

THE COORDINATION OF ALUMINUM IONS IN THE PALYGORSKITE STRUCTURE

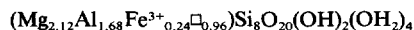
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Abstract—NMR spectra of PF1-1 Floridan palygorskite strongly suggest that Al^{3+} occurs only in octahedral coordination. X-ray microanalysis of the palygorskite fibers indicate a chemical composition defined by the atomic ratios: $\text{Mg}/\text{Si} = 0.34$, $\text{Al}/\text{Si} = 0.27$, and $\text{Fe}/\text{Si} = 0.04$. Considering the NMR and CEC data in this report along with the previously published results of IR and Mössbauer spectroscopic studies, the following structural formula is proposed for PF1-1 palygorskite:



where \square represents the vacant MI octahedral sites in the structure, and Al^{3+} and Fe^{3+} are all exclusively assigned to the octahedral sites.

Key Words:—Al-coordination, MAS-NMR, Palygorskite.

INTRODUCTION

Chemical data collected for a large number of palygorskites show the presence of significant amounts of Al^{3+} in the structure of this mineral (Weaver and Pollard, 1963; Smith and Norem, 1986; Paquet *et al.*, 1987; Newman and Brown, 1987; Jones and Galan, 1988; Singer, 1989). The trivalent aluminum ion is generally assumed to occur in both octahedral and tetrahedral sites in the palygorskite structure. The nuclear magnetic resonance (NMR) spectra of palygorskite, described in this note, raise some doubt about the occurrence of tetrahedral Al^{3+} substitutions in the palygorskite studied. Prior to the NMR analyses, the palygorskite sample was examined with X-ray diffraction and electron microscopy, as briefly described below.

CHARACTERIZATION OF THE PALYGORSKITE SAMPLE

A palygorskite sample from the Hawthorn Formation in the Meigs-Attapulugus-Quincy district (Georgia-Florida) was selected for this study. The sample is known as PF1-1 palygorskite and is available from the Clay Minerals Society's Source Clays Repository at the University of Columbia, Missouri. Detailed data on the chemistry, mineralogy, as well as a description of the geological occurrence of PF1-1 palygorskite are given by van Olphen and Fripiat (1979). This palygorskite was previously studied by many other investigators such as Serna *et al.* (1977), Heller-Kallai and Rozenson (1981), and Woessner (1989). Their results have been

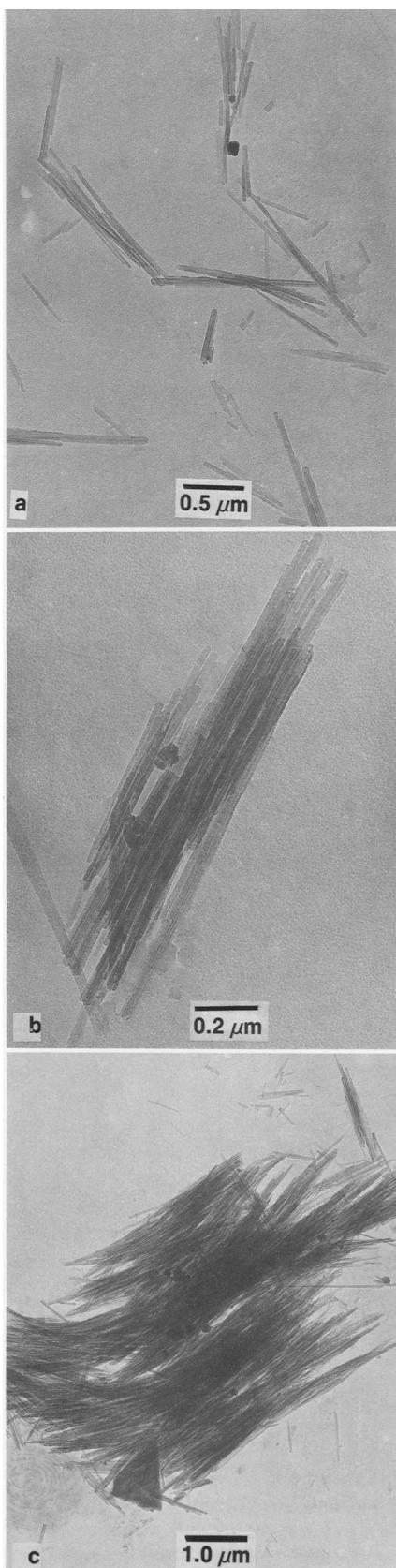
incorporated into the discussion in order to describe the structural state of the palygorskite.

X-ray diffraction analysis of the clay indicates that palygorskite makes up about 85% of the fine ($<2 \mu\text{m}$) fraction. Smectite (10%), quartz (1–3%), apatite (2%), carbonates (1%), and mica ($<1\%$) were identified as the main impurities in the fine fraction. The bulk clay contains, however, significantly larger quantities of quartz, montmorillonite, and mica.

The fine fraction of the sample, containing about 85% palygorskite, was used for NMR analysis after the removal of amorphous iron by dithionite treatment (Mehra and Jackson, 1960).

Electron microscopy of PF1-1 palygorskite

Electron microscopic examination of the fine fraction of the palygorskite was carried out by a JEM 100-CX analytical electron microscope equipped with a KEVEX quantum 5000 X-ray microanalyzer. Palygorskite fibers range in length from 0.2 to 2.0 μm (Figures 1a and 1b). The fibers often occur as bundles consisting of sets of parallel fibers (Figure 1b) or as aggregates displaying a “bird-nest” texture (Figure 1c). Impurities of calcite and apatite, differentiated by their X-ray spectral lines, occur as minute grains in the range of 50 to 100 nm (Figures 1a and 1c). Some of the grains of calcite and apatite appear to be trapped within the bundles or aggregates of palygorskite fibers. In the fine fraction ($<2 \mu\text{m}$), smectite and mica appear in the form of extremely thin platelets and flakes up to 0.3 μm in size (Figure 1b). Micras are distinguished from smectite



by the strong potassium line in their X-ray spectra. The fine lamellae of smectite are sometimes intergrown with the palygorskite fibers and cannot be separated even by the dodecylammonium saturation (Abudelgawad *et al.*, 1985). The presence of these impurities may have been partially responsible for variations in the published structural formulae that were derived from the chemical analyses of bulk palygorskite samples.

X-ray microanalysis of palygorskite fibers

Special attention was paid to the aforementioned impurities while collecting X-ray spectra from palygorskite fibers. Spectra showing K- and P-lines were excluded. Furthermore, palygorskite fibers with smectite intergrowths were also disregarded. The average intensities of 10 measurements were then converted into atomic ratios using the well-known "thin film approximation":

$$N_x/N_{Si} = k_{x/Si}(I_x/I_{Si})$$

where N_x/N_{Si} and I_x/I_{Si} represent the atomic and intensity ratios, respectively, between elements x and Si. The k -factors in the above equation were obtained from well-known layer silicates ($k_{Al/Si} = 1.165$ from kaolinite, $k_{Mg/Si} = 1.386$ from talc, and $k_{Fe/Si} = 0.733$ from annite). The mean intensities with their standard errors and the derived mean atomic ratios, with respect to Si, for the palygorskite fibers are listed below.

	I_x/I_{Si} intensity ratio	N_x/N_{Si} atomic ratio
Mg/Si	0.248 (± 0.020)	0.344
Al/Si	0.231 (± 0.015)	0.270
Fe/Si	0.053 (± 0.020)	0.039

Fe represents the total iron and will be assumed to be in trivalent state in the palygorskite structure, although a small portion of it may be divalent.

The cation exchange capacity (CEC) of the fine fraction of PF1-1 palygorskite was measured using the ammonium acetate extraction method. The CEC was found to be 6 meq/100 g, and this has been attributed to the smectite impurities in the fine fraction. The palygorskite structure was therefore assumed to be electrostatically balanced and to carry no excess charges.

The conversion of the above atomic ratios into a possible structural formula was attempted after consideration of the NMR data described next.

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Figure 1. TEM Images of PF1-1 palygorskite: (a) dispersed palygorskite fibers and minute, but dense, particles of apatite; (b) a typical bundle of palygorskite fibers with fine smectite flakes that seem to have intergrown with the fibers; and (c) a "bird-nest" aggregate of palygorskite fibers with dense grains of calcite and apatite entrapped in the aggregate.

NUCLEAR MAGNETIC RESONANCE SPECTRA OF PALYGORSKITE

High-resolution magic-angle spinning nuclear magnetic resonance (MAS-NMR) ^{27}Al spectra of the palygorskite sample shows the main peak at 3.6 ppm with a full width at half-maximum (FWHM) of about 3 ppm (Figure 2). The spinning side bands (SSB) were relatively intense, indicating that paramagnetic species are not negligible, in agreement with the iron content revealed by X-ray microanalysis. Using the structure of the second SSB in the PF1-1 ^{27}Al MAS spectra, it was possible to get the position of the centers of gravity (δ_{CG}) of both the $1/2 \rightarrow -1/2$ and the $3/2 \rightarrow 1/2$ transitions. The pulse width was lengthened to 3–5 μs in order to increase the intensity of the $3/2 \rightarrow 1/2$ transition. According to Samoson (1985), the difference between the δ_{CG} s is the difference between the second-order quadrupolar shifts, $\Delta\delta_{\text{QS}}$ with

$$\delta_{\text{QS}}(m) = -\frac{3}{40} \left(\frac{\text{QCC}}{\omega_L} \right)^2 F(I, m) \left(1 + \frac{1}{3} \eta^2 \right)$$

and

$$F(I, m) = \frac{I(I+1) - 9m(m-1) - 3}{I^2(2I-1)^2}$$

From $\Delta\delta_{\text{QS}}$, $(\text{QCC})^2 (1 + 1/3\eta^2)$ is easily obtained. For spin $I = 5/2$, the amplitude of the $(m, m-1)$ transition is negligible for $m = 5/2$. QCC is the quadrupolar coupling constant and η is the asymmetry parameter of the electric field gradient tensor. Since the central transition was structureless, we assumed $\eta \approx 1$. The quadrupolar coupling constant QCC was found to be 1.5 MHz for PF1-1, while the isotropic chemical shift $\delta_{\text{CS}} = \delta_{\text{CG}} - \delta_{\text{QS}}$ was equal to 4.7 ppm. Woessner (1989) gave a QCC (0.8 MHz) through direct measurement of the quadrupolar shifts at different magnetic field strengths. His method is more accurate than the one applied here, which suffers from ill-defined maxima in the SSB. However, it is particularly interesting to note that when applicable, the method of Samoson, in its beautiful instrumental and computational simplicity, leads to decent results.

With such a low QCC, the $^{14}\text{Al}/^{16}\text{Al}$ line intensity ratio, obtained from a one pulse spectrum with a narrow pulse (0.5 μs) at high frequency, quantitatively reflects the relative Al nuclei populations. The absence of selective saturation of one of the lines was checked by increasing the delay time ten-fold. The upper limit of the $^{14}\text{Al}/^{16}\text{Al}$ ratio is ≤ 0.01 . This is in conflict with Woessner (1989) who derived an $^{14}\text{Al}/^{16}\text{Al}$ in the range of 0.12–0.15. Thus, all the Al is assigned to [6]-fold coordination in the PF1-1 palygorskite, and the tetrahedral substitutions of Al for Si are assumed to be negligible.

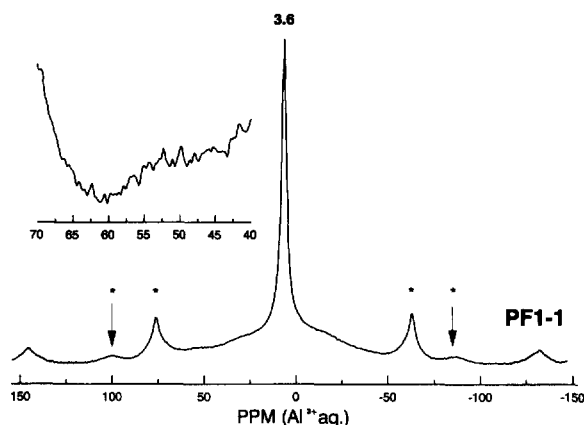
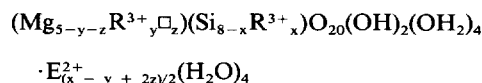


Figure 2. One-pulse ^{27}Al magic-angle spinning nuclear magnetic resonance spectra of PF1-1 palygorskite spinning at 9.1 KHz. Recorded at 130.3 MHz. Acquisition time: 51.2 ms. Delay time: 50 ms. Number of accumulations: 5408. Spinning side bands: (*) central transition SSB, (◻) contribution of the $3/2 \rightarrow 1/2$ transition SSB.

PARTITION OF CATIONS IN THE PALYGORSKITE STRUCTURE

The palygorskite structure was first determined by Bradley (1940). The structure was later confirmed by Drits and Sokolova (1979). Based on this structure, the following structural formula was proposed to account for the chemical variations in this mineral (Bailey, 1980):



where R^{3+} ions are commonly Al^{3+} and Fe^{3+} and \square is the octahedral vacancy. E^{2+} represents the exchangeable cations in the microchannels and its amount $(x - y + 2z)/2$ is assumed to be equal to the excess charge for the half unit cell.

The Mössbauer spectra obtained from PF1-1 palygorskite by Heller-Kallai and Rozenson (1981) showed that all isomer shifts (I.S.) range from 0.39 to 0.41 mm/s indicating that no Fe^{3+} occurs in the tetrahedral sites. Similarly, the present NMR data suggest that the tetrahedral coordination of Al^{3+} is negligibly small in the structure of this mineral. Consequently, Al^{3+} , Fe^{3+} , and Mg^{2+} are all assigned to the octahedral sites in the structure of PF1-1 palygorskite. Octahedra in this structure form ribbons running parallel to the X-direction (Figure 3) and half of the unit cell contains five octahedral sites. As illustrated in Figure 3, there are three distinct octahedral sites M1, M2, and M3 in the structure. M1 and M2 sites are similar to those in dioctahedral 2:1 type layer silicates such as muscovite and montmorillonite. The M1 site has a *trans* OH configuration and is the vacant octahedral site in these

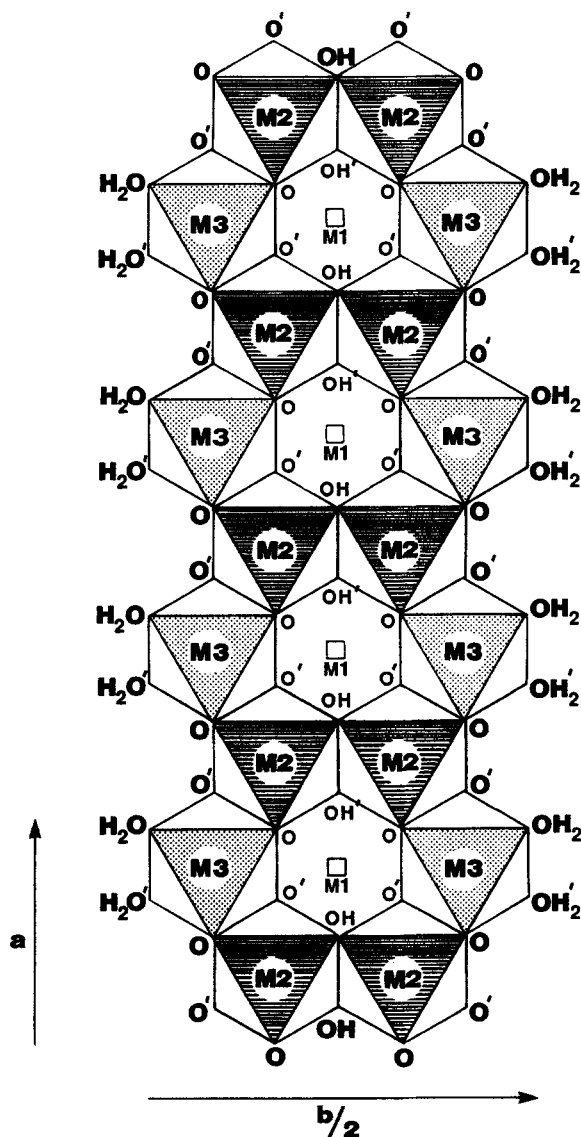


Figure 3. Configuration of the octahedral ribbons in the palygorskite structure having M1, M2, and M3 octahedral sites. Note that O', OH', and H₂O' form the bottom triangles while O, OH, and H₂O belong to the top triangles of the octahedra in this projection.

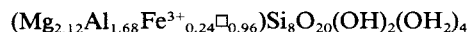
layer silicates. The two M2 sites display a *cis* OH configuration with a pair of OH ions being shared between two adjacent octahedra. The two M3 sites have two water ligands and appear at the edges of the octahedral ribbons. The infrared spectral analysis of the palygorskite by Serna *et al.* (1977), indeed, confirmed that the M1 (*trans*) sites are vacant and the palygorskite ribbons are dioctahedral. They also reached the conclusions that M3 (edge) sites are exclusively occupied by Mg, whereas M2 (*cis*) sites have an average composition (Al_{1.36}Fe³⁺_{0.37}Fe²⁺_{0.03}Ti_{0.07}) with a total occupancy of 1.83.

The Mössbauer spectra of PF1-1 palygorskite reported by Heller-Kallai and Rozenson (1981) showed two distinct doublets with quadrupole splittings (Q.S.) at 0.24 and 0.56 mm/s which were assigned to Fe³⁺ in M3 (edge) and M2 (*cis*) octahedral sites, respectively. The ratio Fe³⁺(M3)/Fe³⁺(M2) was calculated by the above investigators to be 0.66, which shows that a significant portion of Fe³⁺ occupies the M3 (edge) octahedral sites. Furthermore, they proposed an average population of (Al_{1.48}Mg_{0.13}Fe_{0.19}) for the M2 sites with a total occupancy of 1.80, again significantly lower than 2.0.

The real distribution of Mg, Fe, and Al ions over the M1, M2, and M3 sites in the PF1-1 palygorskite structure may be clarified in the future. At present, these ions can all be assigned to the octahedral ribbons without defining their partition over the M2 and M3 octahedral sites. Considering the NMR and CEC data in this report, and the previous IR and Mössbauer spectroscopic studies, the general structural formula of PF1-1 palygorskite can be simplified to:



The subscript *y* is computed from the atomic ratios obtained by X-ray microanalysis to be 0.96 for PF1-1 palygorskite. This computation is based on the assumption that the octahedral cations provide +10 electronic charges. The structural formula of this palygorskite can be then stated as:



The formula yields a full occupancy for both the M2 and M3 sites; whereas, the structural formulae accepted by Serna *et al.* (1977), Heller-Kallai and Rozenson (1981), and Woessner (1989) display significant vacancies in M2 sites with a total octahedral occupancy ranging from 3.65 to 3.81.

ACKNOWLEDGMENTS

We thank Todd Schaefer of Texas Tech University for his assistance during the preparation of the sample and data collection. Special appreciation is due to Kaylyn Dowdy for her meticulous typing of the manuscript.

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(Received 21 April 1992; accepted 11 August 1992; Ms. 2211)