Clays and Clay Minerals, Vol. 23, pp. 452–457. Pergamon Press 1975. Printed in Great Britain

FOLDING IN SEPIOLITE CRYSTALS

C. SERNA, J. L. AHLRICHS and J. M. SERRATOSA

Instituto de Edafologia y Biologia Vegetal, C.S.I.C. Madrid, Spain and Department of Agronomy, Purdue University, West Lafayette, Indiana, U.S.A.

(*Received* 18 *April* 1975; *and in final form* 27 *August* 1975)

Abstract—Fibrous sepiolite crystals derive much of their commercial value from their molecular size channels and grooves. The crystals fold upon drying and these channels and grooves are lost. A model for the folding and unfolding of the crystals is presented. Extensive i.r., X-ray and thermogravimetric evidence shows that folding occurs when approximately half of the water of hydration, which is coordinated to the edge magnesium atoms inside of the channels, is removed. This occurs near 175°C under vacuum and near 300°C in air. When the crystals fold, all remaining water molecules enter a new environment, that of the hexagonal holes of the neighboring silica surface. A true anhydride is produced at about 500°C under vacuum when the final water is lost, but this final dehydration produces no important structural change. Rehydration of the anhydride to the normal hydrated sepiolite does not occur at room temperatures in 100% r.h. However, above, 60°C rehydration does occur.

INTRODUCTION

Sepiolites derive much of their commercial value from their molecular sized channels and grooves. The channels are lost when the crystals fold which occurs when the temperatures are slightly elevated and water is lost from the sepiolite. The conditions necessary for folding and the stages and mechanism of this change are only partially understood.

Crystals fold by rotation of the fibers on axes through the Si–O–Si edge bonds that join the fiber units along the length of their edges as illustrated by Preisinger (1959). Preisinger describes the folded form as sepiolite anhydride and considers that it occurs when the zeolitic and coordinated water are lost from the channels at or before 450°C. The two forms, sepiolite and sepiolite anhydride, can be detected by their characteristic X-ray spacings with reflections of 12·2 Å for sepiolite and 10·4 Å for the sepiolite anhydride. Fernandez Alvarez (1970) reports the same reflections at 12·1 Å and 10·3 Å with an added reflection for the anhydride at 8·18 Å. Hayashi *et al.* (1969) and Imai *et al.* (1969) reported that no structural changes occur below 250°C but that changes begin when the coordinated water is being lost at the higher temperature and that the anhydride structure is finally obtained at about 500°C.

Recently Nagata *et al.* (1974) have shown that sepiolite folds when only half of its water of coordination has been lost. Based on TG and X-ray data they proposed a scheme to explain the changes in sepiolite upon heating.

Crystals will also rehydrate and unfold. Hayashi *et al.* (1969) noted that, after a rehydration treatment, sepiolite heated to 250°C nearly completely returned to the diffraction pattern of regular sepiolite. However, after 450°C there was only slight return of the 12·2 Å diffraction peak. Fernandez Alvarez (1970), using specific surface measurement, found a similar rehydration would occur after the low temperature but not after the high temperature treatment. Nagata *et al.* (1974) consider that the folded stage produced at half dehydration will rehydrate, but the true anhydride does not rehydrate even under hydrothermal conditions.

Our study is designed to clarify the conditions under which sepiolite folds and unfolds and the involvement of the water of coordination in the folding. Interpretation of TGA–DTGA. X-ray powder diffraction patterns and, especially, careful study of the major changes observable in the i.r. spectra of the structural OH during the dehydration and folding process will be used to explain a folding model.

METHODS AND MATERIALS

The Vallecas and Salinelles sepiolites used were described in previous work (Ahlrichs *et al.*, 1975).

TG and DTG analysis were run on air dry samples under atmospheric pressure with a heating rate of 10°C/min. Samples for X-ray powder diffraction analysis were prepared in an "L" shaped vacuum cell with one leg being a large tube for sample heating during evacuation. The second leg was a Lindemann glass capillary with 0·5 mm wall thickness. After evacuation and heating a small portion of the sample powder was shaken into the capillary which was sealed and cut by flame without losing the vacuum. The diffractograms were then obtained using a powder camera (114·7 mm) on a Philips model PW 1010 instrument with a special collimator to obtain reflections at low angles. The lines on the exposed film were converted to a diffractogram with a densitometer.

In the rehydration study, the diffraction patterns were of oriented films of sepiolite in the ambient atmosphere on an automatic goniometer.

Self-supporting films of sepiolite were used for the i.r. studies. Coarse powder was dispersed in water by

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gentle ultrasonic treatment, dried on mylar plastic and removed from the plastic for study. Films were mounted in aluminium film holders and placed in an evacuable cell with two side arms; one with NaCl windows for viewing the sample and the other for heating the sample. Spectra were run on a Perkin-Elmer 225 instrument with an expanded frequency scale. Vacuum studies were conducted at 10^{-4} mm Hg. Rehydration was done by placing self-supporting films in a closed chamber over a free water surface at several temperatures.

RESULTS AND DISCUSSION

TGA–DTGA

Typical TGA and DTGA curves for Salinelles and Vallecas sepiolites are represented by the Salinelles curves in Fig. 1 for the temperature range which includes the crystal folding. The first and major weight loss near 110°C is zeolitic water (Preisinger, 1959). The weight loss which reaches its maximum near 330°C is attributed to loss of the first two molecules of coordination water, and the weight loss near 500°C to the last two. The total of the two weight losses equals the theoretical amount according to the structure of Brauner and Preisinger (1956). The ideal predicts that the sample dried to remove the zeolitic water would have 6·25% of the remaining weight due to coordination water. Experimental results on five samples of the Vallecas sepiolite averaged 6·20% and on three samples of Salinelles 6·27%. While the DTGA peaks at 330°C and at 500°C are very different in shape, the amount of water lost at the two temperatures is only slightly different. The Vallecas averaged 3·25% loss under the first peak and 2·95% under the second. The Salinelles losses were 3·60 and 2·67% respectively.

The greater water loss always occurred in the first peak (330°C). As we will see later, this probably signifies that in this peak all coordinated water on the external edges as well as half of that on internal edges has been lost. The difference between the Vallecas and Salinelles sepiolite is in agreement with this because the Salinelles is less crystalline and thus would have more exterior edges. Therefore, it would lose a higher percentage of its coordinated water in the first peak.

The significant difference between the two peaks is their shape. The 330°C peak is narrow and intense while the 500°C peak is very broad. This suggests that the crystal folds after the removal of the first water of coordination at each edge Mg, after this the second water of coordination is in a very different environment in collapsed channels from which it is removed only at higher temperatures and it encounters diffusion problems which retard its escape from the crystal. Close examination of other works (Fernandez Alvarez, 1970; Hayashi *et al.*, 1969; Imai *et al.*, 1969; Nagata *et al.*, 1974) shows a similar characteristic in DTGA–TGA and DTA curves.

The two temperatures of 330 and 500°C are higher for the respective water losses than subsequent data in this study will show because the system is a dynamic one being heated at 10°C/min rather than being an equilibrium system and because it is not under vacuum. Figure 1 shows that the losses actually begin about 100°C before the peak temperatures, thus the temperatures reported for these phenomena are very dependent on the experimental conditions. Serna (1973) gives thermogravimetric curves obtained under vacuum for Vallecas sepiolite which show much loss of coordinated water starting near 100°C and accomplishing the loss of 61·3% of it by 200°C. His i.r. spectra show that the area under the water deformation band (near 1600 cm^{-1}) has attained a 59·1% reduction by 200°C. This again indicates that under vacuum, more than two of the four coordinated waters per half-cell are gone by 200°C.

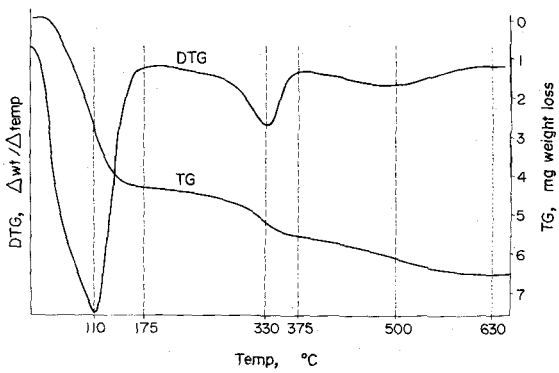


Fig. 1. TG and DTG analysis of the loss of zeolitic and coordination water from Salinelles sepiolite.

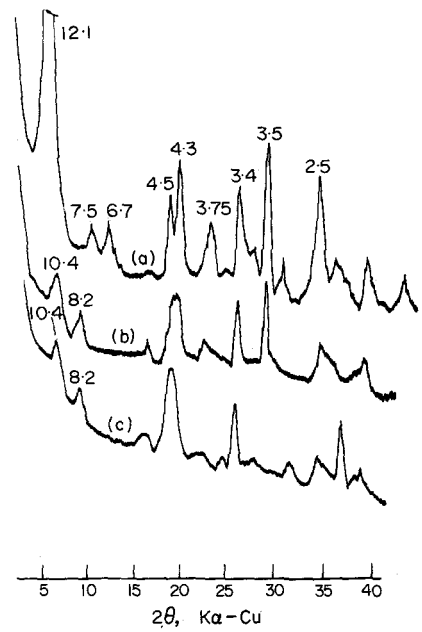


Fig. 2. X-ray powder diffraction patterns of sepiolite under vacuum. (a) At 25°C, 4 hr; (b) 200° C, 4 hr; (c) 530°C, 6 hr.

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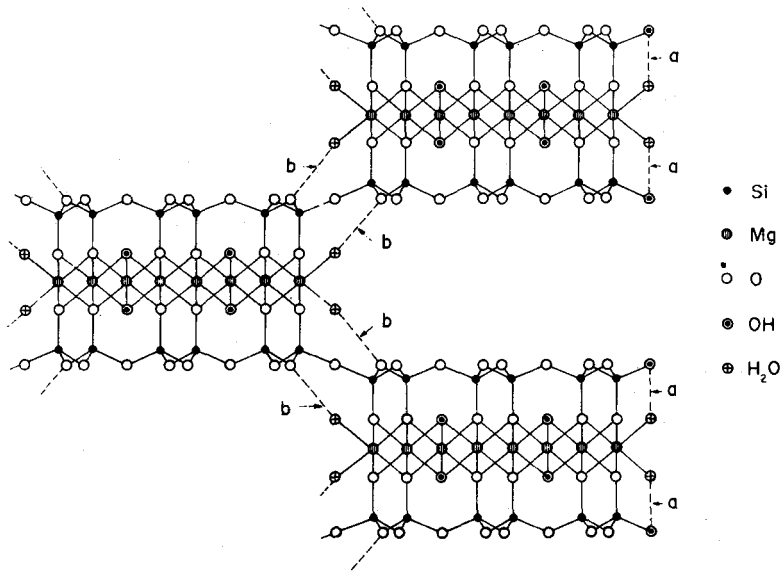


Fig. 3. End view of the right-hand edge of a model sepiolite fiber. (a) water–SiOH bond (b) water–oxygen bond.

X-ray investigation

The X-ray powder diffraction patterns of the heated samples under vacuum (10^{-4} mm Hg) are shown in Fig. 2. The reflections of natural sepiolites at room temperature (Fig. 2a), were generally sharp and strong and the position of each reflection is in agreement with previous work (Caillere and Henin, 1961; Nagata *et al.*, 1974). In the diffraction patterns at 200°C under vacuum (Fig. 2b), reflections at 10·4 Å and 8·2 Å indicate that a new crystalline phase has appeared. Similar results have been shown by Nagata *et al.* (1974) at atmospheric pressure and 300°C. Probably, both conditions (300° in the atmosphere, or 200°C with vacuum) produce similar water loss and it is the removal of part of the coordinated water which produces the folding of the structure.

When the sample is heated to 530°C under vacuum true sepiolite anhydride forms, but the X-ray powder diffraction patterns (Fig. 2c) indicate that no additional structural changes occur with the loss of this last water of coordination.

A model

If sepiolites fold upon loss of approximately half of the waters of coordination, then the normal form without its zeolitic water, can be represented by Fig. 3 and the folded form by Fig. 4. In each figure the right side represents the crystal edge and the left side the interior of the crystal. In Fig. 3 the hydrogen bridges at points *b* from the waters of coordination to the oxygen of the neighboring silica surfaces stabilize the normal sepiolite structure. However, at the crystal edges similar waters of coordination have no neighboring oxygen surface with which to interact. Therefore they should interact with the edge SiOH groups (Ahlrichs *et al.*, 1975) as depicted by the bridging labeled *a*.

In Fig. 4, the loss of one water of coordination at each site eliminates the bridge effect of the two waters and permits the crystal to fold. In the absence of one water of coordination that particular coordination site on the octahedral magnesium can be satisfied by the oxygen of the neighboring silica surface as shown by bond *g*. The folding brings the remaining water molecule, *d* into a position above and partially

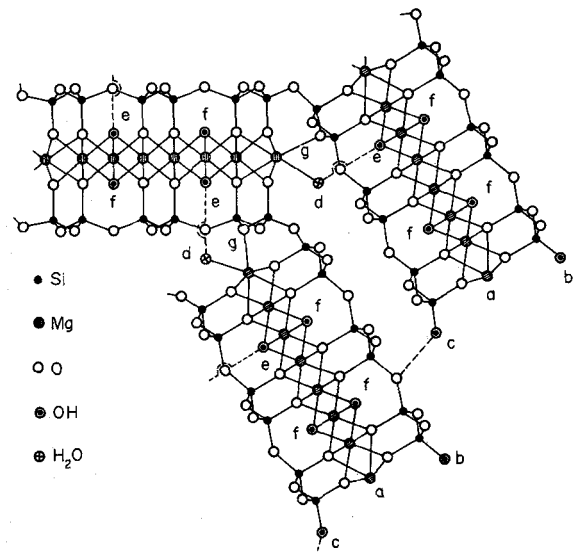


Fig. 4. End view of the right-hand edge of a model sepiolite crystal which folded after losing approximately half of its water of coordination. (a) dehydrated Mg; (b) unperturbed OH of Si; (c) OH of Si perturbed by bond to surface oxygen; (d) remaining internal water; (e) perturbed octahedral OH; (f) unperturbed octahedral OH; (g) Mg to oxygen bond.

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into the hexagonal hole of the neighboring silica surface. The strong orientation of the water molecule by the magnesium ion would lead to the anticipation that the hydrogen ends of the water molecule would perturb the OH of the crystal, labeled *e*, to a higher frequency by a hydrogen–hydrogen repulsion. In contrast it should have little effect on OH *f* unless there is a small secondary inductive effect producing a lower frequency.

On the crystal edge in Fig. 4 we see both SiOH are now liberated from water bonds, since probably no water exists on the edge Mg, *a*, after the first stage of loss of coordinated water. Thus both SiOH *b* and *c* should vibrate at higher frequencies. However, SiOH *c* does approach the neighboring oxygen surface upon folding and therefore should form some hydrogen bond with the indicated oxygen atom.

If this model is correct, it will be difficult for the last part of the water of coordination to leave the crystal because of its entrapment. As explained previously, this view is supported by the thermogravimetric data.

Folded sepiolite with trapped water will be very similar in structural form to sepiolite anhydride. Thus the X-ray powder diffraction changes expected in going from the folded sepiolite of Fig. 4 to the true sepiolite anhydride may be very small and possibly difficult to detect. Our data, Fig. 2(b),(c) show little X-ray powder diffraction difference. This could explain the common assumption (Imai *et al.*, 1969) that sepiolite anhydride begins forming at about 200 or 300°C in air. In reality the true anhydride is not attained until higher temperatures.

I.r. analysis offers much opportunity to study these phenomena. The $(Mg)_3OH$ produces an intense OH band near 3680 cm^{-1} and Ahlrichs *et al.* (1975) have shown the SiOH band to be sufficiently strong to be readily observable at 3718 cm^{-1}.

I.r. observation

(1) SiOH *shifts* (*low temperature*). Figure 5(a) shows that upon heating both the 3718 cm^{-1} band for SiOH and the 3680 cm^{-1} band of $(Mg)_3OH$ become doublets at new frequencies which is as the model predicted. The 3718 cm^{-1} SiOH band, according to the model, is the perturbed low frequency state of the SiOH in the normal structure when the two waters of coordination are present to perturb it. The new highest frequency band at 3738 cm^{-1} is the liberated SiOH *b* of Fig. 4. The normal frequency for hydroxyl in an unperturbed state as seen in dehydrated silica gels (McDonald, 1958) is near 3740 or 3750 cm^{-1} supporting this assignment of the 3738 cm^{-1} band to the liberated SiOH. The 3726 cm^{-1} band is the slightly lower weakly hydrogen bonded SiOH, *c* in Fig. 4.

The SiOH shift occurs at quite low temperatures in vacuum and they are well initiated by 100 and completed by 125°C. It is suggested that at these low temperatures water is already leaving the crystal edges, liberating the SiOH, and the edges are beginning to fold.

(2) $(Mg)_3OH$ *shifts* (*low temperature*). The $(Mg)_3OH$ band at 3680 cm^{-1} begins to shift at 125°C. By 175°C it has completed its shift to two bands of equal intensity but at new frequencies. The major shift is to 3692 cm^{-1} and fits the model prediction, Fig. 4, for the effect of water *d* on hydroxyl *e*. The other band has shown only a slight shift to 3674 cm^{-1}, a lower frequency. If any secondary inductive effect existed, it should be in this direction representing hydroxyl *f* of Fig. 4.

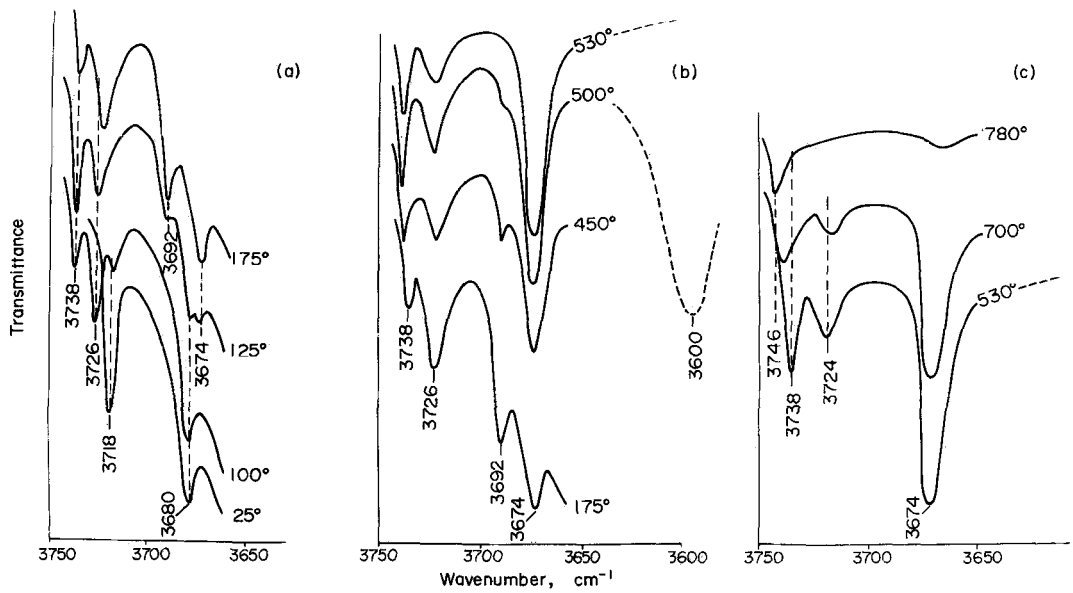


Fig. 5. I.r. spectra of the hydroxyl stretching region of Salinelles sepiolite from (a) 25–175°C; (b) 175–530°C; (c) 530–780°C.

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The nearly equal intensity of the two new $(Mg)_3OH$ bands could be predicted because each fiber unit is approximately twice as long as it is wide and there are only half of the $(Mg)_3OH$ groups to be affected directly by the water molecule as the crystal folds.

(3) *Loss of the second water of coordination.* Between 175 and 400°C very little spectral change is observed. However, at 450°C (Fig. 5b), the last water of coordination rapidly is leaving the crystal and the 3692 cm^{-1} band, thought to arise from the perturbation of one $(Mg)_3OH$ by the water, begins to disappear. It is completely gone by 530°C under vacuum when the last water (see 3600 cm^{-1}) has disappeared. This is the true sepiolite anhydride and only the original or nearly original frequency of the $(Mg)_3OH$ exists. Additional evidence for this mechanism is the apparent increase in intensity of the 3680 to 3674 cm^{-1} band as the 3692 cm^{-1} band disappears. It appears that the 3692 cm^{-1} band is not diminishing due to loss of OH but rather to a return to the original frequency, now that the perturbing water molecules are gone.

The two SiOH bands fluctuate in intensity, but are basically unaffected by the loss of the second water of hydration. This observation suggests that the water coordinated to Mg on the exterior edges of the crystal has already disappeared totally by the time of the folding. Thus the model shows no external water on the folded sepiolite, which is in contrast to the scheme of Nagata *et al.* (1974). This view is supported by the fact that more than half of the water of coordination was lost in the first stage of the TGA when the crystal folded. Also, the model of Nagata *et al.* (1974) would require an additional peak on the DTGA because water still exists in two different environments in his folded, step II crystal. Additionally, at the folding temperature the OH stretching region shows sharp water OH bands at 3590 and 3530 cm^{-1} representing the asymmetric and symmetric vibrations of water in only one environment (Prost, 1973). Thus water on the edges appears to be absent because it would be in a very different environment and would produce new or broader stretching frequencies.

(4) *Loss of the octahedral OH.* Finally, in the last stages of dehydration, Fig. 5(c), the octahedral hydroxyls react and gradually disappear as water by 780°C, leaving no octahedral OH and only the edge SiOH at its 3746 cm^{-1} frequency, typical of silica gels heated to similar high temperatures in vacuum. However part of the SiOH, absorbing at 3724 cm^{-1}, is lost by this temperature, probably because of association with adjacent surfaces (*c* in Fig. 4). This may explain why we and other workers (Nagata *et al.*, 1974; Rautureau and Caillère, 1974) find a weight loss slightly higher than the theoretical amount according to the structure of Brauner and Preisinger (1956).

The i.r.-dehydration data support the theory of crystal folding with the first stage occurring on loss of over half of the coordination water near 175°C, but with the anhydride not formed until 530°C under vacuum. Steric observations would predict a major change in structure at 175°C in vacuum, but little if any added crystal folding when the anhydride is formed at 530°C. Nearly total dehydroxylation and sepiolite anhydride destruction take place by 780°C.

Rehydration of sepiolite. The literature on rehydration of sepiolite is confusing because in the past there was no differentation between folded sepiolite with water and the true sepiolite anhydride. The model (Fig. 4), shows that the folded sepiolite with entrapped water rehydrates easily because the entrapped water and the crystal OH have a hydrogen–hydrogen repulsion as found by the i.r. studies. Our experimental results confirm the easy rehydration at room temperature with normal r.h. which agrees with Fernandez Alvarez (1970) and Nagata *et al.* (1974).

When the anhydride is formed, however, the edge magnesium completes its coordination with the two nearest oxygens of the neighboring silica surface which has been brought into close proximity by the folding. This bonding resists rehydration. In addition the SiOH (*c* in Fig. 4) also has a greater interaction with its neighboring surface oxygen in the anhydride. This was observed as a small displacement of the 3726 cm^{-1} band of the folded sepiolite to a slightly lower frequency in the sepiolite anhydride. Our experimental results show the anhydride does not rehydrate at room temperature and 100% r.h. even in three months. The model suggests that extra energy input might enable rehydration to occur. We found that at 60°C and 100% r.h. the rehydration occurred slowly over several weeks and at 100°C and 100% r.h. it was complete in 21 hr. The starting material was completely anhydride, as shown by i.r. analysis, with no OH stretching or deformation modes of water present. The X-ray powder diffraction patterns in Fig. 6 show the rehydration with time. Pattern (a) is the dry sepiolite anhydride, (b) is after 7 hr at 100°C and 100% r.h. and shows partial rehydration and (c) is after 21 hr showing complete rehydration to normal sepiolite. Preisinger (1963) reports that sepiolite will

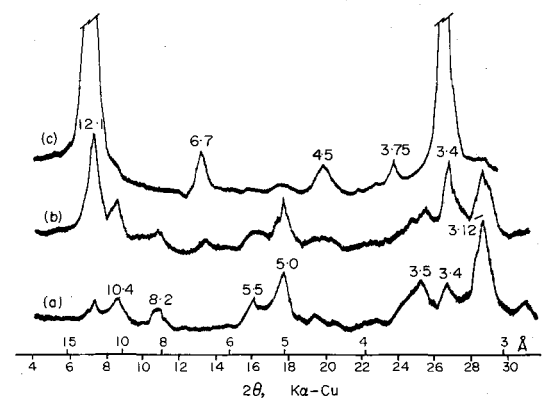


Fig. 6. X-ray powder diffraction patterns of sepiolite anhydride as it alters to sepiolite upon rehydration (a) for 1/4 hr in laboratory air; (b) 7 and; (c) 21 hr in 100% r.h. at 100° C.

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rehydrate but does not define the conditions. However, Nagata *et al.* (1974) did not find the rehydration even under hydrothermal conditions in a sample dehydrated at 600°C in the atmosphere. Their hydrothermal conditions are not reported, but their work would appear to be in conflict with our observations.

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