

MÖSSBAUER STUDIES OF PALYGORSKITE AND SOME ASPECTS OF PALYGORSKITE MINERALOGY

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Abstract— Fe^{3+} ions in palygorskite occupy sites at the edges and in the interior of the aluminosilicate chains. The Mössbauer parameters of the doublets associated with Fe^{3+} ions in edge sites indicate that the sites have a regular 6 coordination. Fe^{3+} ions in the interior of the chains occupy M(1) sites in three of the samples examined and M(2) sites in the fourth. Fe^{3+} ions in edge positions of palygorskite become 5-coordinated when water is lost on heating. They maintain this coordination on dehydroxylation, probably by cross-linking of the chains. The temperatures at which changes occur in the X-ray powder diffraction patterns and the Mössbauer and infrared (IR) spectra differ from sample to sample. The intermediate stages observed also vary, either due to different reaction paths or to different stabilities of the intermediate phases. The deduced distribution of cations in the octahedral sheets is in good qualitative agreement with the observed IR hydroxyl absorptions.

Key Words—Infrared spectroscopy, Iron, Mössbauer spectroscopy, Palygorskite, Sepiolite, Thermal treatment, X-ray powder diffraction.

INTRODUCTION

By using the results of Mössbauer spectroscopy in conjunction with other methods, Heller-Kallai and Rozenson (1980) were able to establish the distribution of cations in dioctahedral phyllosilicates and to follow changes in these minerals on heating. Although more than 100 papers have been published in recent years dealing with Mössbauer studies of various clay minerals, palygorskite and sepiolite do not seem to have been studied by this technique. A preliminary investigation of several samples of palygorskite showed that the Mössbauer spectra contained a doublet with parameters unlike those of any other phyllosilicate previously investigated. A similar doublet was noted in the spectrum of a sample of sepiolite. To verify the intuitive assignment of these doublets to iron occupying sites at the edges of the channels in these structures and to follow the changes in the iron positions in heated samples, the following study was undertaken.

EXPERIMENTAL

Materials

The following samples were used: (1) Palygorskite from Gasden County, Florida, C.M.S. Source Clay PFI-1 (Flor.); (2) Palygorskite from Attapulugus, Georgia, A.P.I. Reference Clay 44, Ward's Natural Science Establishment, Rochester, New York; (3) Palygorskites from (a) Mt. Flinders (Mt. F.) and (b) Mt. Grainger (Mt. G.), Australia; (4) Sepiolite from Vallecas, Spain (Sep. V.); and (5) Sepiolite from Madagascar (Sep. M.). The samples from Mt. Grainger and Mt. Flinders were aliquots of those described previously (Singer and Norrish, 1974; Singer, 1977). They had been treated with a weak acid and with dithionate to

remove carbonates and iron oxides. The Madagascar sample was described by Caillère (1951). The Al, Mg, and Fe contents of the octahedral sheets of some of the samples, calculated from literature data, are shown in Table 5, column A.

Methods

The samples were examined in their original form and after heating in air for 1 hr at temperatures up to 700°C. X-ray powder diffraction (XRD) patterns were recorded of samples sedimented on glass slides with filtered $\text{CuK}\alpha$ radiation and a recording rate of $2^\circ/2\theta/\text{min}$. Infrared (IR) spectra were obtained from self-supporting films of the Florida and Mt. Grainger samples and from KBr disks of all palygorskite specimens, using a Perkin Elmer 237 IR spectrograph. Mössbauer spectra of all samples were recorded and resolved as previously described (Rozenson *et al.*, 1979). Spectra of some of the heated samples showed very broad doublets. Resolution into two or more doublets gave rise to very large errors in the Mössbauer parameters. Attempts were therefore made to constrain some of the parameters by assuming that the samples consisted of a mixture of varying proportions of the original and the dehydroxylated material, but errors of as much as 60% persisted in the line widths and intensities of the doublets, and the decrease in χ^2 was insignificant (~ 20).

RESULTS AND DISCUSSION

Mössbauer spectra of palygorskite

The Mössbauer parameters derived from the spectra of three samples of palygorskite are presented in Table 1. The spectrum of the Attapulugus sample is identical with that of the Florida sample. Two of the spectra are

Table 1. Mössbauer parameters of samples of palygorskite, sepiolite, and heated palygorskite.

Sample ¹	Temp. (°C)	Fe ³⁺ (edge)				Fe ³⁺ (interior)				Site
		I.S.	Q.S.	Γ	%	I.S.	Q.S.	Γ	%	
Mt. F.	R.T.	0.42 (1)	0.24 (1)	0.40 (1)	76 (1)	0.41 (1)	1.06 (1)	0.40 (1)	24 (2)	M (1)
Mt. G.	R.T.	0.41 (1)	0.30 (1)	0.41 (1)	69 (1)	0.40 (1)	1.16 (1)	0.41 (1)	31 (2)	M (1)
Flor.	R.T.	0.40 (1)	0.24 (1)	0.51 (1)	35 (2)	0.40 (1)	0.56 (1)	0.50 (1)	65 (2)	M (2)
Sep. V.	R.T.	0.40 (1)	0.30 (1)	0.62 (2)	20 (3)	0.41 (1)	0.67 (1)	0.60 (1)	80 (3)	M (2)
Sep. M. ²	R.T.					0.39 (1)	0.80 (1)	0.80 (1)	85 (2)	M (1)
Mt. F.*	400	0.36 (1)	0.81 (1)	0.66 (1)	100					
Mt. F.*	500	0.39 (1)	1.10 (1)	1.00 (1)	100					
Mt. F.	600	0.36 (1)	1.09 (1)	0.50 (1)	72 (2)	0.38 (1)	1.78 (1)	0.50 (1)	23 (2)	M (1)
Mt. F.	700	0.37 (1)	1.07 (1)	0.49 (1)	75 (2)	0.38 (1)	1.81 (1)	0.49 (1)	25 (2)	M (1)
Mt. G.*	400	0.37 (1)	0.79 (1)	0.58 (1)	100					
Mt. G.*	500	0.38 (1)	1.06 (1)	0.85 (1)	100					
Mt. G.	600	0.37 (1)	1.08 (1)	0.54 (1)	70 (3)	0.38 (1)	1.78 (1)	0.53 (1)	30 (2)	M (1)
Flor.*	500	0.38 (1)	1.14 (1)	0.66 (1)	100					
Flor.*	600	0.38 (1)	1.22 (1)	0.70 (1)	100					
Flor.*	700	0.38 (1)	1.35 (1)	0.61 (1)	100					

Abbreviations: I.S. = isomer shift relative to Fe; Q.S. = quadrupole splitting; τ = line width, (all in mm/sec).

¹ Asterisks indicate that the spectrum was difficult to resolve (see text).

² Also contains Fe²⁺ in M (2) sites: I.S. 1.41 (1), Q.S. 2.64 (1), Γ 0.39 (1), % 15.

shown in Figure 1. All three spectra show a doublet with quadrupole splitting (Q.S.) between 0.24 and 0.30 mm/sec, which is much lower than that of any other Fe-*ophyllosilicate* reported in the literature. The spectra of the Mt. Flinders and Mt. Grainger samples show an additional doublet with Q.S. equal to 1.06 and 1.16 mm/sec, respectively, resembling that of Fe³⁺ in M(1) [trans] sites, whereas the spectrum of the Georgia samples shows a doublet with a Q.S. of 0.56 mm/sec, corresponding to Fe³⁺ in M(2) [cis] sites of Al-rich *phyllosilicates* (Heller-Kallai and Rozenson, 1980). All isomer shifts (I.S.) range from 0.39 to 0.41 mm/sec, characteristic of Fe³⁺ in 6-fold coordination. The line widths are similar to those observed in other *phyllosilicates*, and no further resolution of the spectra was therefore attempted.

According to the structural model proposed by Bradley (1940), palygorskite is composed of aluminosilicate ribbons with five octahedral sites per unit cell. Chemical analyses show that about four of these sites are occupied. The three inner positions are analogous to those in sheet silicates, i.e., one M(1) and two M(2) sites, whereas the remaining two sites are unlike those in any other *phyllosilicate* except sepiolite. According to Serna *et al.* (1977), all outer sites are occupied by cations coordinated by four oxygen and two H₂O ligands, and one of the three inner sites is vacant. In view of the unique character of the edge sites it seemed reasonable to assign the doublet with the unusually low Q.S. to Fe³⁺ in these positions. The very low Q.S. indicates that the site is relatively undistorted.

To confirm this assignment, Mössbauer spectra of two samples of sepiolite were recorded (Table 1). One of the spectra does, indeed, show a doublet with Q.S. similar to that observed with palygorskite. The other

sample contains some Fe²⁺ and gave rise to a broad doublet with parameters similar to those of Fe³⁺ in M(1) sites in *trioctahedral minerals*. The doublet is probably composite, but it could not be meaningfully resolved.

The presence of a doublet with low Q.S. in sepiolite resembling that in palygorskite, despite the difference in the chemical composition of palygorskite and sepiolite, strongly supports the proposed assignment. It also confirms that this doublet is not due to impurities in the samples. Although the samples from Mt. Grainger and Mt. Flinders were highly purified, it might be argued that minor amounts of an unusual iron-rich impurity may be specifically associated with palygorskite. The presence of this doublet in spectra of four palygorskites from different localities and of a sample of sepiolite, which is the only other *phyllosilicate* structurally similar to palygorskite, discredits this argument.

Effect of heating palygorskite

The effect of heating palygorskite has been studied by several investigators, most recently by Van Scoyoc *et al.* (1979). On heating Georgia palygorskite, zeolitic and coordinated water molecules were given off. When 50% of the coordinated water had been lost, the structure folded, but an ordered state was not reached until 65% of the water had evolved. Loss of water caused an initial decrease in the spacing of the prominent 110 reflection from 10.3 to 9.9 Å. At higher temperatures the chains folded, and a new reflection appeared at 9.2 Å, which decreased to 8.7 Å on further heating. The OH-stretching frequencies changed when only small amounts of coordinated water were lost. The original Al-OH-Al absorption at 3625 cm⁻¹ was gradually replaced by absorptions at 3657 and 3644 cm⁻¹. When the amount of coordinated water was reduced to 35% only

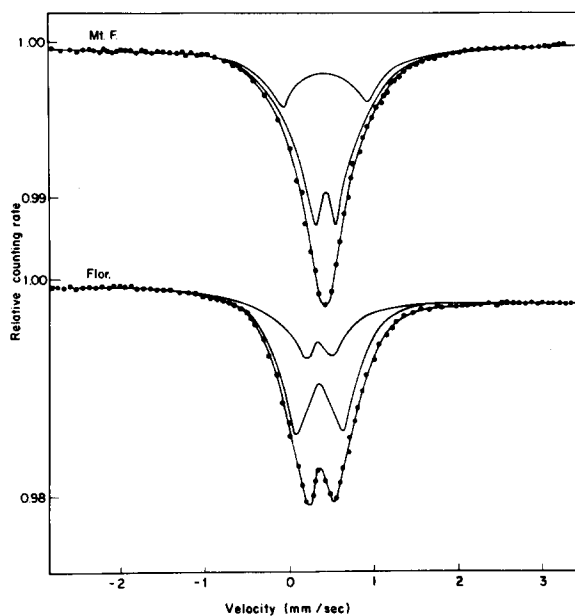


Figure 1. Mössbauer spectra of palygorskites.

one Al-OH-Al absorption persisted, at 3644 cm^{-1} (Van Scoyoc *et al.*, 1979). Whether these spectral features were due to changes in configuration or whether some dehydroxylation took place, leaving Al-OH-Al groups in only one single environment, is unclear from the IR data. Loss of the remaining 35% coordinated water was accompanied by dehydroxylation. Preisinger (1963) proposed a model for palygorskite "anhydride" with $a = 10.7\text{ \AA}$, $b = 15.3\text{ \AA}$, $c = 5.26\text{ \AA}$, $\alpha \sim 90^\circ$. The powder data calculated from these cell dimensions are in good agreement with those obtained from the 8.7-\AA form of the mineral produced in the present study. In the structural scheme of Preisinger the chains are cross-

Table 2. Selected physicochemical constants of palygorskite, Gasden County, Florida.¹

Temp. (°C)	X-ray diffraction spacing larger than 8 Å (Å)	IR absorption in the OH bending region (930–850 cm^{-1}) (cm^{-1})	Mössbauer spectra Q.S. (mm/sec)	Atom ratio: Fe ³⁺ (edge) / Fe ³⁺ (interior)
R.T.	10.4	915 860	0.24	0.56
600	9.8, 9.2	915 875	1.22	* ²
700	practically amorphous	865	1.35	*

¹ C.M.S. Source Clay PFI-1.

² Asterisks indicate that the spectrum was difficult to resolve (see text).

Table 3. Selected physicochemical constants of palygorskite, Mt. Flinders, Australia.

Temp. (°C)	X-ray diffraction spacing larger than 8 Å (Å)	IR absorption in the OH bending region (930–850 cm^{-1}) (cm^{-1})	Mössbauer spectra Q.S. (mm/sec)	Atom ratio: Fe ³⁺ (edge) / Fe ³⁺ (interior)
R.T.	10.4	910 880 850	0.24	1.06
400	10.4	910 870	0.81	* ¹
500	10.4	910 870	1.10	*
600	8.75	865	1.09	1.78
700	8.8	865		

¹ Asterisks indicate that the spectrum was difficult to resolve (see text).

linked, leading to 5 coordination of the cations occupying edge positions.

Some of the thermal changes observed with three samples of palygorskite in this study are shown in Tables 2–4. The XRD data alone suffice to show that loss of water takes different courses in these minerals. With the Florida sample a 9.2-\AA spacing appeared after heating at 500°C . However, a 9.8-\AA spacing, corresponding to the unfolded structure, persisted even after heating at 600°C . After heating at 700°C the sample was practically amorphous.

The Mt. Flinders sample showed an abrupt transition

Table 4. Selected physicochemical constants of palygorskite, Mt. Grainger, Australia.

Temp. (°C)	X-ray diffraction spacing larger than 8 Å ¹ (Å)	IR absorption in the OH bending region ¹ (930–850 cm^{-1}) (cm^{-1})	Mössbauer spectra Q.S. (mm/sec)	Atom ratio: Fe ³⁺ (edge) / Fe ³⁺ (interior)
R.T.	10.3	910 860	0.30	1.16
400	10.3	910 860	0.79	* ²
500	10.3	910 880w 865	1.06	*
550	10.9 9.55	880vw		
600	10.9vw 9.55vw		1.08	1.78

¹ w = weak, vw = very weak.

² Asterisks indicate that the spectrum was difficult to resolve (see text).

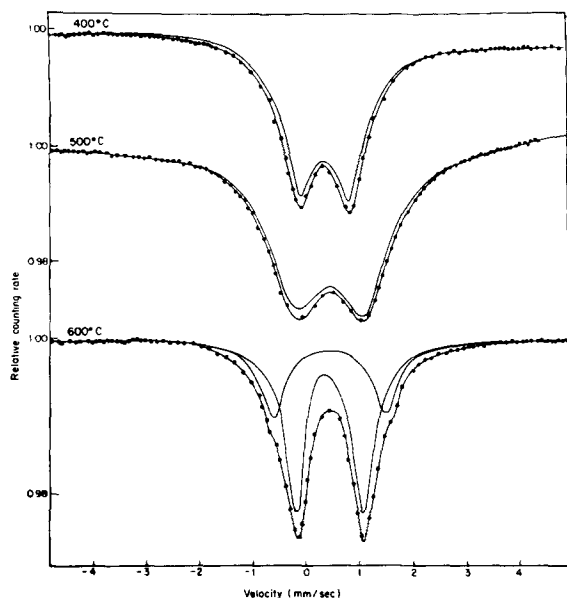


Figure 2. Mössbauer spectra of heated samples of palygorskite from Mt. Flinders, Australia.

from the 10.4- to the 8.75-Å form; the latter form remained stable over a relatively wide range of temperature. The Mt. Grainger sample behaved drastically different from the other two. The 10.3-Å form persisted after heating at 500°C, but at 550°C a new phase crystallized which gave rise to a distinct XRD pattern with strong reflections at 10.9, 9.55, 5.47, and 4.27 Å. A similar, but considerably weaker pattern was recorded after heating the sample at 600°C.

Scanning electron micrographs showed that the samples preserved their acicular shapes after heating at 550°C and, to a lesser extent, after heating at 600°C. The needles were somewhat expanded and rugged, but remained clearly recognizable even when the XRD patterns indicated that a fundamental change in crystal structure had occurred.

Hydroxyl-stretching vibrations and the OH-bending

vibration at about 910 cm^{-1} were detected whenever the 110 reflection was greater than 8.7 Å. The broad absorption at 860–880 cm^{-1} , which was assigned to Mg-OH-Al and Fe-OH-Al associations (see below), was not diagnostic because the "anhydride" form showed an absorption at about 865 cm^{-1} , which became progressively more pronounced as the 8.7-Å form developed.

The Mössbauer spectra require more detailed consideration. The parameters of the heated samples are shown in Table 1, and changes in Q.S. are included in Tables 2–4. It is evident that the Mössbauer parameters began to change at a lower temperature than the XRD pattern or the IR absorption at 910 cm^{-1} , assigned to Al-OH-Al vibrations by Farmer (1979). With increasing temperature of heating a small reduction in I.S. was observed, together with an appreciable increase in Q.S. and line width. It is difficult to resolve the spectra of samples heated at temperatures below that corresponding to complete dehydroxylation (marked with an asterisk in the Tables), probably because Fe^{3+} occurs in a number of sites of somewhat different configuration (Figures 2, 400° and 500°C). After complete dehydroxylation the Mt. Flinders and Mt. Grainger samples gave rise to two doublets with Q.S. values of about 1.08 and 1.80 mm/sec, respectively (Figure 2, 600°C), whereas the Florida sample showed a single, broad doublet with Q.S. \sim 1.35 mm/sec.

The octahedral Fe^{3+} in phyllosilicates becomes 5 coordinated on heating if it occupies M(2) sites and assumes a very distorted 6 coordination if it occupies M(1) sites in the original mineral (Heller-Kallai and Rozenon, 1980). The observed Q.S. for minerals with low iron content ranged from 0.96 to 1.36 mm/sec and from 1.68 to 1.80 mm/sec for 5- and 6-coordinated sites, respectively. Accordingly, the Q.S. of the two doublets of completely dehydroxylated palygorskite from Mt. Flinders and Mt. Grainger (Table 1) correspond to Fe^{3+} in 5 and 6 coordination. The single, unresolved doublet of the Florida sample corresponds to Fe^{3+} in 5-coordinated sites only. If edge sites become 5-coordinated on dehydroxylation, as suggested by Preisinger (1963),

Table 5. Population of octahedral sheets (vacancies not included).

Sample	Column A Octahedral cations per 8 tetrahedral cations			Column B Population of interior of chains per 8 tetrahedral cations ¹			Column C Probability of encountering cation associations				
	Al	Mg	Fe	Al	Mg	Fe	Al-Al	Al-Mg	Al-Fe	Mg-Fe	Mg-Mg
Flor. ²	1.15	2.15	0.36	1.48	0.13	0.19	0.68	0.12	0.17	0.01	0.02
Mt. F ³	0.92	2.70	0.48	0.92	1.07	0.11	0.21	0.45	0.05	0.05	0.24
Mt. G. ⁴	1.84	1.68	0.16	1.84 ⁵ or 1.68 ⁶			1.00				

¹ Deduced from the chemical analyses and Mössbauer spectra (see text).

² Calculated from the chemical analysis in van Olphen and Fripiat (1979, p. 128).

³ Singer (1977).

⁴ Calculated from the chemical analysis given by Singer and Norrish (1974).

⁵ Vacancies in edge sites.

⁶ Al in edge sites.

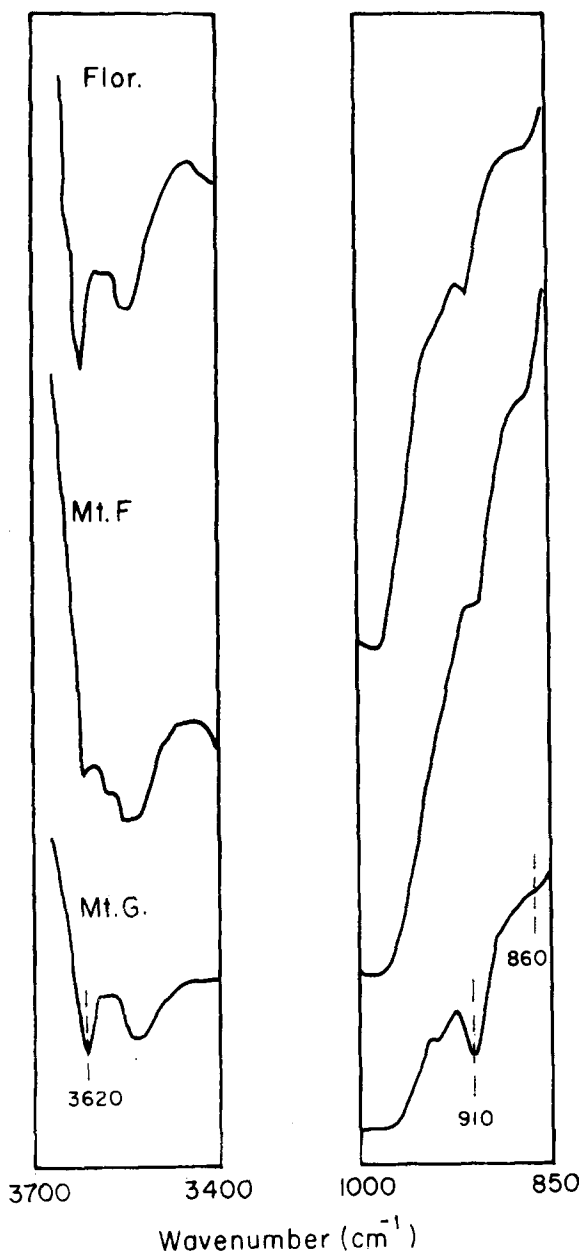


Figure 3. Infrared spectra of palygorskites.

at least two nonequivalent 5-coordinated sites are expected in the dehydroxylated Florida sample, i.e., edge sites and sites in the interior of the chains which originally had an M(2) configuration. In the dehydroxylated Mt. Flinders and Mt. Grainger samples Fe^{3+} should be present in 5-coordinated edge sites and in distorted 6 coordination derived from M(1) sites, as was indeed observed. The Mössbauer spectra thus confirmed the cross-linking of the chains in palygorskite dehydroxylate proposed by Preisinger (1963), although the details of his proposed structure, with fully hydroxylated, trioctahedral chains, are incorrect.

Samples heated at intermediate temperatures showed an increase in Q.S. of the doublets corresponding to the edge sites. The I.S. values ranged from 0.37 to 0.42 mm/sec throughout, indicating that Fe^{3+} did not become tetrahedrally coordinated. It may therefore be inferred that Fe^{3+} in edge positions tends to retain a single coordinated H_2O molecule as established by Serna *et al.* (1977) for Mg in similar positions. The edge sites thus change from an original octahedral configuration with four O and two OH ligands to a 5-coordinated configuration with four O and one OH ligand and finally to a 5-coordinated configuration with five O ligands. It is, of course, possible that intermediate phases with 4-coordinated Fe^{3+} , i.e., with four O ligands, were briefly formed, but escaped detection.

Infrared spectra of the Florida and Mt. Flinders samples show that dehydroxylation of the Al-OH-Al association was complete only when the mineral reached the folded 8.7-Å form. Whether dehydroxylation of iron-containing hydroxyl associations occurred at a lower temperature than that of hydroxyl associations, as was observed with other dioctahedral phyllosilicates (Heller-Kallai and Rozenson, 1980), is difficult to establish. The initial changes in the Mössbauer spectra, which were observed on heating the samples, are due to modifications of the edge sites. After heating the samples at higher temperatures the spectra are difficult to resolve, but this may be due to distortion of the sites which form in the course of folding and crosslinking of the chains and does not necessarily indicate that dehydroxylation of Fe associations is incomplete.

Population of the octahedral sites

Serna *et al.* (1977) affirmed that most of the Mg ions in Georgia palygorskite occupy positions at the edges of the channels and are bonded to coordinated water. They based their conclusion on (1) the fact that no IR absorption was observed at 3680 cm^{-1} , as would have been expected for three neighboring Mg ions in a trioctahedral structure, and (2) the observation that only one kind of coordinated water was present. However, only the second argument is valid, because, as Serna *et al.* (1977) themselves demonstrated, the interior of the chains is dioctahedral. Thus, even if Mg occupied positions in the interior, associations of the type $(\text{Mg Mg } \square)\text{OH}$ (\square = vacancy) and not $(\text{Mg Mg Mg})\text{OH}$ would be expected to predominate. The conclusion that Fe ions occupy edge positions preferentially in the Mt. Grainger and Mt. Flinders samples, based on the Mössbauer spectra, receives support from an earlier study of acid attack of these samples (Singer, 1977). Singer showed that octahedral cations were extracted in the order $\text{Fe} > \text{Mg} > \text{Al}$ and attributed this to their decreasing accessibility. It is reasonable to assume that cations occupying positions at the edges of the chains are more accessible than those in the interior, suggesting that Fe, and to a lesser degree Mg, tend to occupy

edge positions in these samples. The Mössbauer spectrum of the Florida sample shows that Fe³⁺ does not occupy edge positions preferentially. These positions may therefore be populated predominantly by Mg, as suggested by Serna *et al.* (1977) for the sample from Georgia.

The Fe, Mg, and Al content of the octahedral sheets of the samples studied is shown in Table 5, column A. If Fe ions are assigned to edge positions on the basis of the Mössbauer spectra and the remaining edge positions are filled with Mg ions, the composition of the interior of the chains can be deduced from the chemical composition. The results are shown in Table 5, column B, and the probabilities of encountering various associations in the interior of the chains, deduced from these data, are shown in Table 5, column C. In calculating the probabilities, two assumptions were made: (1) All edge positions which are not occupied by Fe are filled by Mg; and (2) The cations occupying the interior of the chains have no preference for any particular nearest neighbor. If some Al ions occupy edge positions, the number of Al containing associations are overestimated, whereas the number of Mg containing associations are underestimated. Similarly, vacancies in edge sites would cause the calculated number of Mg-containing groups to be too low. In the Mt. Grainger sample there are insufficient Fe and Mg ions to fill the edge positions completely. The remaining sites may be vacant or filled by Al ions. In either case the interior positions are expected to be occupied predominantly or entirely by Al ions.

The estimates in Table 5, column C, must be regarded as approximations, but they are consistent with the IR spectra. Serna *et al.* (1977) showed that it is difficult to differentiate between structural and adsorbed water without deuteration. It is evident from Figure 3, however, that the OH-stretching region of the three samples differs profoundly. The Mt. Grainger sample shows only two strong OH-stretching absorptions. These are similar to the two dominant absorptions observed with the Florida sample. The sample from Mt. Flinders shows a different distribution of absorption bands. This is in agreement with the probabilities deduced in Table 5, column C: in the Mt. Grainger sample Al-OH-Al associations are almost the only ones present; they predominate in the Florida sample, but in the Mt. Flinders sample other associations are of similar or greater importance.

The OH-bending vibrations of palygorskite have not previously received much attention. A band at about 910 cm⁻¹ in the spectrum of attapulgite has been assigned to Al-OH-Al vibrations, and one at about 870–875 cm⁻¹ to carbonate impurities (Farmer, 1979). The Mt. Flinders and Mt. Grainger samples do not contain carbonate, yet the Mt. Flinders sample shows a pronounced broad absorption extending from about 890 to 960 cm⁻¹. By analogy with other dioctahedral phyllo-

silicates it seems reasonable to assign this band to OH associations involving Mg and Fe ions. The band is practically absent in the Mt. Grainger sample, as predicted in Table 5, column C.

CONCLUSIONS

Mössbauer data of three samples of palygorskite and their dehydroxylates indicate that Fe³⁺ occupies edge sites with relatively regular 6 coordination and M(1) or M(2) sites in the interior of the chains. On heating, Fe³⁺ ions in edge positions become 5 coordinated, first by retaining one molecule of coordinated water per site and at higher temperatures possibly by cross-linking of the chains. The Mössbauer parameters are thus compatible with the model of palygorskite dehydroxylate proposed by Preisinger (1963).

The distribution of cations in the octahedral sheets deduced from the Mössbauer spectra and the chemical analyses agrees with the IR spectra and the reactivity of the samples. Scanning electron micrographs of the heated samples show that the acicular form is maintained throughout the dehydration and dehydroxylation process, but the thermal stability of the samples differs considerably.

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Резюме—Ионы Fe^{3+} в палыгорските занимают места по краям и внутри алюмосиликатных цепей. Мессбауэровские параметры дуплетов связанных с краевыми ионами Fe^{3+} указывают на то, что эти места имеют шестикратную регулярную координацию. Ионы Fe^{3+} внутри цепей занимают места M(1) в трёх исследованных образцах и места M(2) в четвёртом образце. Ионы Fe^{3+} , находящиеся на краевых местах палыгорскита, становятся 5-координированными в результате потери воды вследствие нагрева. Они сохраняют эту координацию при дегидроксилировании, вероятно благодаря образованию поперечных связей в цепях. Температура, при которой наблюдаются изменения в порошковых рентгенограммах и в мессбауэровских и инфракрасных спектрах, различна в зависимости от образцов. Наблюдаемые промежуточные стадии также изменялись либо вследствие различных путей протекания реакций, либо вследствие различной устойчивости промежуточных фаз. Выведенное распределение катионов в октаэдрических слоях находится в хорошем количественном согласии с данными, наблюдаемыми при инфракрасной абсорбции гидроксила. [E.C.]

Resümee—Die Fe^{3+} -Ionen im Palygorskit besetzen Plätze an den Ecken und im Innern der Aluminiumsilikatketten. Die Mössbauerparameter der Dubletts, die von den Fe^{3+} -Ionen auf den Eckplätzen herrühren, deuten darauf hin, daß diese Plätze eine regelmäßige 6-Koordination haben. Die Fe^{3+} -Ionen im Innern der Ketten besetzen in drei der untersuchten Proben M(1)-Plätze und in der vierten Probe M(2)-Plätze. Bei Wasserabgabe durch Erwärmen werden die Fe^{3+} -Ionen in den Eckpositionen von Palygorskit 5-koordiniert. Sie behalten diese Koordination nach der Dehydroxilierung bei, was wahrscheinlich auf eine Querverbindung von Ketten zurückzuführen ist. Die Temperaturen, bei denen Veränderungen in den Röntgenpulverdiffraktometerkurven sowie in den Mössbauer- und Infrarot(IR)-Spektren auftreten, sind in den einzelnen Proben verschieden. Die beobachteten Zwischenstadien variierten entweder aufgrund unterschiedlicher Reaktionswege oder unterschiedlicher Stabilität der Übergangphasen. Die abgeleitete Verteilung der Kationen in den Oktaederschichten stimmt gut mit der beobachteten IR-Hydroxyl-Absorption überein. [U.W.]

Résumé—Les ions Fe^{3+} dans la palygorskite occupent les sites périphériques et à l'intérieur des chaînes aluminosilicates. Les paramètres de Mössbauer des doublets associés avec les ions Fe^{3+} dans les sites périphériques indiquent que ces sites ont une coordination-6 régulière. Les ions Fe^{3+} à l'intérieur des chaînes occupent les sites M(1) dans trois des échantillons examinés et les sites M(2) dans un quatrième. Les ions Fe^{3+} dans les positions périphériques de palygorskite deviennent coordonnés-5 lorsque l'eau est perdue à l'échauffement. Ils gardent cette coordination lors de la déshydroxylation, probablement par la liaison transverse des chaînes. Les températures auxquelles des changements se passent dans les clichés de diffraction poudrée aux rayons-X et dans les spectres de Mössbauer et d'infrarouge (IR) varient d'échantillon en échantillon. Les étapes intermédiaires observées varient aussi, soit à cause de voies de réaction différentes, soit à cause de stabilités différentes des phases intermédiaires. La distribution déduite de cations dans les feuillets octaédriques s'accordent qualitativement bien avec les absorptions hydroxyl IR observées. [D.J.]