A RANDOM INTERGROWTH OF SEPIOLITE AND ATTAPULGITE

by

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ABSTRACT

The smectic clays from Cabo de Gata region, Almeria, Spain, are composed mainly of montmorillonite, but they contain appreciable quantities of fibrous clay minerals, some of which are of the palygorskite type. However, there also is a mineral that has properties intermediate between those of palygorskite and sepiolite. Its structure seems to be a random intergrowth of both.

INTRODUCTION

A pink papyraceous material overlying the montmorillonite in some parts of the bentonite deposit in Sierra de Gata region, Almeria, Spain, has been described previously (Martin Vivaldi, Cano Ruiz and Fontboté, 1956). It was characterized as a mineral from the sepiolite–palygorskite group, without qualification as sepiolite or attapulgite because of peculiarities of the X-ray diffraction photographs, notably the appearance of a broad reflection covering the region from 12 to 10 Å. In the present paper new data are given for this mineral and for several samples from the sepiolite–palygorskite group in the same deposit.

MATERIAL AND EXPERIMENTAL TECHNIQUES

Material

A short description of the deposit from Sierra de Gata was given in the paper cited above; a full description of that deposit and one at Serrata de Nijar will be published elsewhere (Martin Vivaldi and Linares Gonzalez, in preparation). Pink papyraceous clay sample no. 123, from the Sierra de Gata region (in the quarry at the place named "Los Trancos") fills cracks in the montmorillonite mass. Sample no. 126 is a grayish brown clay that was sandwiched between quartz veinlets and altered volcanic rock

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(Fig. 1 and Plate 1). Sepiolite–palygorskite clay also is found in some samples (*e.g.* no. 113) in the Serrata de Nijar deposit.

The pink material was separated as far as possible from the white mont-

FIGURE 1.—Location map and sketch map of the quarry at "Los Trancos" in Sierra de Gata region, Almeria, Spain, showing location of samples 123 and 126.

morillonite mass in sample 123. Separation was impossible in sample no. 126 as no external macroscopic differences were observed. The same was true for sample no. 113, although the fraction finer than $2\,\mu$ (e.s.d.) was enriched in the fibrous mineral. The study of the pink material from sample no. 123, therefore, is more complete.

Experimental Techniques

X-ray diffraction photographs were taken with modified Philips cameras of 114.7 mm radius (Martin Vivaldi, Girela Vilchez and MacEwan, 1959), using CuK_α radiation. Diffraction photographs were made for glycolated and glycerated samples. Oriented aggregates were prepared by pressure (Mitchell, 1953). Fifteen percent very pure kaolin (medical grade) was added as an internal standard. An automatic differential thermal apparatus operated at 11 °C per minute was used (Martin Vivaldi, Girela Vilchez and Rodriguez Gallego, 1959). Thermogravimetric analyses (TGA) were made by heating samples at a series of temperatures until constant weight was attained. Base exchange capacity was determined by saturation with ammonium acetate and washing with methyl alcohol, followed by distillation of ammonia over sulfuric acid and titration with NaOH solution. Chemical analyses were made following the methods given by Jakob (1944). Free silica was determined by boiling samples 10 min with 5 percent Na_2CO_3 solution (Ross and Hendricks, 1945).

Electron micrographs were made with "Philips Metalix" type 11980 and RCA electron microscopes. Very dilute aqueous clay suspensions, made alkaline with ammonia, were prepared and drops evaporated on Formvar film mounted on a grid.

EXPERIMENTAL RESULTS

X-ray Diffraction

Table 1 shows *d* spacings and relative intensities, estimated by visual inspection from powder photographs of samples no. 123 and no. 126. Table 2 includes X-ray data from two photographs of oriented aggregates of sample no. 113. Photographs with aggregates normal to the X-ray beam were taken to avoid the appearance of basal reflections from montmorillonite.

While photographs of sample no. 113 match diffraction lines from a normal attapulgite, photographs of samples no. 123 and no. 126 both show a broad line in the 10–12 Å region, with a central value of 11 Å. The rest of the lines (some of which are broad), neglecting the montmorillonite lines, do not fit well any of those produced by attapulgite or sepiolite. These photographs resemble attapulgite in the low-angle region and sepiolite in the high one.

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Fig. 2 shows differential thermal curves for samples no. 123 and no. 126 as well as curves for sepiolite from Vallecas and attapulgite from Attapulgus for comparison. The curve of sample no. 126 is not very informative as
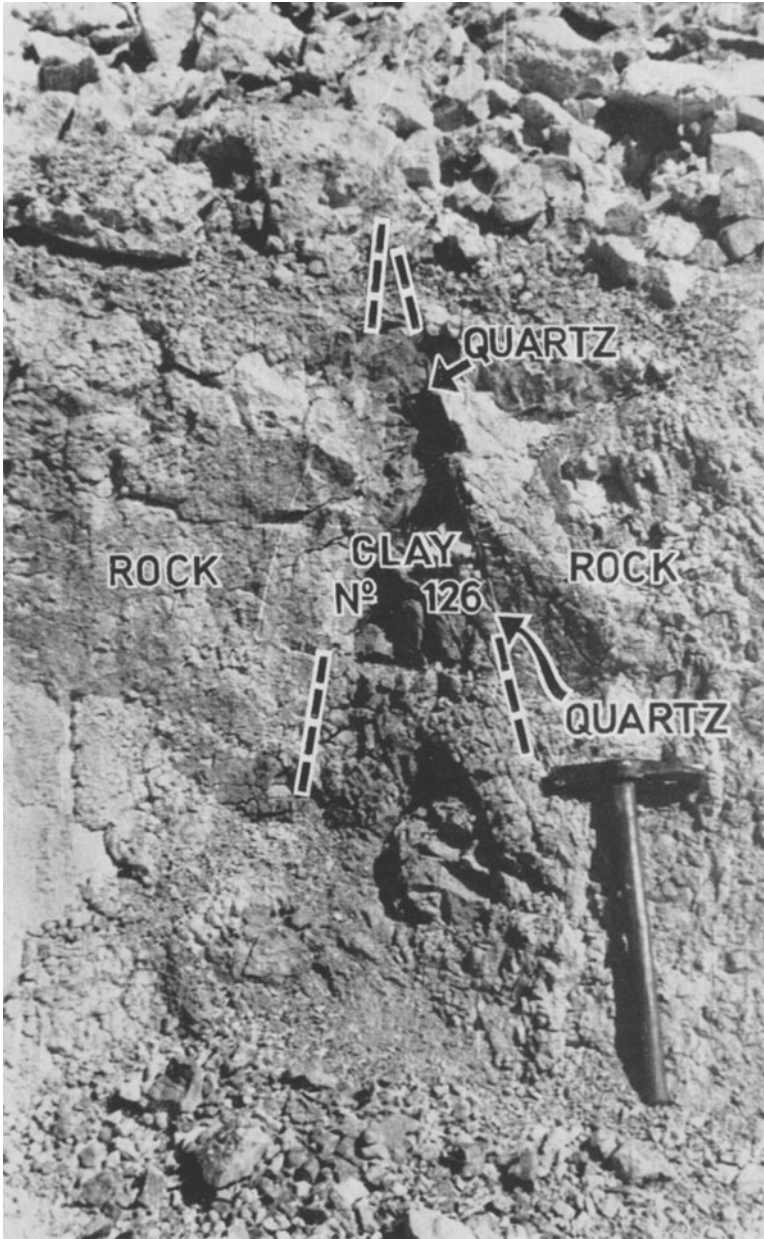
PLATE 1.—Photograph of outcrop of sample no. 126.

abundant montmorillonite is present (peak at 645 °C). The curve of sample no. 123 is a very interesting one as peaks in the 100–200 °C and 800–1000 °C regions resemble those of sepiolite, but in the 300–500 °C region the peak is almost a singlet and resembles peaks from attapulgite.

TABLE 1.—d SPACINGS CALCULATED FROM X-RAY POWDER PHOTOGRAPHS; I VALUES ESTIMATED VISUALLY

No. 123		No. 126	
d	I	d	I
12–10	vs.b	17.0	vs
8.58	vw	11.0	vw.b. diff.
6.45	w.b	8.4	w
5.40	vw.b	7.3	vis
4.48	m	6.4	vw
4.28	mw[1]	5.6	w
3.69	w.b	4.52	s
3.25	m	4.25	w
3.12	w[1]	4.04	s
2.61	vw	3.75	mw
2.54	m.b	3.34	ms
2.33	vis	3.32	vs
2.24	vw	2.97	vw
2.14	vw.b	2.81	vw
2.05	vw	2.58	vs
2.00	vw	2.49	w
1.77	vis	2.16	vw
1.70	vis	2.11	w
1.67	vw	1.81	vw
1.55	vis	1.77	vw
1.50	w.b	1.70	w
1.42	vis	1.66	vw
1.30	vw	1.61	w
1.28	vis	1.53	w
1.25	vis	1.49	s
		1.36	w
		1.29	w
		1.24	vw

[1] Superimposed on a band.

T. G. A.

Fig. 3 reproduces the thermogravimetric curve for sample no. 123. Here again the curve agrees with the behavior of sepiolite inasmuch as an inflection point is shown at about 400 °C. Notwithstanding, the inflection in the region 600–1000 °C is lower than for sepiolite and more like attapulgite.

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TABLE 2.—d SPACINGS CALCULATED FROM X-RAY POWDER PHOTOGRAPHS;
I VALUES ESTIMATED VISUALLY; SAMPLE NO. 113

O.A. parallel to the X-ray beam		O.A. perpendicular to the X-ray beam	
d	I	d	I
17.6	s	10.5	s
10.5	s	6.50	vis
8.92	vis	5.43	vis
6.50	vis	4.48	vs
4.48	vw	4.20	s
4.22	w	3.81	w
3.94	vis	3.68	w
3.79	mw	3.28	s
3.47	vis	2.95	vw
3.34	vis	2.58	mw
3.22	vis	2.45	mw
2.99	w	2.17	vw
2.91	vw	2.12	vw
		1.79	vw
		1.67	vw
		1.56	vw
		1.54	vw
		1.50	vw
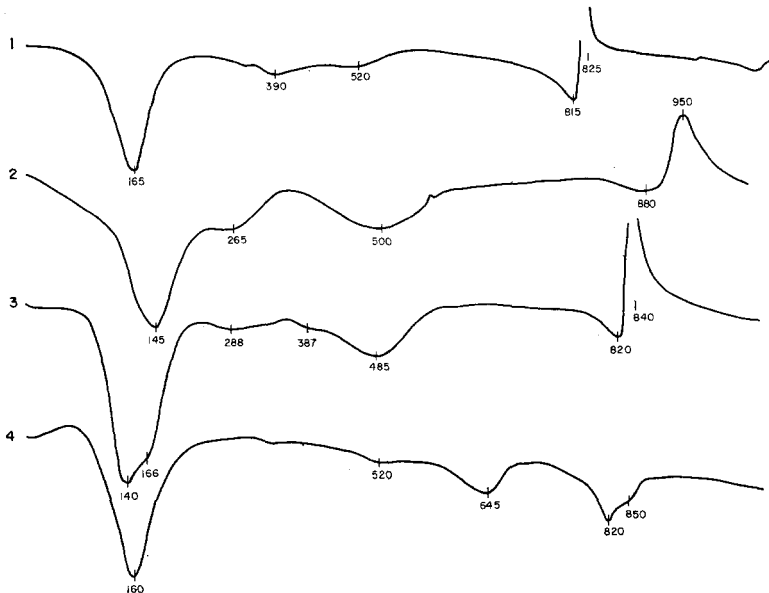
FIGURE 2.— DTA curves of several sepiolite–palygorskite samples: (1) Sepiolite from
Vallecas (Spain). (2) Attapulgite from Attapulgus (Georgia, U.S.A.). (3) Sample
No. 123. (4) Sample No. 126.

Base Exchange and Soluble Silica

The base exchange capacity for sample no. 123 is 38 meq/100 g, and the silica gel content is 1.2 percent. The base exchange capacity value covers values typical of members of the sepiolite–palygorskite group.
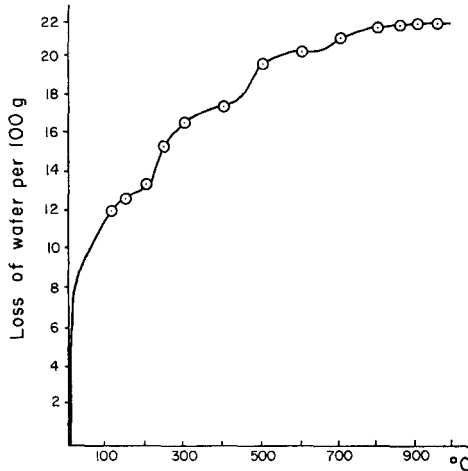

FIGURE 3. — Thermogravimetric analysis curve of sample no. 123.

Chemical Analysis

Table 3 includes the results of chemical analysis for samples no. 123 and no. 113. The presence of montmorillonite in sample no. 113 makes it difficult to draw a helpful conclusion. But as it has been enriched in the fibrous mineral, the low figures of MgO are in accordance with the X-ray diffraction data: that is, the mineral must be attapulgite.

Al_2O_3 and MgO values in sample no. 123 seem to come from a mixture of sepiolite and attapulgite, but it could be an aluminum sepiolite like the one described by Rogers, Quirk and Norrish (1956).

TABLE 3.— CHEMICAL ANALYSES, CALCULATED
ON A DRY BASIS, OF SAMPLES NO. 113 AND NO. 123

Oxides	Sample No. 113	Sample No. 123
SiO_2	67.25	60.80
Al_2O_3	18.70	8.29
Fe_2O_3	1.31	4.81
MgO	4.24	14.80
CaO	1.88	1.41
TiO_2	0.74	—
$H_2O +$	6.30	9.02

Electron Microscope Photographs

Plates 2*a* and 2*b* show photographs of sample no. 123. In Plate 2*a* (magnification, 4000 X) almost all particles are bundles of fibers. The thin fibers near the center of the photograph are about 0.1 μ in diameter and 4 μ long. The same is seen in Plate 2*b* at a magnification of 13,000 X; the bundles are made up of very flexible and thin fibers that look like sepiolite rather than attapulgite.

DISCUSSION

The determinations presented above and several now in progress show that sepiolite–palygorskite clays are common in all bentonites from Cabo de Gata (Almeria). In certain places attapulgite seems to be the only fibrous mineral present (Serrata de Nijar no. 113), but in other places (Sierra de Gata) we have either a mixture of sepiolite and attapulgite or a fibrous mineral having a different structure owing to a new arrangement of tetrahedra.

To determine if the broad line at 12–10 Å could be resolved into two independent reflections, a photograph of sample no. 123 with kaolinite added as an internal standard was carefully photometered. Fig. 4 is a photometric tracing of the low-angle region. Only a simple and well defined peak at 11 Å is apparent.

It might be thought that this reflection could be from a structure in which the tetrahedra are rotated to a position intermediate to those giving rise to sepiolite and attapulgite structures. Inspection of Fig. 5 indicates that such an alternative is impossible.

It seems, then, logical to imagine that the rotation of tetrahedra suitable to give sepiolite or attapulgite structures is produced at random, thus giving about 50 percent of each structure for the mineral. This would account for the 110 reflection at 11 Å and the *b* axis having an average value between those of sepiolite and attapulgite. A modification in position and intensity, and a broadening of reflections would be produced. Figure 6 is an idealized scheme of the structures of sepiolite, attapulgite, and the new mineral.

Chemical analysis supports this hypothesis. If, as we think (Martin Vivaldi and Cano Ruiz, 1956a, 1956b) the structural water of sepiolite–palygorskite minerals begins to be expelled at about 100 °C it is possible to calculate its molal formula from a chemical analysis recalculated on a dry basis (that is, without the water driven off below 100 °C).

Table 4 shows the results of such a calculation for some analyses taken from the literature with the moles of sesquioxides recalculated as MgO. As can be seen, this method gives results in accordance with formulas calculated from proposed structures for attapulgite and sepiolite (Bradley,
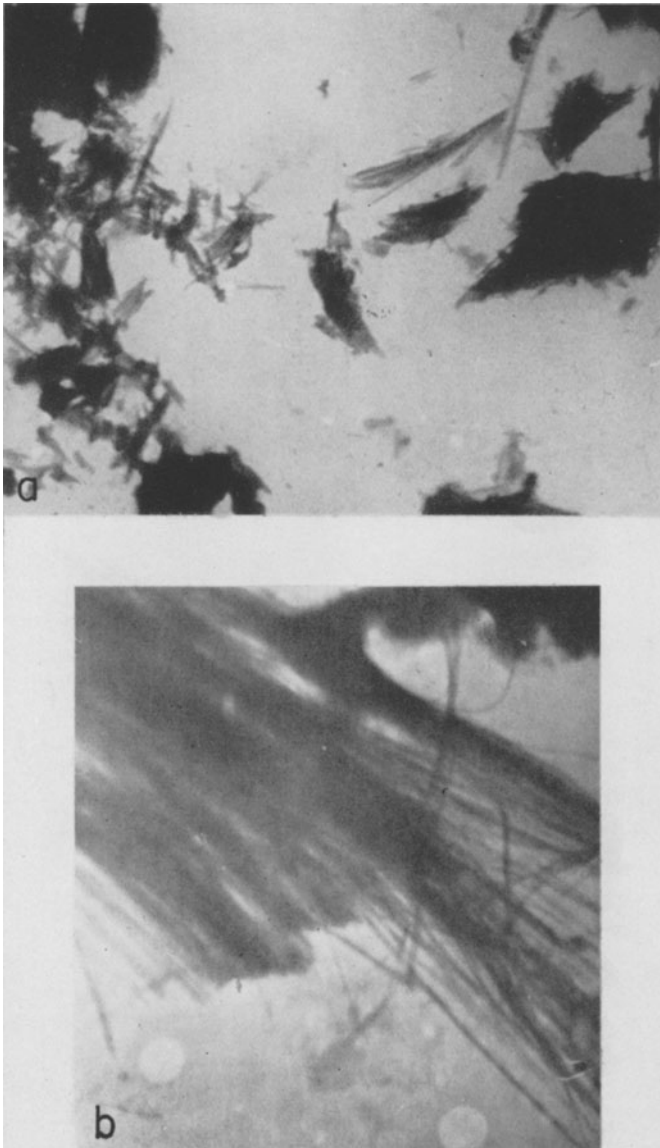
PLATE 2.—Electron micrographs. *a*, sample no. 123, 4000× (Philips). *b*, sample no. 123, 13,000× (RCA).

1940; Nagy and Bradley, 1955). A lattice such as the one proposed would give an average of the formulas for sepiolite and attapulgite, that is

$$10\,SiO_2 \cdot 6.5\,MgO \cdot 6.5\,H_2O.$$

The calculated formula for sample no. 123 is very close to this idealized
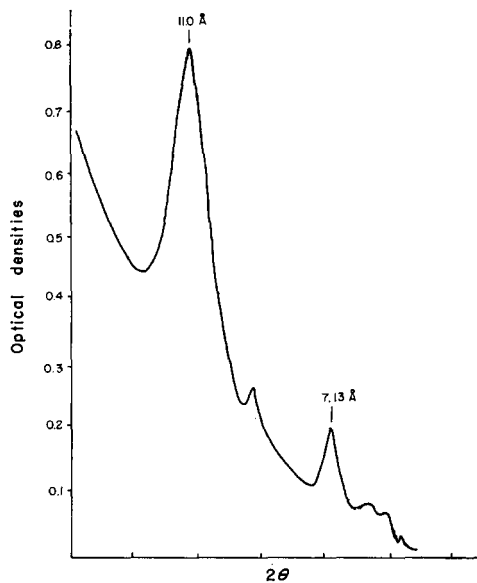
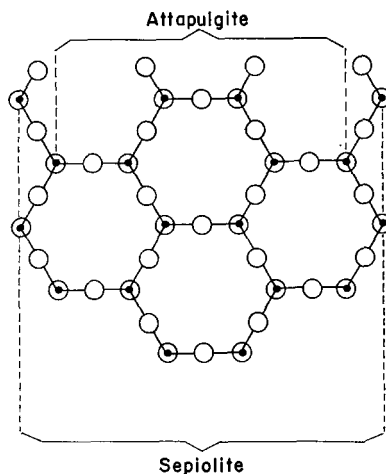FIGURE 4.—Microphotometric curve from low angle region of powder photograph: sample no. 123.

FIGURE 5.—A tetrahedral layer (Si_2O_5) showing intervals at which silica tetrahedra invert for sepiolite and attapulgite.

formula. Impurities and imperfections in the ideal scheme would account for the difference.

That the DTA and TGA curves produced by the mineral under discussion are intermediate between those given by sepiolite and attapulgite is in favor of the proposed structure. Even though we feel a more delicate
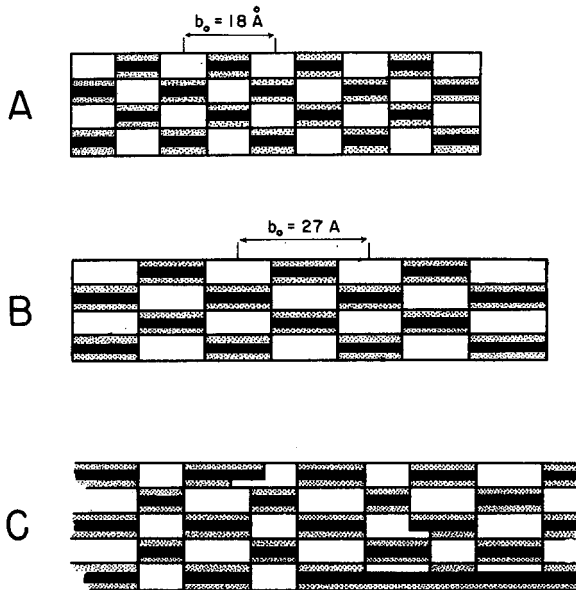

FIGURE 6.—Simplified schematic illustration of crystal structure of attapulgite (A), sepiolite (B), and a random intergrowth of both (C) showing several irregularities.

analysis of diffraction effects is needed to verify the proposed structure, we are presenting it as a very suggestive confirmation of the ability of tetrahedra to rotate in the Si_2O_5 layer. This problem has been discussed by Bradley (1955), who thinks that inversion of tetrahedra is very common and that it is a way by which several silicates can gain relief from stresses arising from difficulties of fitting of octahedral and tetrahedral layers having different b dimensions.

It is well known how differences in chemical composition of such a layer sensibly modify its dimensions (Brindley and MacEwan, 1953). It is also true that the higher the temperature the easier is the adjustment for layers differing in size. Sepiolite and attapulgite are crystals originating at moderate temperature, and with the high content of Mg a fitting of the layers probably is permitted thanks to the regular and systematic rotation of tetrahedra.

In some cases, as in the one of sample no. 123, physical and chemical conditions could have been such that Al and Mg provided by the sur-

TABLE 4.—CHEMICAL ANALYSIS OF SEVERAL SEPIOLITE–PALYGORSKITE CLAYS AND THEIR MOLAL FORMULAS CALCULATED ON A DRY BASIS

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	H_2O+	H_2O-	$TrO + K_2O + Na_2O$	Formula
1.—	54.83	0.28	0.45	—	24.51	0.55	10.74	8.18	0.38	$12SiO_2 \cdot 8MgO \cdot 8H_2O$
2.—	52.76	1.46	0.50	0.26	22.52	—	10.53	11.02	—	$12SiO_2 \cdot 8MgO \cdot 8H_2O$
3.—	54.34	6.29	3.87	—	12.98	0.01	13.04	8.00	0.91	$8SiO_2 \cdot 5MgO \cdot 6H_2O$
4.—	55.03	10.24	3.53	—	10.49	—	10.13	9.73	0.47	$8SiO_2 \cdot 5MgO \cdot 6H_2O$
5.—	54.95	7.49	4.34	—	13.37	1.27	8.16	10.45	—	$10SiO_2 \cdot 7MgO \cdot 5H_2O$

1.—Sepiolite from Yavapai County, Arizona, U.S.A. (Grim, 1953).
2.—Sepiolite (Robertson, 1957).
3.—Attapulgite, Queensland (Rogers, 1954).
4.—Attapulgite, Attapulgus, Georgia (Grim, 1953).
5.—Sample No. 123.

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roundings prohibited growth of crystals of either the sepiolite or atta-
pulgite structural type. Two choices are then possible: either a mixture of
the two kinds of crystals will grow with attapulgite using up the alu-
minum; or only a single kind of crystal of the type proposed would form
with the aluminum spent in its attapulgite like regions. This may be the
nature of the defect crystal we found.

ACKNOWLEDGMENTS

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