

THE ELECTRON-MICROPROBE ANALYSIS OF PALYGORSKITE

DORIAN G.W. SMITH

Department of Geology, University of Alberta, Edmonton, Alberta T6G 2E3

DAVID NOREM

Dome Petroleum Limited, P.O. Box 200, Calgary, Alberta T2P 2H8

ABSTRACT

Fifteen samples of palygorskite, from widespread localities, have been investigated. The ubiquitous impurities and extremely fine grain-size pose serious problems in many analytical procedures. The electron microprobe, however, gave satisfactory analyses of mixtures of the <2- μm fraction with colloidal graphite. Of the samples studied, four had previously been misidentified. Analysis of two others was ruled out by non-clay impurities that could not be eliminated. Of the remaining nine, for which X-ray powder patterns were also obtained, only five proved to be nearly pure palygorskite; the other four contain sepiolite intergrown with illite or chlorite in various amounts. The average structural formula obtained for palygorskite by the microprobe technique is $(\text{Mg}_{1.923}\text{Al}_{1.819}\text{Fe}^{3+}_{0.228}\square_{1.030})[\text{Si}_{7.769}\text{Ti}_{0.223}]\text{O}_{21} \dots \dots \text{Ca}_{0.103}\text{K}_{0.017}\text{Na}_{0.026} \dots \dots$ (based on twenty-one oxygen atoms, since neither water nor hydroxyl can be determined by the microprobe). Attapulgitic samples from Gadsden (Florida) and Attapulgis (Georgia) proved to be mixtures of palygorskite, sepiolite, montmorillonite and illite. The ubiquity of non-clay-mineral impurities and the intimate association with other clay minerals suggest that many compositions of palygorskite in the literature should be regarded with caution. Thus of forty-seven such compositions, supposedly representing pure palygorskite or attapulgitic, the statistical package CLAYSTAT (Gold *et al.* 1983) found twenty-five that probably contain between 10 and 61 vol. % impurities in the form of other clays.

Keywords: clay minerals, palygorskite, attapulgitic, electron-microprobe analysis, CLAYSTAT, X-ray diffraction.

SOMMAIRE

On a étudié quinze échantillons de palygorskite de différents gîtes. Les impuretés omniprésentes et le grain extrêmement fin créent de sérieux problèmes d'analyse. La microsonde électronique, cependant, est capable d'analyser des mélanges, avec graphite colloïdal, de la fraction dont le grain est inférieur à 2 μm . Quatre des quinze échantillons avaient été erronément déterminés comme palygorskite; deux ne pouvaient être analysés à cause d'impuretés impossible à éliminer. Sur les neuf autres, qui-ont chacun donné un diagramme de poudre en diffraction X, cinq seulement se sont avérés être de la palygorskite presque pure; les quatre derniers contiennent de la sépiolite en intercroissance avec illite ou chlorite, en différentes proportions. L'analyse à la microsonde électronique mène à la formule structurale moyenne $(\text{Mg}_{1.923}\text{Al}_{1.819}\text{Fe}^{3+}_{0.228}\square_{1.030})[\text{Si}_{7.769}\text{Ti}_{0.223}]\text{O}_{21} \dots \dots \text{Ca}_{0.103}\text{K}_{0.017}\text{Na}_{0.026} \dots \dots$ (calculée sur 21 atomes d'oxygène, vu que la microsonde

ne peut déterminer ni eau, ni hydroxyle). Des échantillons d'attapulgitic, prélevés à Gadsden (Floride) et Attapulgis (Georgie), ont été identifiés comme mélanges de palygorskite, sépiolite, montmorillonite et illite. L'omniprésence d'impuretés non-argileuses et l'association intime à d'autres minéraux argileux portent à craindre que nombre de compositions assignées à la palygorskite, dans les publications minéralogiques, sont sujettes à caution. Sur 47 compositions publiées et censées représenter de la palygorskite ou de l'attapulgitic, le programme statistique CLAYSTAT (Gold *et al.* 1983) en a décelé 25 qui contiennent probablement de 10 à 61% (en volume) d'impuretés argileuses.

Mots-clés: minéraux argileux, palygorskite, attapulgitic, microsonde électronique, CLAYSTAT, diffraction X.

INTRODUCTION

Clay minerals as a group pose unique problems to the mineralogist who attempts to determine precise compositions and the extent of compositional variations or solid solutions. Not only are these minerals commonly intimately intermixed with one another (and with other clay-sized minerals), but also, the extremely fine grain-size normally renders complete separation of the different mineral components of a clay impractical. Furthermore, even modern methods of *in situ* microbeam analysis, such as electron- or ion-microprobe techniques, have inadequate resolution in many instances. The high-resolution capabilities of analytical electron-microscopy have not yet been developed to the point where they can provide the quantitative information required for accurate determination of composition and a complete understanding of variations that are possible. Amongst clay minerals, the fibrous species, such as palygorskite and sepiolite, pose special problems. Not only are they fine grained in two of their three dimensions, but also they contain water that is easily liberated by an electron beam. Furthermore, mineral impurities appear to be ubiquitous; many of the compositions reported in the literature probably reflect, to a greater or lesser extent, the presence of these impurities. It is, then, hardly surprising that there is not complete agreement amongst various investigators about either the structures of such minerals or their structural formulae.

The aims of this study were to explore the poten-

tial of the electron microprobe for examining the morphologies and compositional variations amongst a suite of palygorskite and "attapulgitite" specimens, and to identify the sample-preparation techniques and analytical strategies that would yield the most satisfactory results. It was felt that such a study might help to identify the extent of true compositional variations and to distinguish these from apparent variations that are actually due to the presence of impurities. Finally, although the view is now widely held that the term *attapulgitite* is a synonym for palygorskite with a short-fibre morphology, it has been considered by some to be a separate mineral. Thus Weaver & Pollard (1975), noting chemical differences, maintained the view that "future studies will probably indicate they are two distinct species." It was hoped, therefore, that a careful microanalytical investigation would throw more light on this matter.

Fifteen samples identified in hand specimen as palygorskite or attapulgitite were obtained from the museum collection at the University of Alberta and from mineral dealers. The two samples identified as attapulgitite macroscopically resemble common clay. However, all of the samples identified as palygorskite are asbestiform in appearance and could be described by either of the terms "mountain leather" and "mountain cork". In the course of this study, four samples were identified as other clay or asbestiform minerals (rectorite/allevardite, actinolite and sepiolite). Other asbestiform minerals are clearly often confused with palygorskite. Sample numbers and localities are given in the Appendix.

EXPERIMENTAL PROCEDURES

All samples were analyzed on an ARL SEMQ electron microprobe equipped with an Ortec EEDS-II energy-dispersion spectrometer. The instrument was operated at 15 kV with a probe current of ~4 nA. The data were processed using the FORTRAN IV program EDATA2-M (Smith & Gold 1979). X-ray-diffraction measurements were carried out on a Norelco Philips goniometer and generator. A Cambridge Instruments S250 SEM was used to obtain the scanning images reproduced here.

SEM examination

The morphology of palygorskite was examined by standard secondary-electron imaging techniques. However, it may be noted that the fibrous nature of these clays made it necessary to apply a double thickness of gold to samples to eliminate problems due to static charging. Not only is the morphology of the palygorskite observable, but the frequency, size and, in cases, the identity of the impurities present in the samples are also apparent. Thus many

samples were found to be intergrown with a variety of other minerals including calcite, dolomite, gypsum and quartz.

The typical palygorskite fibre was found to be <0.5 μm in diameter; and thus single-grain electron-microprobe analysis is impossible. Typical images are shown in Figure 1. Multigrain analysis might also be difficult in most cases, because impurities are commonly so ubiquitous that even with a focussed beam they cannot be excluded from the volume excited by the beam. The use of chemical treatments to remove impurities from the samples was avoided because of uncertainties about effects that such treatment might have on composition. Since palygorskite is a hydrous mineral and dehydration is likely to occur, heating by the electron beam must be kept to a minimum.

Block mounts

A common and simple method of mineral and rock preparation for microprobe investigation is to make block mounts similar to those used in reflected-light microscopy. These samples are then coated with a thin layer of carbon to provide electrical conductivity. Such mounts were prepared of each sample using a polyester resin. It was hoped that it would be possible to focus the electron beam on aggregates of fibres and thus obtain satisfactory spectra. However, several insurmountable difficulties were encountered. These are: a) poor polishing characteristics, b) the presence of impurities in many samples, and c) partial inundation of the sample by the mounting medium.

The ideal surface for quantitative electron-microprobe analysis is flat, but this was rarely achieved in the polishing of block mounts of palygorskite, the sample surfaces often becoming shredded and pitted. The poor quality of polish is perhaps not surprising, considering that the polishing powder used is 0.25 μm in diameter, whereas the SEM examination of gold-coated samples showed the typical palygorskite fibre to be only 0.1 to 0.5 μm in diameter. Rather than polishing the mounted sample, the powder has a tendency to shred individual fibres from the block mount, leaving a rough, ragged surface. An additional problem is the tendency of the fibres to trap small particles of lead from the polishing lap. These could not be removed by the final cleaning process and often resulted in substantial Pb peaks in the X-ray-emission spectra. Polishing with a paper lap was tried, but poorer surfaces resulted, even after several hours of polishing. Examination of the block mounts in a reflected light revealed areas with an adequate polish at the sample-plastic interface, where the palygorskite had been inundated by the resin. These areas were mapped for microbeam analysis. The ubiquitous impurities, noted during

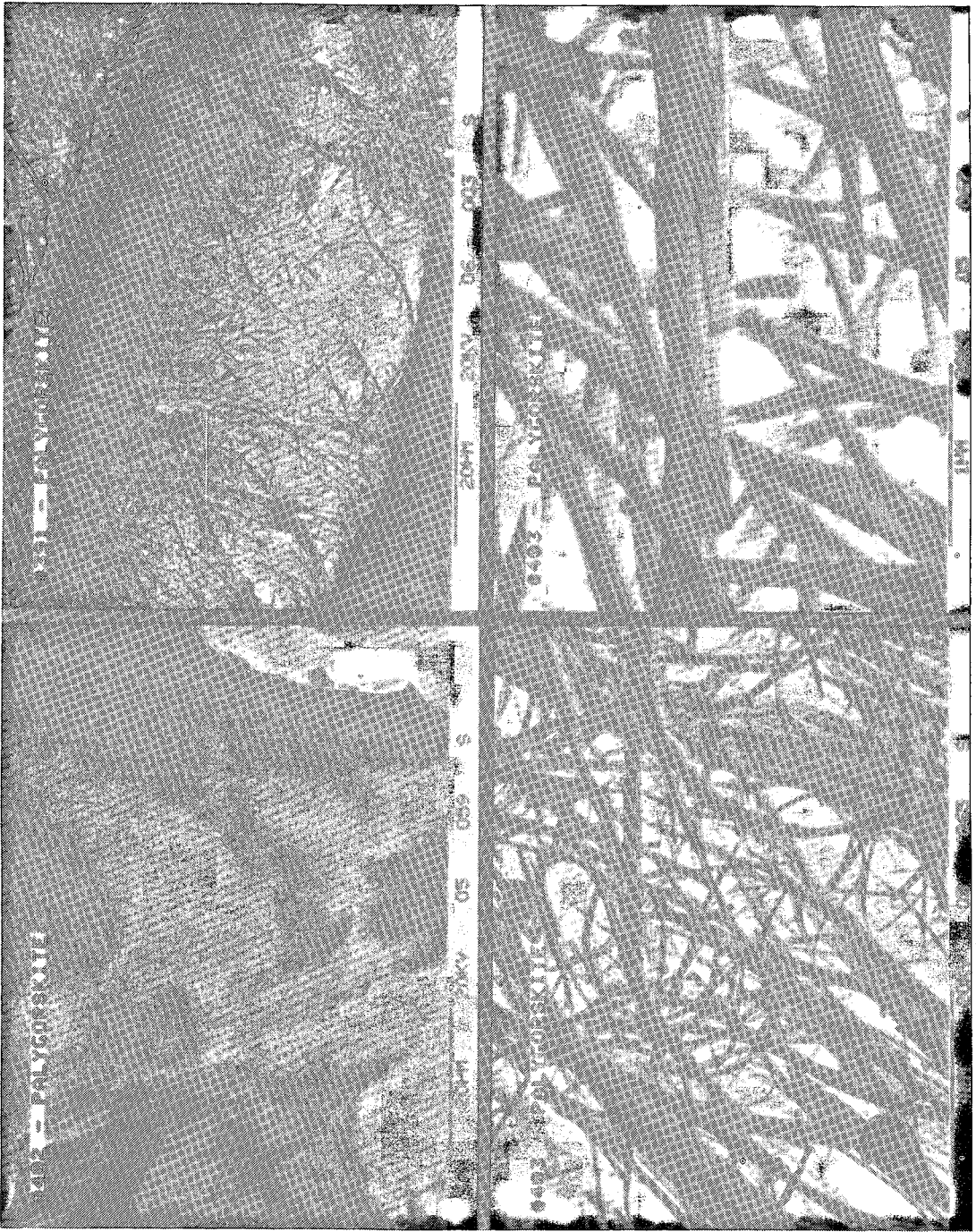


FIG. 1. Scanning images of typical palygorskite samples. The sample numbers on the photos correspond to those in the text. The magnification (scale bar) and instrument operating voltages are indicated immediately beneath each photograph. Note that sample 403 clearly shows the composite nature of the fibres, which gives them a ribbed appearance.

SEM examination, were immediately apparent in back-scattered-electron images as a result of their nonfibrous morphology and differences in average atomic number. Dolomite, calcite and other clay minerals were most common. Quartz, pyrite or gypsum were, however, also present in some samples. Impurities were predominantly in the 1- to 5- μ m range, and hence it was not possible to remove them. It was, in fact, often impossible to find polished areas large enough for analysis (the minimum rastered area used was $6 \times 6 \mu\text{m}$).

Occasionally, areas of the block mounts were well polished and free of impurities. When these areas were analyzed, they were found to contain a large proportion of the plastic mounting medium. The palygorskite appears to have been wetted by this plastic during block-mount preparation; because the volume excited by the beam contained an unknown amount of plastic, these areas were also unsuitable for quantitative analysis. Nevertheless, all block mounts were analyzed, with the objective of comparing the results obtained with results from the same samples where other techniques of preparation were used. Results of block-mount analyses are shown in Table 1. The exact composition of the plastic is not known, but it is certainly dominated by H, C, O and N, with minor amounts of P, S and Cl. Thus most of the mass of plastic in the excited volume was of too low an atomic number for detection by the energy-dispersion spectrometer. In the case of one sample (392), no satisfactory results could be obtained because of the abundance of impurities.

In processing spectra from block mounts, two unknowns had to be dealt with: the amount of plastic material in the excited volume, and the amount of water in the palygorskite. Since both of these have approximately the same atomic number, they were both treated in the same manner. During iterative

corrections, the difference between the oxide total and 100% was treated as H_2O . The results after the corrections had been completed are shown in Table 1. Subsequently, the H_2O , along with any Cl, Pb and P, were removed from the results using the EDATA2-M routine DLET. As will be seen later, these results, although roughly comparable with those of later analyses, are less than satisfactory; the presence of a considerable proportion of plastic is indicated by the Cl values in the initial results.

It was concluded, therefore, that the standard method of mounting mineral and rock specimens for microprobe analysis is not satisfactory for palygorskite. Not only are there problems in the mounting technique itself, but also prior purification of samples is necessary.

Clay discs

Palygorskite-graphite films were prepared using techniques similar to those described by Smith & Cavell (1980). The palygorskite was first suspended in distilled water using a common blender and sonic probe. Standard techniques of settling (Folk 1959) were used to collect the $<1 \mu\text{m}$ fraction. The concentration of palygorskite in this fraction was determined; the palygorskite was then mixed with a suspension of colloidal graphite prepared from Acheson "aquadag". The graphite provides the deposited film with the conductivity necessary for microprobe analysis. The palygorskite-graphite films were prepared by drawing suspensions through porous ceramic discs using a suction device.

In the suspension and settling of clay minerals, 10 g of material suspended in 500 mL of water commonly poses no problem, but if this much palygorskite is blended and disaggregated, the result is a fibrous mush. A much more dilute suspension of 2.5

TABLE 1. MICROPROBE RESULTS FROM BLOCK MOUNTS
(Wt.% oxides, H_2O by difference)

Sample	Area ⁺	Time*	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	Cl	K ₂ O	CaO	TiO	Fe ₂ O ₃ *	H O**
B390	361	20	0.15	9.23	10.15	48.14	0.09	0.00	0.15	0.00	0.00	31.52
B391	361	20	0.22	10.23	11.14	52.31	0.08	0.00	0.09	0.00	1.24	24.73
B393	361	20	0.16	6.84	8.14	37.50	0.10	0.15	0.54	0.00	1.20	45.37
B399	2256	20	0.34	8.05	9.92	44.98	0.11	0.10	0.13	0.17	0.44	35.31
B402	361	20	0.34	9.10	12.30	54.10	0.51	0.58	0.65	0.00	1.03	21.03
B403	361	20	0.00	7.29	9.45	46.63	0.11	0.00	0.10	0.00	1.39	37.50
B404	361	20	0.22	3.90	4.84	20.04	0.16	0.00	0.16	0.00	1.18	68.88
B406	361	20	0.21	6.98	7.39	37.28	0.12	0.42	0.62	0.27	1.43	44.01
B407	2256	20	0.40	6.87	8.28	38.38	0.08	0.69	1.01	0.39	2.65	40.85

⁺ Refers to the unit area rastered (in μm^2) during data collection.

* Time is duration in seconds of rastering over a given area. Total collection time for all samples was 240 s. live time.

** H_2O is calculated by difference from 100%. In reality, much of this difference will be made up of components from the plastic. However, the difference between H_2O and these components will not have large effects on matrix corrections.

* All Fe assumed to be present as Fe^{3+} .

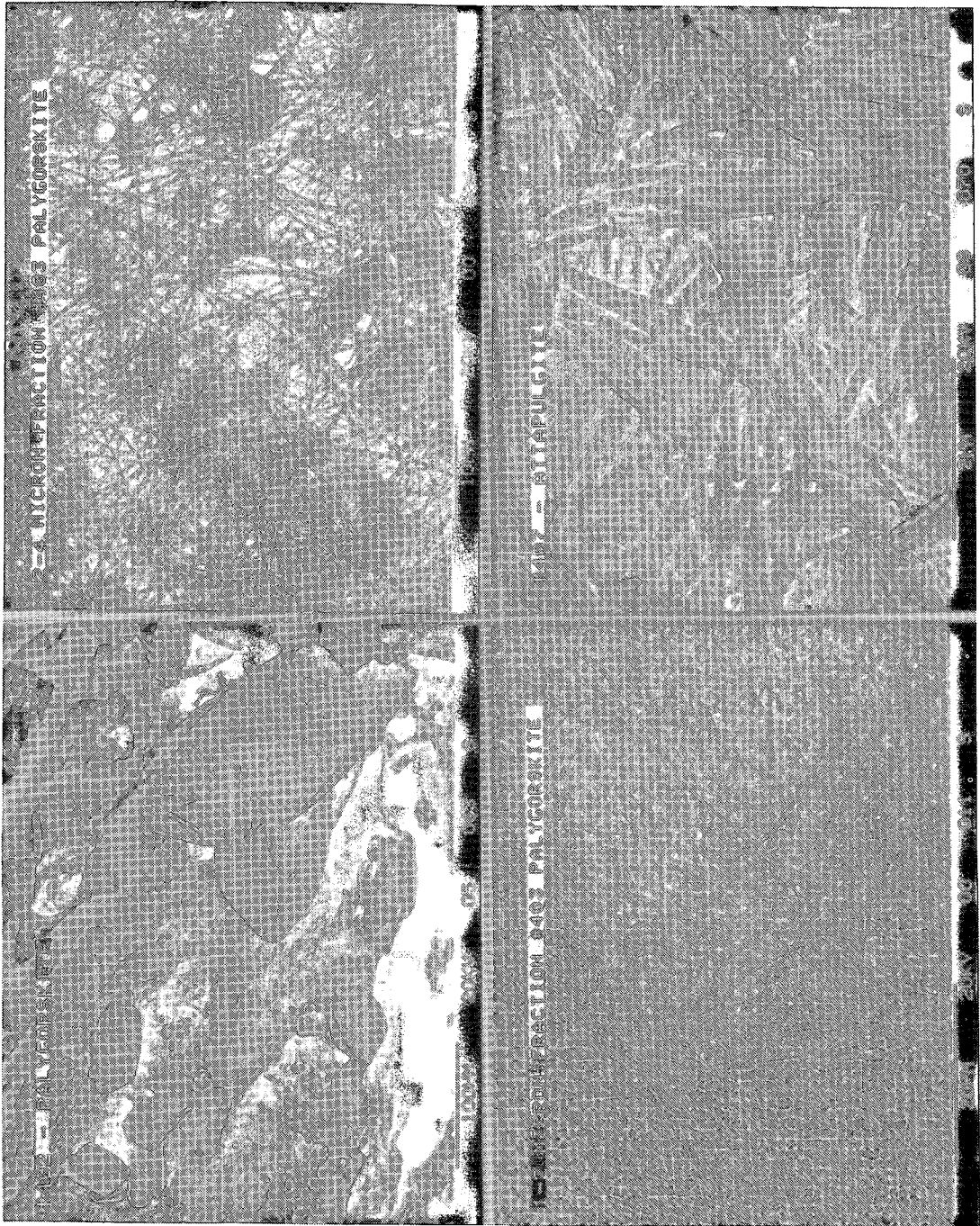


FIG. 2. Scanning images of palygorskite and attapulgite showing the ubiquitous contaminants, which pose severe problems in analysis. Sample 402 shows large crystals of calcite, which can be successfully eliminated by selecting the $<2 \mu\text{m}$ fraction for analysis. The $2\text{--}4 \mu\text{m}$ fraction of sample 403 shows the presence of ubiquitous calcite impurities. As may be seen, these may be effectively eliminated by using the $1\text{--}2 \mu\text{m}$ fraction. Sample 407 shows the short fibres so characteristic of attapulgite. Below the label "attapulgite", the flat area may be a sheet of illite.

g of palygorskite in 500 mL of distilled water usually proved satisfactory. Palygorskite crystals also have a tendency to flocculate rapidly, preventing settling. The use of a chemical dispersant, a common method of solving this problem, was avoided as far as possible because of the difficulty of completely removing it from the film prior to analysis. Repeated washing and centrifuging were used to rid the suspensions of electrolytes. Most samples required four or five washings before flocculations ceased. But the technique was not always successful; with some samples, flocculation occurred even after 12 washings. In those cases, 2 or 3 drops of 4% $(\text{NaPO}_3)_6$ were added to the suspensions to aid dispersion.

After disaggregation, impurities (usually carbonates) were generally found to be of similar size to the palygorskite fibres, but since the ratio of their surface area to their mass is significantly lower than that of the palygorskite and their density greater, they could be removed because they settled more rapidly.

Sample 403, which contains abundant impurities, was chosen to test the effectiveness of this method of purification. It was separated into >4, 2-4 and 1-2 μm fractions. Films prepared from each fraction

were gold-coated twice for examination with the SEM. The 1-2 μm fraction proved to be the least contaminated, and appeared to be wholly suitable for analysis (Fig. 2). With all samples, a portion of the <1 μm or 1-2 μm fraction was gold-coated and observed with the SEM to see if the impurities had been successfully removed before films were made. Occasionally, further settling and separation were necessary. In only one case, the mountain leather from Alameda (sample 393), was the separation unsuccessful. In that material, the carbonate grains are extremely fine-grained, and settling did not separate them from the palygorskite.

Films prepared using the recommended 60 mg total weight of clay and graphite (Smith & Cavell 1980) are far too thick and show irregular and wrinkled surfaces. In one case the film was $\frac{1}{2}$ mm thick. This anomalous thickness is probably due to the fibrous morphology of the clay. Rather than settling to form close-packed films, as do most clay minerals, palygorskite samples settle to form an open network of fibres with considerable void space (Figs. 1, 2). By halving the amount of suspension used, smoother and thinner films were obtained.

TABLE 2. MICROPROBE RESULTS FROM DISCS
(Wt.% oxides, H_2O by difference)

Sample	Area ⁺	Time*	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	Cl	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	H ₂ O
D390	9025	20	0.55	10.22	12.21	55.96	0.00	0.00	0.00	1.03	0.28	0.58	19.19
D390	2256	20	0.16	10.51	12.63	58.60	0.00	0.00	0.00	0.83	0.19	0.60	16.50
D390	361	20	0.00	10.68	13.03	60.16	0.00	0.00	0.00	0.88	0.19	0.57	14.51
D391	9025	20	0.92	16.96	13.37	49.14	0.00	0.08	0.12	0.00	0.15	5.27	14.04
D391	2256	20	0.81	17.31	13.67	50.58	0.00	0.00	0.08	0.00	0.00	5.36	12.20
D391	361	20	0.52	17.30	14.08	51.39	0.00	0.00	0.16	0.07	0.00	5.58	10.91
D392	9025	20	0.73	9.74	13.16	57.86	0.00	0.00	0.20	0.94	0.12	2.80	13.45
D392	2256	20	0.26	9.71	6.22	59.89	0.00	0.00	0.17	2.08	0.11	2.81	11.64
D392	361	20	0.11	10.09	14.14	62.79	0.00	0.00	0.20	1.93	0.17	2.92	7.68
D399	9025	20	0.14	9.27	12.30	54.23	0.00	0.00	0.00	0.00	0.00	4.65	19.44
D399	2256	20	0.00	9.48	12.70	56.65	0.00	0.00	0.00	0.00	0.00	4.96	16.23
D399	361	20	0.00	10.11	13.50	61.21	0.00	0.00	0.00	0.00	0.00	4.70	10.50
D402	9025	20	0.90	6.44	15.67	47.59	0.29	0.09	3.00	0.49	0.44	3.26	21.91
D402	2256	20	0.38	6.49	15.93	48.28	0.27	0.12	3.00	0.49	0.51	3.28	21.28
D402	361	20	0.28	6.62	16.65	51.29	0.22	0.00	3.17	0.47	0.39	3.35	17.58
D403	9025	20	0.53	9.81	12.56	57.67	0.00	0.00	0.00	0.20	0.00	4.00	15.24
D403	2256	20	0.02	10.18	13.18	60.67	0.00	0.09	0.08	0.21	0.00	4.20	11.40
D403	361	20	0.00	10.22	13.40	63.32	0.00	0.00	0.08	0.16	0.00	4.26	9.58
D404	9025	20	0.62	9.04	12.75	52.52	0.00	0.08	0.14	0.10	0.00	1.90	22.90
D404	2256	20	0.14	9.33	13.38	55.65	0.00	0.07	0.12	0.12	0.00	1.92	19.33
D404	361	20	0.03	9.48	13.77	57.65	0.00	0.07	0.13	0.11	0.00	1.90	16.87
D406	9025	20	0.89	9.96	10.09	54.23	0.30	0.00	0.49	0.26	0.30	3.57	19.92
D406	2256	20	0.59	10.52	10.65	59.95	0.32	0.00	0.55	0.31	0.35	3.64	15.13
D406	361	20	0.43	10.87	11.04	60.05	0.30	0.08	0.54	0.28	0.36	3.89	12.19
D407	9025	20	0.69	9.36	11.04	53.37	0.40	0.08	0.82	1.02	0.36	4.02	18.86
D407	2256	20	0.34	9.61	11.46	55.91	0.30	0.06	0.85	1.01	0.41	4.01	16.07
D407	361	20	0.07	9.89	11.71	58.09	0.35	0.08	0.83	1.07	0.46	4.24	13.25

⁺ Refers to the unit area rastered (in μm^2) during data collection.

* Time is duration in seconds of rastering over a given area. Total collection time for all samples was 240 s. live time.

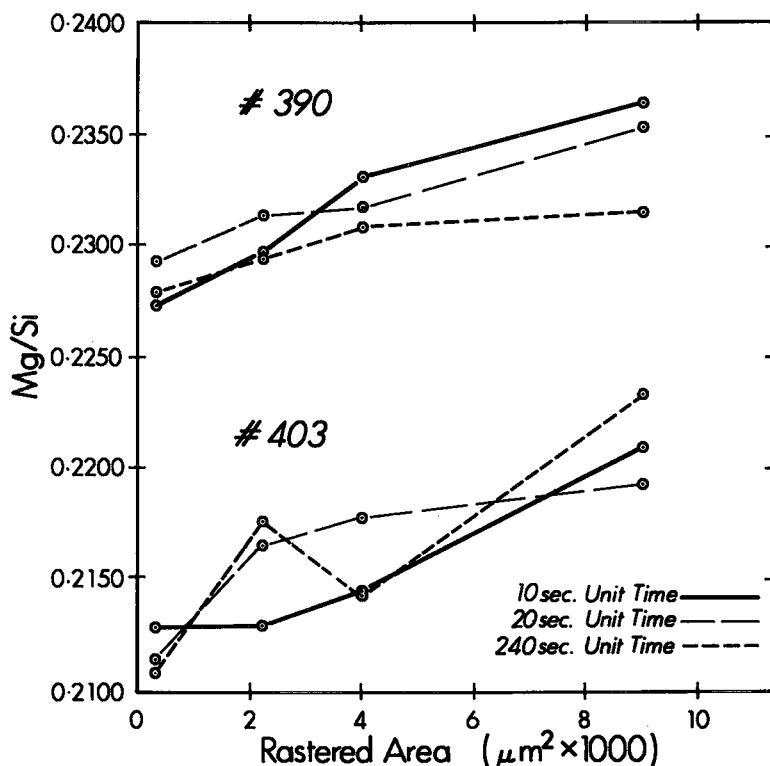


FIG. 3. Mg/Si ratio versus area rastered for disc mounts of samples 390 and 403, both samples of relatively pure palygorskite. The different curves represent the effects of leaving the beam on the sample for different periods of time.

A second problem resulting from the morphology of palygorskite is the difficulty in obtaining sufficient conductivity in the films. Although 14 wt.% graphite was used, conductivity in all cases was found to be low, and attempts to analyze the discs failed owing to static charging at the sample surface. It seems that the 14 wt.% graphite, which is suitable for most clays, is inadequate to fill the gaps in the films of fibrous palygorskite. Rather than prepare new discs with a greater proportion of graphite, a thin coat of carbon ($\sim 100 \text{ \AA}$) was deposited on each. The additional conductivity provided by the carbon film was sufficient and resulted in resistivities across the discs of $< 50 \text{ M}\Omega$.

Stability of the clay-graphite film

Palygorskite is a mineral containing a large amount of water, both co-ordinated and zeolitic. Dehydration studies by Serna *et al.* (1977) suggest that the zeolitic water can be removed under a vacuum of $< 10 \text{ mm Hg}$ at room temperature. Dehydration studies under evacuated conditions (Van Scoyoc *et al.* 1979) showed that some of the co-ordinated water is lost from palygorskite at

120°C , and that at 150°C approximately 50% of the co-ordinated water is lost. The vacuum in the SEMQ during analysis was always better than 10^{-5} mm of Hg.

In electron-microprobe analysis, much of the beam energy is dissipated as heat in the sample. With the combination of vacuum and heat, it is inevitable that some of the zeolitic water and, possibly, even some of the co-ordinated water will be lost during analysis. The vacuum in the instrument was kept constant, but the amount of heating of the film by the electron beam is a function of the electron flux per unit area per second. In a test to examine the effects of heating on the analysis of the palygorskite, both the rastered area and the time the electron beam was rastered over an area were varied.

RESULTS OF DISC ANALYSIS

In an electron-microprobe analysis, it is not possible to determine the H_2O content directly. However, water content can be inferred if no other components, other than those measured, that is, are present in significant quantities. Thus the results presented in Table 2 show these inferred water con-

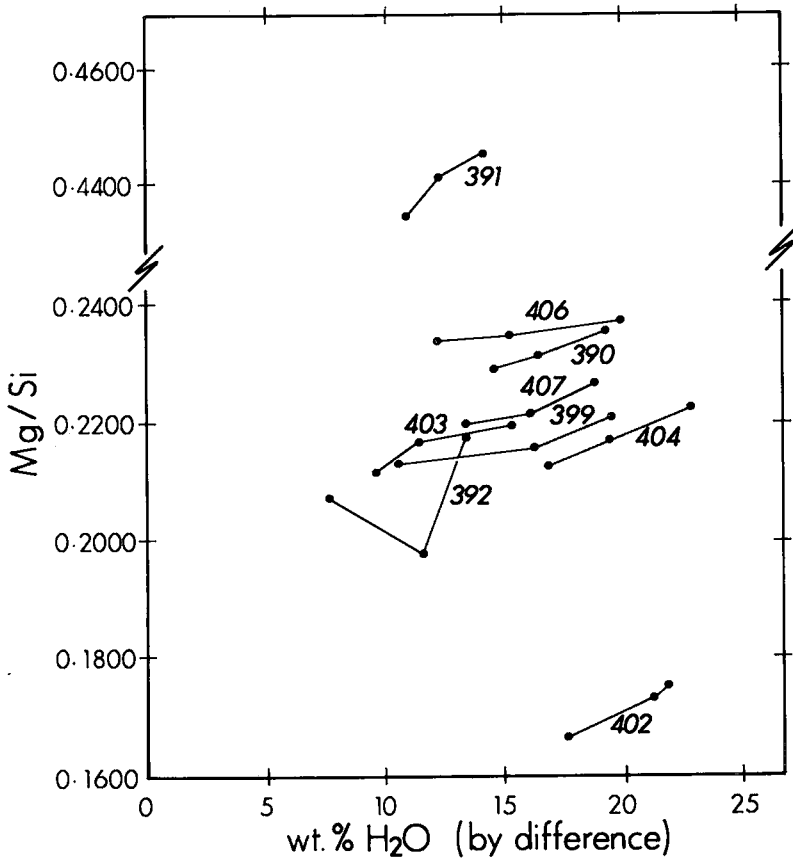


FIG. 4. Mg/Si wt. ratio versus H₂O wt.% by difference for all samples used in this study. Note that all samples show the same general trend. The substantial differences in Mg/Si ratio between 391 and 402 and other samples are related to the presence of major amounts of other clay minerals found to be present as contaminants (see Table 3). The cause of the drop in the case of 392 remains unknown.

tents. Clearly, water retention is related to both the size of the rastered area and the time the beam remains on an area. Decreasing the rastered area increases the electron flux/area/s and thus increases the heating of the clay. Increasing the time that the beam is rastered over a given area also results in greater heating of the palygorskite fibres. Increased heating drives out both zeolitic and co-ordinated water from the clay.

These tests also show an effect on the ratio of Mg/Si, the cause of which remains in doubt. The effect is illustrated in Figure 3, where the values of the Mg/Si ratio for samples 390 and 403 are plotted against area rastered. The ratio apparently decreases as the area rastered decreases, suggesting that there is an effect on the apparent concentration of one or both of these elements associated with beam loading. Since the inferred content of water is also related to beam loading (see above), the indicated Mg/Si ratio is plotted against the inferred water content for

all of the samples in Figure 4. This shows that the trend of increasing Mg/Si with increasing inferred H₂O (*i.e.*, increased area of rastering) is consistent for all samples, with only 1 anomalous data-point (sample 392) out of 27. Possible causes for this behavior will be discussed later.

It is also apparent from Figure 4 that samples 391 and 402 are completely anomalous with respect to all the other samples in their Mg/Si ratio. Sample 392, although close to the cluster of other samples, has an anomalously low inferred amount of H₂O. In order to compare the results of these analyses with those from polished mounts on a more absolute basis, the disc (D) and block mount (B) results obtained with rastering areas of 361 μm are shown recalculated H₂O-free in Table 3. This table also shows the modal proportions calculated from the analytical results by methods that will be discussed shortly. In view of the difficulties encountered in the block-mount analyses, in many respects the results

TABLE 3. COMPARISON OF RESULTS OF BLOCK MOUNT AND DISC ANALYSES* WITH CALCULATED MODAL COMPOSITIONS

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	P	S	I	C	χ ²
D390	0.00	12.49	15.24	70.35	0.02	1.03	0.22	0.67	96	3	0	1	0.6003
B390	0.22	13.47	14.82	70.30	0.00	0.22	0.00	0.00	90	9	0	2	0.6812
D391	0.58	19.42	15.80	57.69	0.18	0.08	0.00	6.25	83	16	0	1	0.1599
B391	0.00	13.59	14.80	69.49	0.00	0.12	0.00	1.64	89	8	0	3	0.3659
D392	0.13	10.91	15.31	67.99	0.23	2.09	0.18	3.16	98	1	0	1	0.0117
B392	-	-	-	-	-	-	-	-	-	-	-	-	-
D393	-	-	-	-	-	-	-	-	-	-	-	-	-
B393	0.29	12.49	14.91	68.84	0.27	0.99	0.00	2.20	92	6	0	2	0.0947
D399	0.00	11.30	15.08	68.37	0.00	0.00	0.00	5.25	93	6	0	1	0.4169
B399	0.52	12.44	15.33	69.53	0.15	0.21	0.27	0.68	96	2	0	2	0.3698
D402	0.34	8.05	20.25	62.38	3.86	0.57	0.47	4.07	52	6	42	0	0.0448
B402	0.00	11.53	15.58	68.51	0.73	0.83	0.00	1.31	95	0	3	2	0.3794
D403	0.00	11.18	14.65	69.25	0.09	0.17	0.00	4.72	94	6	0	0	0.5034
B403	0.00	11.66	15.12	69.81	0.00	0.16	0.00	2.23	98	2	0	0	0.3949
D404	0.04	11.41	16.57	69.38	0.16	0.13	0.00	2.31	97	0	1	2	0.2315
B404	0.70	12.55	15.56	64.38	0.00	0.51	0.00	3.37	90	2	0	8	0.2659
D406	0.49	12.42	12.62	68.66	0.61	0.32	0.41	4.45	84	15	1	0	0.4738
B406	0.38	12.47	13.20	66.58	0.75	1.10	0.48	4.35	76	18	6	0	0.0160
D407	0.08	11.46	13.56	67.26	0.96	1.24	0.53	4.91	81	13	6	0	0.2716
B407	0.60	11.61	14.00	64.88	1.16	1.72	0.66	4.47	71	17	11	1	0.0073

*All analyses recalculated H₂O, P, S & Cl free. #406 & 407 probably contain minor real amounts of P (0.34%, 0.40%, respectively). B=block; D=disc; P palygorskite, S sepiolite, I illite, C trioctahedral chlorite (or for 406 & 407, montmorillonite). Note B392 and D 393 were not analysed because of carbonate contamination.

are surprisingly similar. However, there are some notable differences and anomalies. In several instances the Mg and Fe values are significantly different (e.g., 391, 399, 402). In one case, 402, there is also a marked discrepancy in the content of K. Ca values are also rather variable. The differences in the Fe contents are particularly surprising. They could be due, in some instances at least, to retention of fine-grained Fe-oxides or Fe-hydroxides, which are apparent as a stain on some of the hand specimens, in the <2 μm fraction used to make the discs. In the analysis of block mounts, every opportunity was taken to avoid impurities by using the spatial resolution of the instrument. In the case of the discs, however, every attempt is made to obtain an entirely homogeneous sample. Thus any contaminants remaining in the sample will tend to be mixed evenly throughout the disc. In this regard it will be noted that the results on block mounts of the finer-grained "attapulgitic" samples, 406 and 407, which are naturally homogenized, are quite similar to the results from discs.

The compositions of the two attapulgitic samples, 406 and 407, do not differ greatly from those of palygorskite despite the different morphologies and finer grain-size. The fibres are much shorter than in any palygorskite, only 1-2 μm long. Although they do have relatively high contents of Fe, these are not

higher than those of all of the samples of palygorskite. However, the Al contents are lower than for palygorskite. Previous analyses of sample 406 (from Attapulgis, Georgia) in Kerr *et al.* (1950) reported no P. However, results by Smith & Cavell (1980) for sample 407 from nearby Gadsden County, Florida, do include P, although this was attributed to the (NaPO₃)₆ added as a dispersant. No dispersant was used with the sample in this study, so that possibly the P is structurally bound.

X-RAY-DIFFRACTION RESULTS

The anomalies in analytical results prompted an X-ray-diffraction investigation of the samples, with a view to confirming the identities of particular samples and perhaps revealing the presence of any contaminants not apparent in the SEM investigation. One of the advantages of the disc mounts used in the microprobe work is that the introduction of about 15 wt.% colloidal graphite still leaves them quite suitable for direct investigation by X-ray diffractometry. Thus the identical samples analyzed by microprobe could be studied by the X-ray technique. The discs were examined without further preparatory treatment and under ambient conditions in the laboratory using CuKα radiation.

The diffractometer traces are, as expected, domi-

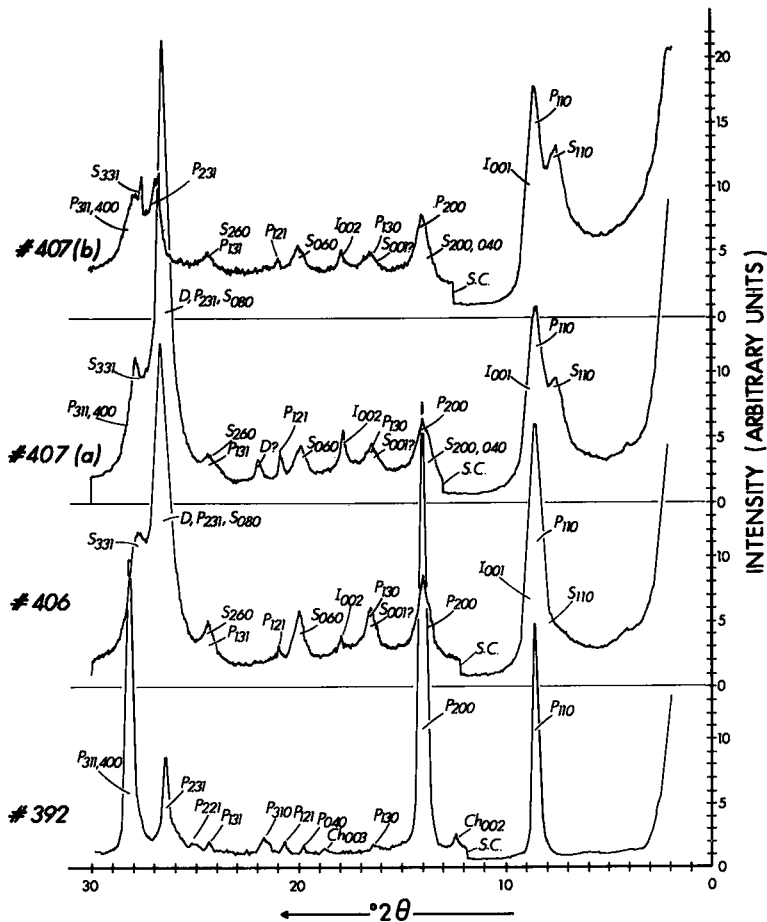


FIG. 5. Diffractometer traces for samples 392, 406 and 407. P palygorskite, S sepiolite, Ch chlorite, I illite, D ceramic disc. 407(a) is a graphite-free film mounted on a glass disc. 407(b) is the clay-graphite film analyzed on a ceramic disc. $\text{CuK}\alpha$ radiation; 1° divergence slits; s.c. = scale change, $\text{FSD} = 1 \times 10^4$ for 2° – 12° and 4×10^3 for 12° – 30° ; $\text{TC} = 2$ s; scan speed = $\frac{1}{2}^\circ 2\theta/\text{min}$.

ated by the 110 peak of palygorskite at approximately 10.5 \AA . The only exception to this was sample 391, which showed a 001 chlorite peak as the most intense line. Several other samples showed very weak chlorite peaks. Typical traces are shown in Figure 5. Sample 392 shows the pattern characteristic of essentially pure palygorskite, and sample 406 (from Attapulgis, Georgia) shows the broadened peaks characteristic of attapulgite. Sample 407 shows a pattern similar to 406 but with the low-angle peak of sepiolite. The 001 peak of illite is largely buried in the high-angle flank of the palygorskite 110 peak. However, the small 002 illite peak is well defined. In the region around 3.34 \AA there are several peaks, not only from palygorskite, sepiolite and illite, but also from the ceramic discs on which the clay-graphite mixtures were prepared. The presence of

peaks due to disc material is clearly illustrated by a comparison of 407(a), obtained from a specially prepared graphite-free film on a glass disc, and 407(b) from the clay-graphite mixture on a ceramic disc used throughout the rest of this study. The thickness of the superimposed clay-graphite films will, of course, control the observed intensities of any peaks from the ceramic discs. Any quartz impurities would also produce a strong peak in this region. Sample 407 was further investigated after preparation as a thin smear on a glass slide. The clay was Ca-saturated, glycerol- and glycol-treated, and then examined under carefully controlled humidity. This revealed the presence of some smectite, probably montmorillonite, in addition to the other three components.

The intensities of the X-ray-diffraction peaks do

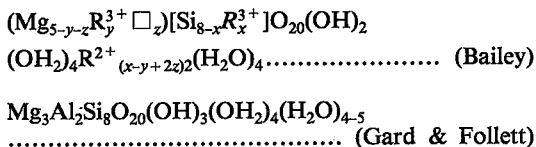
not permit more than qualitative estimates of the relative proportions of the clay-mineral constituents in such mixtures. However, Gold *et al.* (1983) have shown that rather accurate estimates of such relative proportions can be obtained by means of a statistical approach if good compositional data are available for the mixtures. The disc-mount results of Table 3 were, therefore, processed through the program CLAYSTAT, which is a development of the original program described by Gold *et al.* (1983). All samples were treated as mixtures of sepiolite, palygorskite, illite and chlorite. Chlorite was zero in 406 and 407; in view of the X-ray-diffraction results, these were rerun with montmorillonite in place of chlorite. The results are also shown in Table 3. Only five of the disc samples are essentially pure palygorskite (>94%); the others contain between 17 and 49 wt.% contaminants in the form of other clay minerals.

The reliability of these estimates of modal proportions is limited by the fact that the number of analyses in the CLAYSTAT database is low for palygorskite (22) and sepiolite (10), and the average compositions of both minerals may be unduly affected by any one or all of the several different clay-mineral impurities that may be present. However, it is noteworthy that of 47 sets of analytical data for supposedly pure palygorskite or attapulgite collected from the literature, CLAYSTAT found that 25 probably contained between 10 and 61% impurities in the form of other clays, with sepiolite and illite being the most common probable contaminants.

DISCUSSION OF RESULTS

The X-ray-diffraction results have shown clearly that significant amounts of clay-mineral impurities can be present in samples believed on the basis of SEM examination to be essentially uncontaminated. This suggests that analytical data for palygorskite (and other fibrous clays) should be regarded with considerable caution unless it is clearly demonstrated by X-ray-diffraction techniques that the samples *actually analyzed* are quite pure. Four of the compositions that have been found to represent essentially pure palygorskite (390, 392, 403 and 404) give the following average structural formula. Note here that sample 399 was not included because of the very large differences between the Fe contents indicated by the disc and the block analyses. Also note that the (OH) and H₂O present in Bailey's (1980) formula are omitted in the case of the recalculated H₂O-free microprobe analyses, and that hence in the calculation oxygen is increased from 20 to 21 to compensate for hydroxyl. $(Mg_{1.923}Al_{1.819}Fe^{3+}_{0.228} \square_{1.030})[Si_{7.769}Ti_{0.008}Al_{0.223}]O_{21} \dots Ca_{0.103}K_{0.017}Na_{0.026} \dots$ The formulae of Bailey (1980) and Gard

& Follett (1968) are shown below for comparison:



The general consensus seems to be that four of five available octahedral sites in the structure are filled in most samples of palygorskite. Thus Weaver & Pollard (1975) reported a mode of 3.90 octahedral cations and a normal distribution about this figure. The average composition of palygorskite reported here is even closer to 4; 3.97 octahedral cations are indicated. The Ca, K and Na reported in these analyses are assumed to be exchangeable cations; the total number of such cations is well within the range reported by Weaver & Pollard.

X-ray diffraction has clearly shown that at least one of the two "attapulgite" samples included in this study (that from Gadsden County, Florida, which is an A.P.I. reference clay) is actually a mixture of palygorskite, sepiolite, illite and a smectite, probably montmorillonite. This mixture is largely confirmed by the statistical calculation of the modal composition of the clay. However, the virtual absence of smectite from this statistical mode probably reflects both the minor amount of montmorillonite present and the near-equivalence in composition of palygorskite on the one hand and sepiolite plus montmorillonite on the other. When the four samples used to obtain the above formula were recalculated by CLAYSTAT in terms of montmorillonite and sepiolite alone, the average values obtained showed that palygorskite can be represented by 64% montmorillonite and 36% sepiolite, with very small residues.

The other attapulgite (from Attapulgus, Georgia) shows weaker peaks for sepiolite and illite but surprisingly similar proportions of these two components when it is processed by CLAYSTAT. It is noteworthy that all of the compositions of attapulgite tabulated by Weaver & Pollard (1975) show significant amounts of sepiolite (15-35%) and lesser amounts of illite (0-7%) when processed through CLAYSTAT. Furthermore, even better statistical fits are obtained if nontronite (rather than montmorillonite) is included in the components chosen, 3-15% of this mineral being indicated. This raises a question as to whether this mixed character is typical of all samples of attapulgite, perhaps accounting for the chemical differences alluded to by Weaver & Pollard (1975). A more exhaustive study using the combined microanalytical, X-ray diffraction and statistical treatment employed in this study would be useful in attempting to clarify this point.

The small but consistent changes in the Mg/Si ratio with rastering area that were found in the ana-

lytical study could be taken to suggest that, to some extent, one of these elements is mobile under the influence of the electron beam. Since it is improbable that the framework-forming SiO_4 tetrahedra are disturbed, it seems more likely that Mg is affected. Many minerals, particularly hydrous minerals, are degraded to some extent beneath the electron beam and often, as in the case of the feldspars, relatively weakly bonded elements, such as Na, are partly removed from the analytical volume. In other minerals, such as the zeolites, for example, some elements (*e.g.*, Ba) have been shown to be concentrated in the analytical volumes, probably having been brought there by the migration and liberation of zeolitic water at the point of analysis. Although the palygorskite also contains loosely bound water similar to that found in zeolites, it would appear that, if anything, the Mg has migrated away from the point of analysis.

One further possibility needs to be considered, however. On the ARL SEMQ microprobe used in this study, the position of the beam-scanning coils above the final aperture causes a significant change in the ratio of aperture current to probe current when rastering over areas greater than about $500 \mu\text{m}^2$. Although it is difficult to see how this might affect the *relative* proportions, it is possible that the somewhat different sizes of the excited volumes for these two elements could give rise to slightly different measured intensities when part of the rastered beam is blanked by the final aperture. Because it is known that the effect does not occur with small areas of rastering, the results obtained from $361 \mu\text{m}^2$ areas (a magnification of 5000 times when imaging) have been used, wherever possible, in the calculation of the anhydrous compositions in Table 3 and in calculating the structural formula. It should be noted, however, that if indeed the changes in the Mg/Si ratio are real and reflect degradation of the sample beneath the beam, then the figures for Mg given in the structural formula may be up to about 5% (relative) too low.

CONCLUSIONS

Many samples identified macroscopically as palygorskite are in reality a mixture of several species, both clay and non-clay minerals. Careful scanning-electron microscopy and X-ray diffraction are commonly necessary to determine the nature and extent of contaminants, or whether a sample is pure palygorskite, or has been sufficiently purified for analysis. Many compositions of palygorskite in the literature have been found to be suspect in this regard.

The results obtained in this study do not support the view expressed by Weaver & Pollard (1975) concerning palygorskite and attapulgite that "future

studies will probably show they are two distinct species". However, it has been shown that the two samples of attapulgite examined in this study are actually a mixture of palygorskite, sepiolite, smectite and illite and that many published compositions of attapulgite can be recalculated in terms of these components, leaving very small residues. It would, therefore, seem worthwhile to carry out careful X-ray-diffraction work on some of these samples to see if that technique confirms the presence of these other clay minerals.

Palygorskite, although a difficult material to analyze, may be tackled by electron-microprobe techniques. Most of the problems encountered have to do with sample purification. In fact, once a sample has been purified, preparation for the microprobe is a quick and simple procedure, with the most time-consuming part being the determination of the suspension concentration prior to mixing with colloidal graphite. Problems unique to palygorskite (*i.e.*, clay-graphite thickness and conductivity) result from the fibrous nature of this clay. These are easily countered by using less suspension to prepare the discs, and by supplementing conductivity with a thin coat of carbon. An interesting facet of the analytical study is the behavior of Mg and Si when the size of the rastered area is varied. A trend of decreasing Mg/Si with decreasing area of rastering is definite, but the reasons behind it are obscure. Further study of this phenomenon might be of benefit to the microanalysis of all such hydrous minerals, including perhaps the zeolite group.

ACKNOWLEDGEMENTS

The electron-microprobe facilities at the University of Alberta are supported by the Natural Sciences and Engineering Research Council, operating grant #A4254 to the first author. We are grateful to Mr. George Braybrook of the Department of Entomology, University of Alberta, for assistance in acquiring SEM images and to Prof. M. Dudas, Department of Soils, University of Alberta, for the X-ray-diffraction results from the smear mount of sample 407.

REFERENCES

- BAILEY, S.W. (1980): Structures of layer silicates. *In* Crystal Structure of Clay Minerals and their X-ray Identification (G.W. Brindley & G. Brown, eds.). *Mineral. Soc., Mon.* 5, 1-124.
- FOLK, R.L. (1959): *Petrology of Sedimentary Rocks*. Hemphills', Austin, Texas.
- GARD, J.A. & FOLLETT, E.A.C. (1968): A structural scheme for palygorskite. *Clay Minerals* 7, 367-370.

- GOLD, C.M., CAVELL, P.A. & SMITH, D.G.W. (1983): Clay minerals in mixtures: samples preparation, analysis, and statistical interpretation. *Clays Clay Minerals* 31, 191-199.
- KERR, P.F. *et al.* (1950): Analytical data on reference clay materials. *API Project 49, Clay Mineral Standards, Prel. Rep. 7*. Columbia University, New York.
- SERNA, C.J., VAN SCOYOC, G.E. & AHLRICH, J.L. (1977): Hydroxyl groups and water in palygorskite. *Amer. Mineral.* 62, 784-792.
- SMITH, D.G.W. & CAVELL, P.A. (1980): Electron microprobe analysis of clay minerals. *Proc. XI Gen. Mig. Int. Mineral. Assoc.* (1978), 90-98.
- _____ & GOLD, C.M. (1979): EDATA2: A FORTRAN IV computer program for processing wavelength- and/or energy-dispersive electron microprobe analyses. In *Proc. 14th Ann. Conf. Microbeam Anal. Soc.* (San Antonio, Texas, 1979; D.E. Newbury, ed.). San Francisco Press, San Francisco.
- VAN SCOYOC, G.E., SERNA, C.J. & AHLRICH, J.L. (1979): Structural changes in palygorskite during dehydration and dehydroxylation. *Amer. Mineral.* 64, 215-223.
- WEAVER, C.E. & POLLARD, L.D. (1975): *The Chemistry of Clay Minerals*. Elsevier, Amsterdam.

Received October 26, 1985, revised manuscript accepted February 3, 1986.