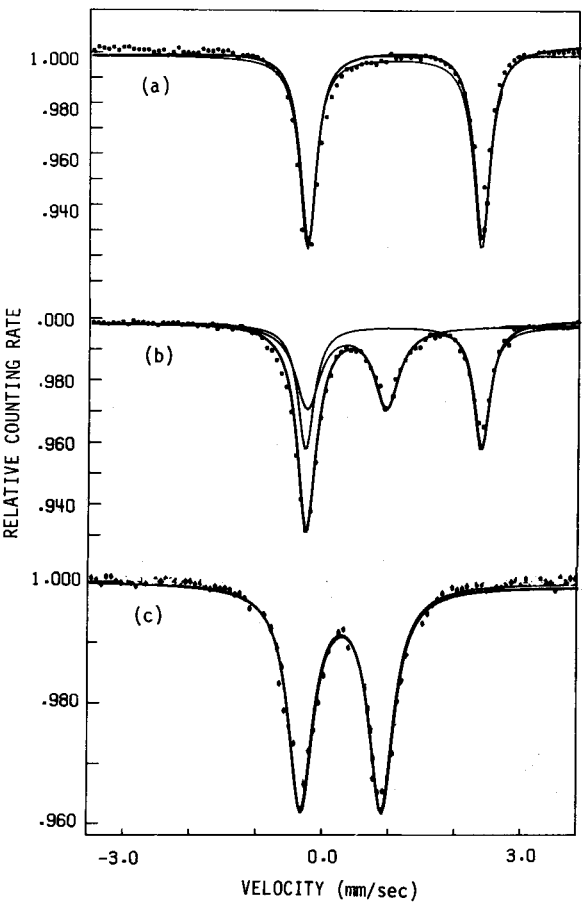


Figure 4. Mössbauer spectrum of phengite 77L27: (a) original sample; samples heated at: (b) 400°C for 5 days; (c) 700°C for 3 hr.

NATURE OF DEHYDROXYLATES IN LIGHT OF MÖSSBAUER SPECTRA

Assignment of doublets of the dehydroxylates

The increase in Q.S. observed with the heated specimens may be inferred to be due to structural changes associated with dehydroxylation of the sites. This inference is confirmed by comparing the IR spectra with the Mössbauer spectra. The assignment of the doublets to the two possible sites presents some problems. Wardle and Brindley (1971) showed that in pyrophyllite, octahedrally coordinated Al occupies

Table 4. Mössbauer parameters of celadonite.

Temp (°C)	Fe^{3+} M(2)				Fe^{3+} dehydroxylate M(2)				Fe^{2+} M(2)				% Hematite	χ^2
	I.S.	Q.S.	Γ	%	I.S.	Q.S.	Γ	%	I.S.	Q.S.	Γ	%		
25	0.38 (1)	0.42 (1)	0.42 (2)	75 (2)					1.12 (1)	2.40 (2)	0.39 (3)	25 (2)		200
420	0.39 (1)	0.43 (2)	0.60 (3)	60 (4)	0.38 (1)	1.16 (2)	0.60 (2)	28 (4)	1.12 (1)	2.36 (3)	0.39 (3)	12 (4)		199
530	0.38 (1)	0.44 (1)	0.62 (3)	20 (4)	0.38 (1)	1.18 (3)	0.60 (2)	80 (4)					8	230
600					0.38 (1)	1.28 (2)	0.63 (2)	100 (4)					44	233

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Table 5. Mössbauer parameters of phengite.

Sample	Temp (°C)	Fe^{3+} M(2)				Fe^{2+} M(2)				Fe^{3+} dehydroxylate M(2)				χ^2
		I.S.	Q.S.	Γ	%	I.S.	Q.S.	Γ	%	I.S.	Q.S.	Γ	%	
77L27	25					1.13 (1)	2.68 (2)	0.38 (2)	100					199
77L27	400[1]					1.13 (1)	2.65 (2)	0.38 (3)	52 (4)	0.39 (1)	1.20 (2)	0.49 (3)	48 (4)	205
77L27	700[2]									0.39 (1)	1.20 (2)			203
77L27	700[2,4]									0.39 (1)	1.18 (3)			217
1378	25	0.38 (1)	0.74 (1)	0.60 (2)	35 (5)	1.13 (1)	2.90 (1)	0.40 (1)	65 (5)					240
1378	250[3]	0.38 (1)	0.82 (1)	0.60 (3)	45 (5)	1.12 (1)	2.84 (2)	0.40 (3)	55 (5)					250
1378	600					1.11 (1)	2.80 (4)	0.41 (3)	10 (2)	0.39 (1)	1.21 (1)	0.61 (3)	90 (2)	221
1378	700									0.39 (1)	1.23 (4)	0.61 (3)	100	219

[1] 4-day heating.
[2] 3-hr heating.
[3] 10-day heating.
[4] Heated in vacuum.

M(2) positions and that on dehydroxylation the coordination is reduced to 5. By analogy it may be inferred that Fe^{3+} ions in the phengite, celadonite, and beidellite studied, which occupy M(2) sites in the original minerals, will be 5-coordinated after dehydroxylation. (Unfortunately, no pyrophyllite containing sufficient Fe for a reliable Mössbauer study was available.)

The post dehydroxylation coordination of cations which occupy both M(1) and M(2) sites in dioctahedral minerals (e.g., Fe^{3+} in montmorillonite, muscovite, and particularly in nontronite) does not seem to have been considered. If the structure of pyrophyllite dehydroxylate is used as a prototype, the cations which originally occupied M(1) sites (vacant in pyrophyllite) must become 6-coordinated after dehydroxylation of minerals in which both M(1) and M(2) sites are occupied by Fe. Two doublets would be expected—one corresponding to Fe^{3+} in 5 coordination, the other with Fe^{3+} in a distorted octahedral environment. In fact, the spectra of heated montmorillonite, muscovite, and nontronite can be resolved into two Fe^{3+} doublets, in contrast to those of heated celadonite, phengite, and beidellite, which gave rise to only one doublet. Thus, it is likely that Fe^{3+} occupying M(2) and M(1) sites in the original minerals became respectively 5- and 6-coordinated after dehydroxylation. The question then arises which of the doublets corresponds to 5-coordinated and which to 6-coordinated Fe^{3+}. Comparison with the spectra of dehydroxylated beidellite, phengite, and celadonite suggests that the doublet with the smaller Q.S. should be assigned to Fe^{3+} in 5-coordination. The very large values of the Q.S. of the second doublets indicate that the octahedral environment is very distorted.

This assignment receives further support from a study of the changes occurring when nontronite is heated to progressively higher temperatures. The original spectrum showed two doublets with Q.S. = 0.32 and 0.69 mm/sec, assigned to Fe^{3+} in M(2) and M(1) sites, respectively. After heating the sample to 400°C, the spectrum was resolved into two doublets with Q.S. = 0.53 and 1.16 mm/sec, respectively. If the doublet with Q.S. = 0.53 mm/sec were assigned to Fe^{3+} which originally occupied M(1) sites, a decrease in Q.S. on heating would have to be postulated, which is contrary to all other results obtained.

The fact that samples with Fe exclusively in M(2) sites give rise to a single doublet after dehydroxylation indicates that Fe does not migrate from M(2) to M(1) sites during the short periods (one hour) of heating employed. The relative intensity of the two doublets of nontronite does not alter significantly on heating, also confirming that no migration of cations occurs. The relative intensities of the doublets in the iron-poor muscovite and montmorillonite seem to change on heating, but the errors involved in resolving the spectra at intermediate temperatures of heating are considerable. The values of the relative areas of the doublets are particularly prone to error. Although the Mössbauer spectra of montmorillonite and muscovite do not, therefore, disprove the migration of cations on heating the samples for one hour, or even three hours, the spectra of nontronite, beidellitic montmorillonite, celadonite, and phengite strongly suggest that under these conditions cations maintain their original sites. Moreover, cation migration after more prolonged periods of heating was clearly shown by the Mössbauer spectra (Rozenson and Heller-Kallai, 1980).

Lindqvist (1962) and Bailey (1975) suggested that the increase in the *b* parameter with dehydroxylation of dioctahedral layer silicates indicates redistribution of the octahedral cations over all the octahedral positions. The Mössbauer spectra of this study do not support this conclusion. The increase in *b* merely indicates a change in structure on dehydroxylation.

The Q.S. of Fe^{3+} in montmorillonite, beidellite, and muscovite are larger than those of Fe^{3+} in corresponding sites of the iron-rich minerals nontronite, celadonite, and phengite. This difference persists on dehy-

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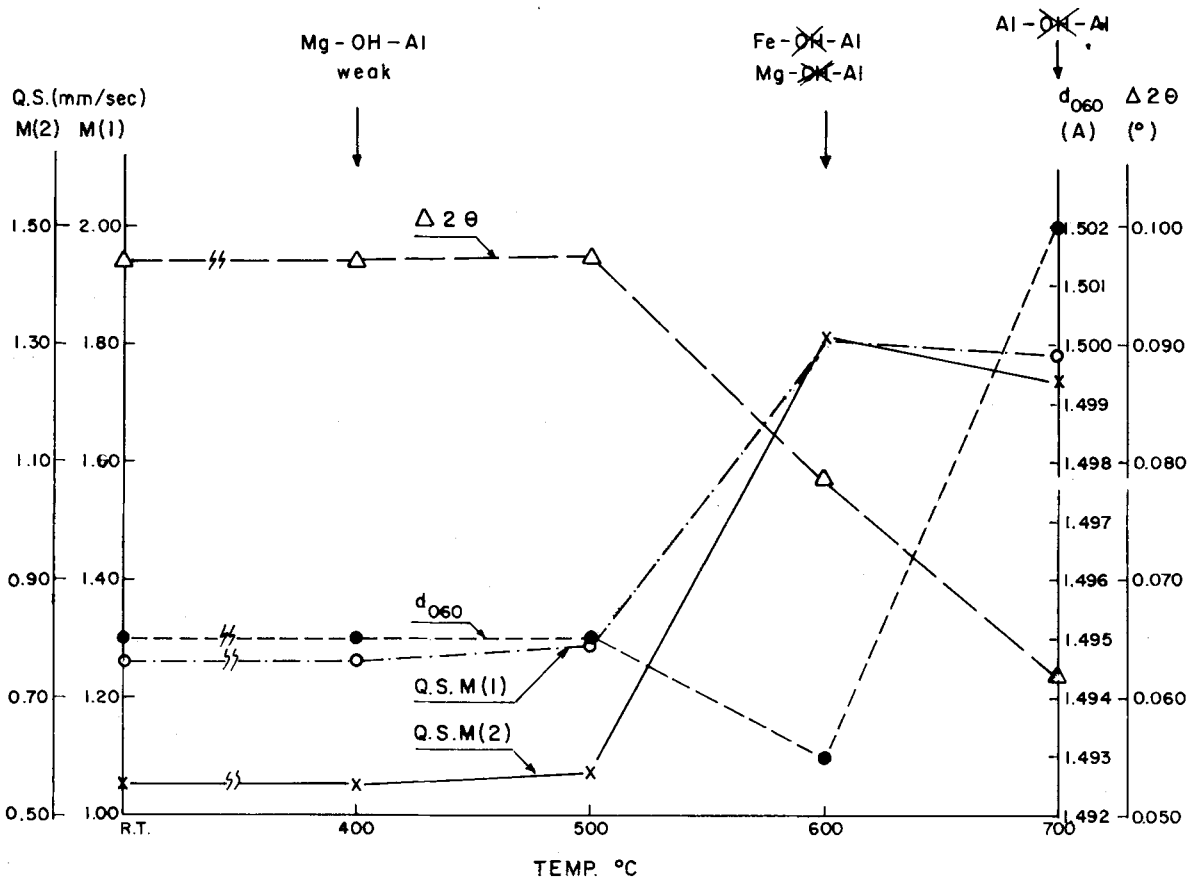


Figure 5. Correlation between Q.S., $\Delta 2\theta$, d(060), and temperature of heating of natural montmorillonite. Fe-OH-Al etc. indicates the temperature at which the corresponding IR absorption band disappeared.

droxylation. If a larger Q.S. of Fe^{3+} doublets indicates greater site distortion, as is generally accepted (Bancroft, 1974), it may be concluded that sites occupied by Fe^{3+} in iron-poor minerals are more distorted after dehydroxylation than those in their iron-rich counterparts, as was previously observed for the original minerals (Rozenson and Heller-Kallai, 1977).

The Mössbauer parameters

The quadrupole splittings of the Fe^{3+} doublets of the dehydroxylated samples are large. The smaller splittings, from 1.0 to 1.3 mm/sec, have been assigned to Fe^{3+} in 5-coordination, and the larger, from 1.6 to 1.8 mm/sec, to Fe^{3+} in distorted 6-coordination. These assignments were based on structural considerations and not on the Mössbauer parameters. It is customary in mineralogical studies to assign Fe^{3+} doublets according to their Q.S.—the larger the deviation from cubic symmetry, the greater the Q.S. It is difficult, however, to anticipate which of two sites, one with 5, the other with 6 ligands, would have the larger Q.S., even if their distortion were similar. Only two minerals are known in which Fe^{3+} may occur in 5-coordination: replacing Al in andalusite (Burnham and Buerger, 1961) and in yoderite (Fleet and Megaw, 1962).

Halenius (1978) assigned two doublets in the spectra of andalusite to Fe^{3+} in 6- and 5-coordination, but in view of the small isomer shift of the latter, the question arises whether some Fe^{3+} may be present in tetrahedral coordination (Rozenson and Heller-Kallai, 1980). Abu Eid *et al.* (1978) obtained only one Fe^{3+} doublet for yoderite, and the assignment is uncertain. Fe^{3+} occurs in 5-coordination in $BaFe_{11}O_{19}$ (Townes *et al.*, 1967) and gives rise to a doublet with the very large Q.S. of 2.01 mm/sec (Kreber *et al.*, 1975), but the site is so distorted that the structure cannot serve as a general model. Several structures have been reported in which Fe^{3+} occurs in very distorted 6-coordination, and the associated doublets have a very large Q.S., e.g., 1.8 mm/sec for andalusite (Rozenson and Heller-Kallai, 1980) and 1.97 mm/sec for epidote (Dollase, 1971). By analogy with the structure of pyrophyllite dehydroxylate (Wardle and Brindley, 1972) it is to be expected that the 6-coordinated sites in dehydroxylated phyllosilicates

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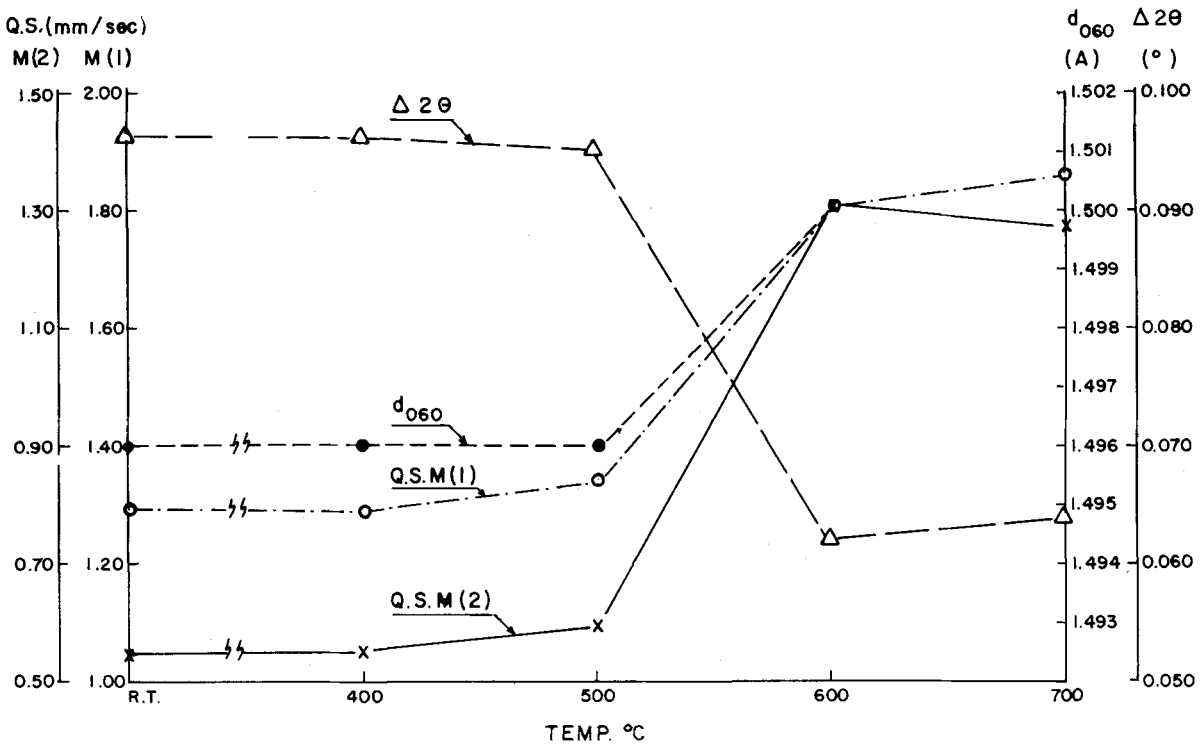


Figure 6. Correlation between Q.S., $\Delta 2\theta$, d(060), and temperature of heating of Li montmorillonite.

are very distorted. The criterion of site symmetry cannot therefore be used for any *a priori* assignment of the doublets with large Q.S. to sites either with 5- or 6-coordination.

Fe^{3+} in 4-coordination gives rise to doublets with smaller I.S. than Fe^{3+} in 6-coordination, due to the greater covalency of the bonds. Isomer shifts associated with Fe^{3+} in 5-coordination are therefore expected to be intermediate. Fe^{3+} in 5-coordination in $BaFe_{11}O_{19}$ shows a doublet with a very small I.S. which, like the large Q.S., may be attributed to the very considerable distortion of the sites (Rozenson and Heller-Kallai, 1980). The I.S., therefore, is not a reliable criterion for site assignment. In the phyllosilicate dehydroxylates examined, moreover, the doublets have similar isomer shifts. Thus neither the Q.S. nor the I.S. are diagnostic for assigning the doublets to sites with Fe^{3+} in 5- or 6-coordination, but they are compatible with assignments proposed on structural grounds.

The line widths of the Fe^{3+} doublets, particularly those of heated iron-poor specimens, are large. This may be due to a combination of two factors: (1) the high degree of disorder of the crystallites, evidenced by XRD patterns, which probably leads to a variety of cation environments, and (2) relaxation effects in samples containing low concentrations of Fe^{3+} (Rozenson *et al.*, 1979).

THE DEHYDROXYLATION PROCESS

On heating montmorillonite to 300°C, all OH bending vibrations were reduced in intensity, the Al-OH-Mg vibration being the most affected. On heating to higher temperatures this vibration became continuously weaker, but when KBr was present, it regained intensity. Heller-Kallai (1976) inferred that dehydroxylation is preceded by protonation of the OH group adjacent to the site of negative charge, but that this is reversible in the presence of a proton acceptor.

Al-OH-Mg absorption bands disappeared entirely at 600°C, together with the Al-OH-Fe absorption bands. At this stage the Q.S. of both Fe^{3+} doublets increased sharply, but only a very minor decrease in d(060) was observed, showing that although considerable changes occurred in the configuration of some of the octahedral sites, this did not appreciably alter the dimensions of the octahedral sheets. Only when most of the Al-OH-Al groups were dehydroxylated at 700°C, and $\Delta 2\theta$ reached its lowest value, was the geometry of the entire sheet modified and d(060) increased to 1.502 Å.

The localized character of some of the changes occurring in the octahedral sheets is also illustrated by Li-montmorillonite. The perturbation of the IR spectra indicates that Li penetrates into the octahedral sheets at

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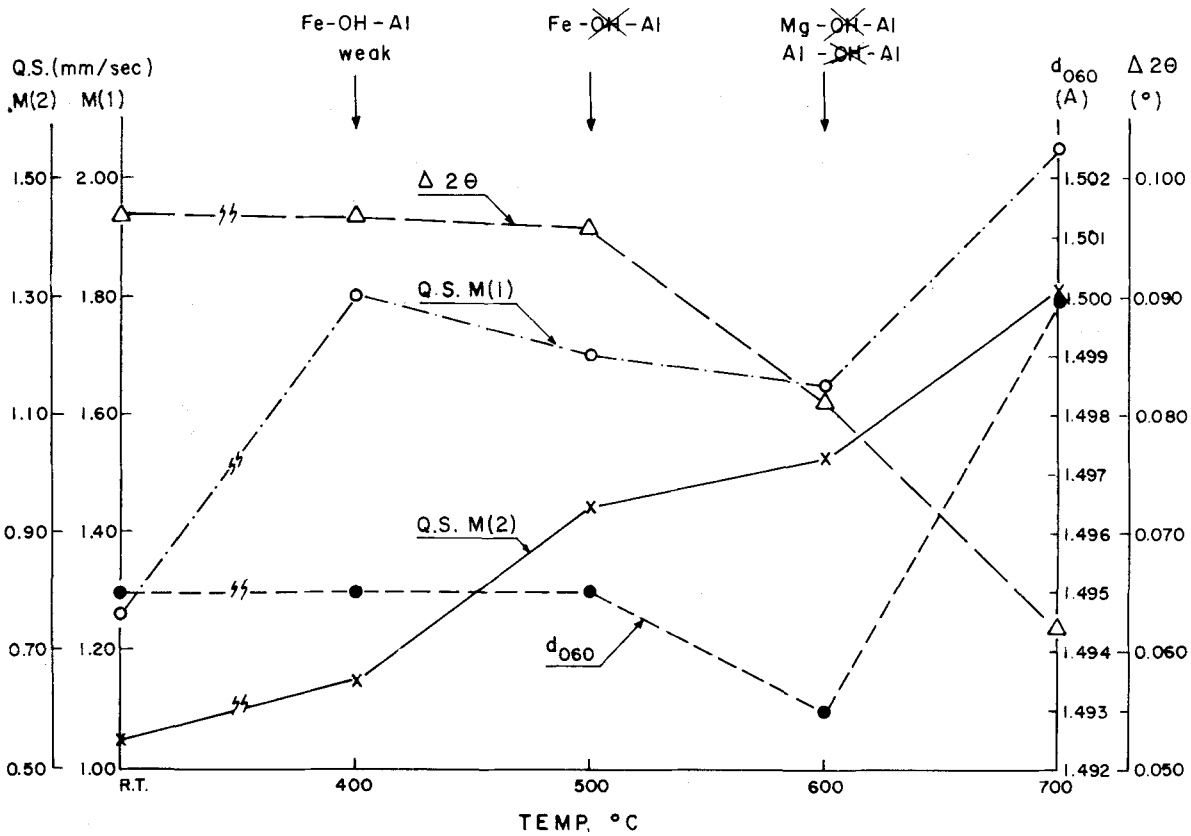


Figure 7. Correlation between Q.S., $\Delta 2\theta$, d(060), and temperature of heating of a mixture of natural montmorillonite and KBr. Fe-OH-Al etc. indicates the temperature at which the corresponding IR absorption band disappeared.

relatively low temperatures, but this was not associated with any change in the quadrupole splitting of either of the Fe^{3+} doublets, in $\Delta 2\theta$ or in d(060). The temperature at which dehydroxylation was completed was lower than that for the natural montmorillonite. None of the parameters of the dehydroxylate recorded differed from those of dehydroxylated natural montmorillonite, but the d(060) reflection could not be detected after heating at 700°C, showing that the presence of Li in the octahedral sheets reduced the stability of the dehydroxylate.

The configuration of the octahedral sheets of smectites has not been definitely established. In montmorillonite Fe^{3+} occupies M(2) sites preferentially, but some Fe^{3+} also occurs in M(1) sites (Rozenson and Heller-Kallai, 1977). The distribution of the other octahedral cations is uncertain (Grim and Güven, 1978). It was inferred from the Mössbauer spectra that Fe^{3+} ions which originally occupy M(1) and M(2) sites become 6- and 5-coordinated, respectively, after dehydroxylation. By analogy it seems probable that other cations which originally occur in M(1) and M(2) sites become similarly coordinated. If in montmorillonite, as in muscovite, octahedral Al and Mg ions predominantly occupy M(2) sites, Li which penetrates into the octahedral sheets on heating is expected to occupy vacant M(1) positions. If some Al and Mg ions initially occupy M(1) sites leaving some M(2) sites vacant, Li ions may also penetrate into M(2) positions. Whatever its coordination after dehydroxylation, the configurational effect of Li ions on the octahedral sheets is apparently confined to the immediate vicinity of the sites involved and the overall parameters are not significantly affected. The stability of the entire structure is, however, reduced.

The changes observed when montmorillonite was heated with KBr at 400–500°C were attributed to deprotonation of the Fe-OH-Al groups by reaction with KBr (Heller-Kallai, 1975, 1976). This does not affect the overall size of the octahedral sheets nor the environment of most of the Al ions. The effect of deprotonation, like that of Li penetration into the octahedral sheets, is localized. Only when most of the Al-OH-Mg and Al-OH-Al groups were dehydroxylated, after heating at 600°C, were significant changes recorded in d(060) and $\Delta 2\theta$, as in the absence of KBr. With Li-montmorillonite the presence of KBr raises the temperature at which the final values of d(060) and $\Delta 2\theta$ are reached.

In summary, changes occurring on heating mont-

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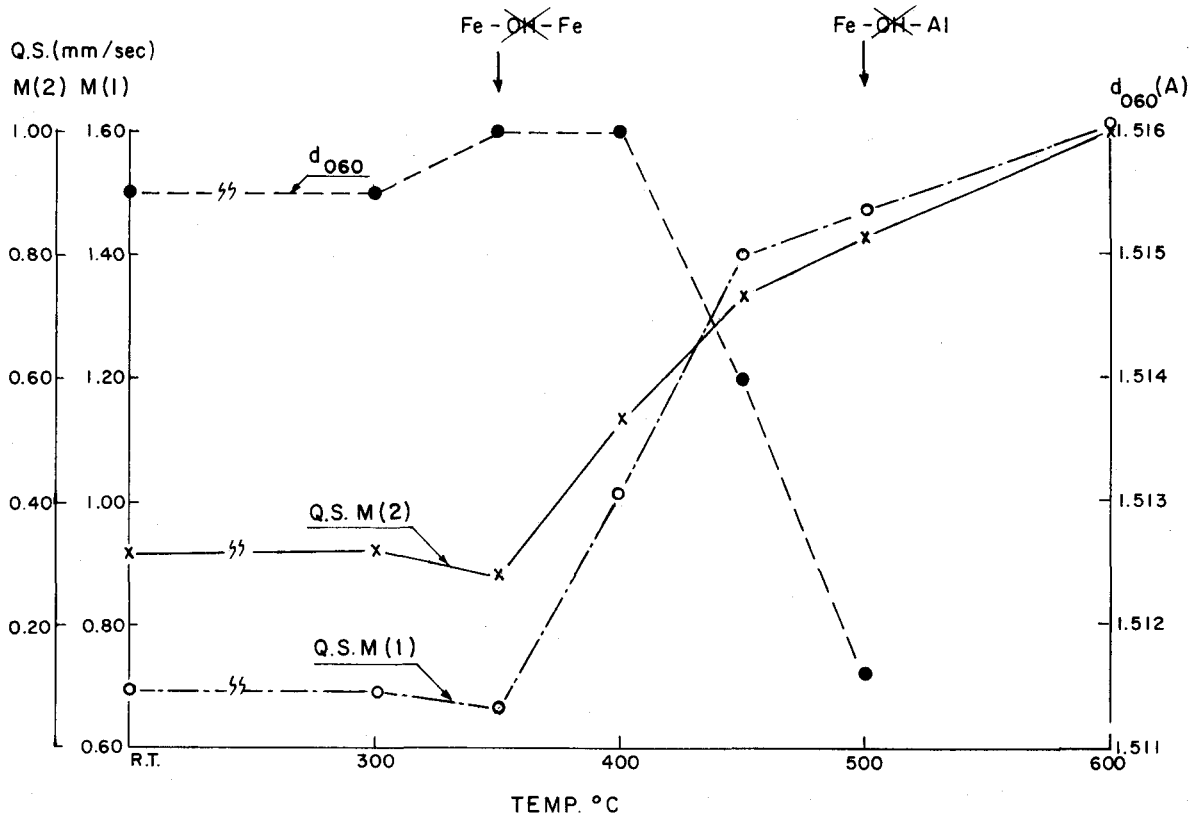
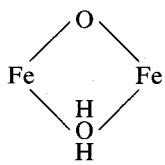


Figure 8. Correlation between Q.S., d(060), and temperature of heating of nontronite. Fe-OH-Fe etc. indicates the temperature at which the corresponding IR absorption band disappeared.

morillonite initially tend to be confined to selected sites in the octahedral sheets, without affecting the overall dimensions of the sheets or even the geometry of adjacent sites. Only when most of the octahedral groups are dehydroxylated are the parameters of the entire sheet affected.

Nontronite differs from montmorillonite in several respects. It has been shown that the overall distribution of Fe^{3+} in the octahedral sheets is random, i.e., the ratio of Fe^{3+} in M(2) and M(1) sites is 2:1 (Rozenson and Heller-Kallai, 1977). If it is assumed that octahedral Al is also randomly distributed, the probabilities that in the sample investigated octahedral groups are of the type Fe-OH-Fe or Fe-OH-Al are 47 and 29%, respectively. The probability that Al-OH-Al groups occur is only 4%. The disappearance of Fe-OH-Fe absorption bands after the sample was heated to 350°C was not associated with significant changes in d(060) or in the quadrupole splitting of the Fe^{3+} doublets. Since Fe-OH-Fe are the dominant octahedral associations in nontronite, it is difficult to envisage dehydroxylation of these groups without such changes. It is probable, therefore, that proton migration of the type



precedes dehydroxylation and that proton migration, rather than dehydroxylation, causes the Fe-OH-Fe absorption band to disappear. This assumption is supported by the observation that, in contrast to the effect observed with montmorillonite, heating nontronite with KBr delays the disappearance of the Fe-OH-Fe vibrations, probably due to the fact that partial $K \rightleftharpoons H$ exchange reduces the probability of proton transfer. At higher temperatures the quadrupole splittings increased, indicating that dehydroxylation occurred. The Fe-OH-Al absorption band disappeared, but the associated changes in d(060) were relatively small. Dehydroxylation was completed at lower temperatures than with montmorillonite and the dehydroxylate was less stable.

Nontronite differed from all other samples examined in one respect; while the increase in Q.S. on heating

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occurred abruptly in all the other samples examined, it was gradual with nontronite, extending over a temperature range of about 250°C. It seems that the octahedral sheets of this iron-rich mineral assume some intermediate configuration before reaching that of the dehydroxylate. Celadonite, which is also rich in iron, shows an abrupt change in Q.S., possibly due to the greater rigidity of the structure.

In other respects the dehydroxylation of celadonite resembles that of nontronite, whereas muscovite corresponds to montmorillonite. Dehydroxylation of Fe-OH-Al groups in muscovite occurred at a much lower temperature than that of Al-OH-Al groups. Celadonite was dehydroxylated at a lower temperature than muscovite, losing Fe-OH-Fe and Fe-OH-Mg before Al-OH-Mg groups.

The dehydroxylates of the iron-rich minerals nontronite and celadonite were unstable. Celadonite partially disintegrated on heating to 530°C, and gave a weak Mössbauer spectrum of hematite. Nontronite disintegrated on heating to 600°C, in contrast to montmorillonite and muscovite dehydroxylates, which were stable to this and even higher temperatures.

OXIDATION OF Fe^{2+}

The proportion of Fe^{2+} in the samples, deduced from the Mössbauer spectra of the unheated minerals, is included in Tables 1–5. On heating the samples, the Fe^{2+} doublets became progressively weaker, but no change was observed in the other parameters of the doublets. After dehydroxylation all Fe was in the trivalent form, even when the samples were heated in vacuum, and the doublets associated with Fe^{3+} derived from Fe^{2+} could not be differentiated from those of Fe^{3+} in the original minerals. Such results were obtained with all samples containing Fe^{2+}, but were particularly well demonstrated by the phengites studied, one of which contained only Fe^{2+} and the other both Fe^{2+} and Fe^{3+}, yet the dehydroxylates were identical.

In none of the samples examined was a change observed in the Mössbauer parameters of the Fe^{2+} doublets that could be correlated with dehydroxylation of Fe^{2+}. It appears that dehydroxylation of Fe^{2+} is preceded or accompanied by oxidation. It may be speculated that on oxidation charge balance is maintained by the loss of protons. The bond strength between Fe and the remaining hydroxyl is thereby reduced, facilitating loss of this group by combination with a structural proton to form water. Oxidation of Fe^{2+} may thus be associated with dehydroxylation.

It was noted previously that, on oxidation at ambient temperatures, Fe^{2+} in montmorillonite became indistinguishable from Fe^{3+} by Mössbauer spectroscopy (Rozenson and Heller-Kallai, 1978). In the original mineral Fe^{2+} occupied M(2) sites preferentially. If oxidation is associated with deprotonation of one hydroxyl group and loss of the other, a doublet with large Q.S. would arise, which is similar to that characteristic of Fe^{3+} in M(1) sites and would coincide with it. If deprotonation were not associated with loss of the second hydroxyl group, a doublet with different Q.S. would be expected. The Mössbauer spectra, therefore, suggest that oxidation of structural Fe in montmorillonite and other phyllosilicates may entail dehydroxylation, even at low temperatures. Deprotonation of some of the hydroxyl groups tends to isolate others, some of which may then be preserved in the structure beyond the stage at which most of the dehydroxylation takes place.

CONCLUSIONS

The Mössbauer spectra, interpreted in the light of the known crystal structures, showed that iron which originally occupied M(2) sites became 5-coordinated, and that in M(1) sites, 6-coordinated on dehydroxylation. By analogy it can be speculated that other octahedral cations became similarly coordinated. The 6-coordinated sites are very distorted.

Samples with high iron content disintegrate at lower temperatures than their iron-poor counterparts, expelling iron oxide from the structure. Disintegration may even precede complete dehydroxylation.

No migration of octahedral cations was observed under the thermal regime employed in this study (1–3 hr heating; $T \leq 700$°C), in contrast to samples subjected to more prolonged heat treatment, described by Rozenson and Heller-Kallai (1980).

The XRD, XRF, IR, and Mössbauer data show that dehydroxylation does not occur uniformly throughout the structure. In iron-poor minerals proton migration is followed by dehydroxylation of Al-OH-Mg and Al-OH-Fe groups. The associated structural changes, like those accompanying the migration of Li from interlayers into octahedral sheets on heating, are localized and do not affect the overall parameters. These parameters are changed only when most of the Al-OH-Al groups have been dehydroxylated. Dehydroxylation of iron-rich minerals commences with Fe-OH-Fe and Fe-OH-Mg groups.

The presence of KBr, acting as a proton acceptor, affects the course and temperature of dehydroxylation, but not the configuration of the 5- and 6-coordinated sites of the product.

Fe^{2+} in the minerals is oxidized either before or during dehydroxylation.

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Резюме—Моссбауероская спектроскопия диоктаэдрических листовых силикатов показала, что при дегидроксилировании железо, которое первоначально занимало места M(2) и M(1), становилось соответственно 5- и 6-координированным. 6-координированные места являются очень деформированными. Не происходит никакой миграции катионов во время прокаливания образцов в течение от 1 до 3 часов при 600°–700°C.

Используя комплекс нескольких физикохимических методов, можно выделить несколько последующих фаз процесса дегидроксилирования (1) миграция протонов; (2) локализованное дегидроксилирование индивидуальных ассоцнаций без значительных изменений в общей конфигурации октаэдрических листов; и (3) потеря большинства гидроксильных групп с сопутствующими изменениями размеров ячеек. Проникновение Li в октаэдрические листы не влияет на ход реакции, но понижает температуру дегидроксилирования и устойчивость продуктов.

С дегидроксилированием было связано или предшествовало ему окисление любого присутствующего двухвалентного железа. Fe^{3+}, полученное из Fe^{2+} было неотличимо Моссбауеровской спектроскопией от железа первоначально присутствующего в трехвалентной форме. Высокие концентрации Fe понижают температуру дегидроксилирования и уменьшают устойчивость дегидроксилата до такой степени, что частичная дезинтеграция может предшествовать полному дегидроксилированию. [N.R.]

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Resümee—Die Mössbauerspektroskopie von dioktaedrischen Phyllosilikaten zeigte, daß das Eisen, das ursprünglich die M(2) und M(1) Plätze besetzte, bei der Dehydroxylierung 5- bzw. 6-koordiniert wird. Die 6-koordinierten Plätze sind stark verzerrt. Beim Erhitzen der Proben auf 600°–700°C für 1–3 Stunden findet keine Wanderung der Kationen statt.

Mehrere aufeinanderfolgende Stadien des Dehydroxylierungsprozesses können durch die Verwendung einer Kombination von mehreren physikochemischen Methoden unterschieden werden: (1) eine Wanderung von Protonen; (2) eine lokalisierte Dehydroxylierung einzelner Bereiche ohne wesentliche Änderung in der gesamten Konfiguration der oktaedrischen Schichten; (3) Verlust der meisten Hydroxylgruppen mit daraus folgenden Veränderungen der Zelldimensionen. Das Eindringen von Li in die oktaedrischen Schichten beeinflußt den Reaktionsverlauf nicht, reduziert jedoch die Dehydroxylierungstemperatur und die Stabilität der Produkte.

Vor der Dehydroxylierung oder gleichzeitig damit oxidiert das vorhandene zweiwertige Eisen. Fe^{3+}, das aus Fe^{2+} hervorgegangen ist, konnte mittels Mössbauerspektroskopie nicht von Eisen unterschieden werden, das schon immer in dreiwertiger Form vorlag. Hohe Fe-Konzentrationen erniedrigen die Dehydroxylierungstemperatur und können die stabilität des Dehydroxylats bis zu einem Ausmaß reduzieren, daß es vor der vollständigen Dehydroxylierung teilweise zerfällt. [U.W.]

Résumé—La spectroscopie de Mössbauer de phyllosilicates dioctaédrales montre que lors de la déshydroxylation, le fer qui occupait originalement les sites M(2) et M(1) devenait, respectivement coordonné-5 et -6. Les sites coordonnés-6 sont très déformés. Il n'y a aucune migration d'ions pendant l'échauffement des specimens pour 1–3 heures à 600°–700°C.

Par l'utilisation de plusieurs méthodes physicochimiques, différentes étapes successives du procédé de déshydroxylation pouvaient être distinguées: (1) la migration de protons; (2) la déshydroxylation localisée d'associations individuelles sans que des changements significatifs ne se produisent dans la configuration générale des feuillets octaédraux; (3) la perte de la plupart des groupes hydroxyles avec des changements concomitants dans les dimensions des mailles. La pénétration de Li dans les feuillets octaédraux n'affecte pas la suite des réactions mais réduit la température de déshydroxylation et la stabilité des produits.

La déshydroxylation était précedée ou accompagnée de l'oxidation de n'importe quel fer divalent présent. On ne pouvait distinguer par spectroscopie de Mössbauer Fe^{3+} derivé de Fe^{2+}, du fer initialement présent dans la forme trivalente. De hautes concentrations de Fe abaissent la température de déshydroxylation et réduisent la stabilité du déshydroxylate à tel point qu'une désintégration partielle peut précéder une déshydroxylation complète. [D.J.]

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