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STRUCTURAL HYDROXYLS IN SEPIOLITES

J. L. AHLRICHS,* C. SERNA and J. M. SERRATOSA
Consejo Superior de Investigationes Cientificas, Madrid, Spain

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Abstract—Three sepiolite clays studied showed evidence for the presence of structural hydroxyl groups in three to five different environments depending on the composition of the clay. A 3720 cm^{-1} i.r. frequency is shown to be characteristic of SiOH at crystal edges which are very abundant in sepiolites. This band has not been seen by most workers because the Nujol, fluorolube or KBr used in sample preparation perturb it sufficiently to obscure it under other OH stretching bands. The 3680 cm^{-1} band is confirmed as being from the $(Mg)_3OH$ and evidence of a very small band near 3640 cm^{-1} is suggested to arise from limited trioctahedral substitution. The very crystalline Ampandrandava sepiolite shows only the above three bands. The intermediately crystalline Vallecas shows a 3620 cm^{-1} band in addition which is characteristic of dioctahedral systems and is due to either some vacancy sites or to the presence of attapulgite. This dioctahedral band is greater in the less crystalline Salinelles sepiolite; in addition, it has a smaller 3585 cm^{-1} band. Mg–Al–vacancy and Mg–Fe'''–vacancy are suggested as the source of the 3620 cm^{-1} and 3585 cm^{-1} bands.

INTRODUCTION

Characteristic i.r. spectra of sepiolite clays show only one hydroxyl stretching band near 3680 cm^{-1} attributable to structural hydroxyls (Hayashi *et al.*, 1969; Fernandez Alvarez, 1972). However, Cannings (1968) reported an additional higher frequency band near 3740 cm^{-1} in an acid washed Vallecas sepiolite. Mendelovici (1973) reported a similar band in a sample of attapulgite. It has been suggested to arise from SiOH, and Prost (1973) suggests that it is an artifact of crystal disruption during sample preparation. There is also the possibility of bands below 3680 cm^{-1} but these would be difficult to see in sepiolites because of the strong absorption of coordinated and zeolitic water, and because of the difficulty in removing the coordinated water.

The hypotheses for this study are: (1) that there is a true high frequency hydroxyl stretching band above 3700 cm^{-1} in sepiolite due to structural SiOH on edges of the silica sheet because the structural model of sepiolite predicts large numbers of SiOH in this location; (2) that sepiolite must have some band or bands at slightly lower frequency than the 3680 cm^{-1} $(Mg)_3OH$ because of some trioctahedral substitution of the other structural metal ions for magnesium; and (3) that the crystals logically would contain some vacancies to produce even lower frequency dioctahedral type OH bands at 3620 cm^{-1} or lower.

METHODS AND MATERIALS

The sepiolites used were from Vallecas (Spain), Ampandrandava (Madagascar) and Salinelles (France). The Vallecas sample was originally carefully selected for purity and is routinely used at the C.S.I.C. laboratories. The Ampandrandava was hand picked under a microscope from a large crystal selecting only clean and apparently pure crystal fibers. The Salinelles was from sample No. 2-22766 of the Paris museum.

Coarse powders of the samples were dispersed in water where necessary by gentle ultrasonic treatment with a Philips unit producing 40 kHz. Self supporting films were prepared by drying suspensions on mylar plastic and removing them after drying. Several spectra are reported from suspensions dried onto IRTran-2 or AgCl windows or from KBr discs. Infra-red spectra were run on a Perkin–Elmer 225 instrument.

Deuterium exchange studies were done on a standard laboratory vacuum system including a mercury diffusion pump. Sample films were mounted in aluminum foil holders and placed inside an evacuable holder with two side arms; one with CaF_2 windows for viewing the samples and the other for heating the sample during evacuation.

RESULTS AND DISCUSSION

Hydroxyl from SiOH

The structure of sepiolite (Preisinger, 1959) with its short, alternating, talc-like units provides a large number of crystal edge sites which should terminate in SiOH groups. Figure 1(a) shows the cross section (001) of an individual fiber unit. If this fiber unit is not connected to a similar unit through an Si–O–Si bond at any one of the corners, then that terminal Si–O– or Si– should acquire a proton or a hydroxyl respectively. Sites for SiOH along the fiber should occur at intervals of about 5·2 Å at the opposite sides of bisected ditrigonal voids. Since these crystals are long fibers in the direction of the *c*-axis one can expect a maximum possible SiOH to $(Mg)_3OH$ ratio

* Visiting scientist from the Department of Agronomy, Purdue University, West Lafayette, Indiana 47907, U.S.A.

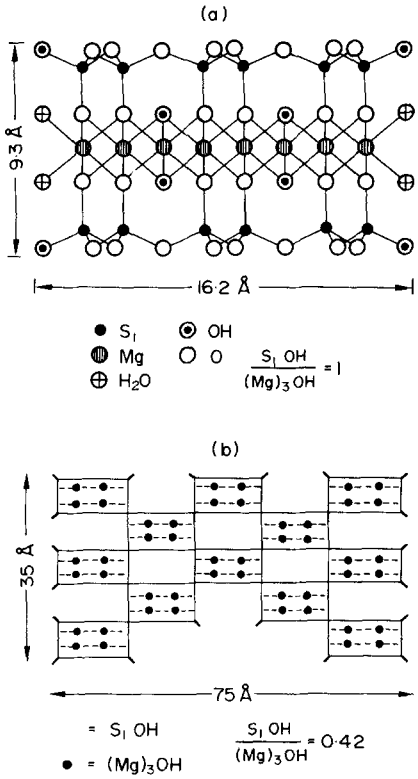

Fig. 1. Sepiolite models (a) atomic sketch of the 001 plane of a single sepiolite fiber; (b) schematic 001 view of a small sepiolite crystal composed of 12 single fibers.

of one, which would exist in such an individual fiber of sepiolite of infinite length. Larger crystals will have lower SiOH to $(Mg)_3OH$ ratios as illustrated by Fig. 1b for a very regular crystal of 75 × 35 Å. Crystals with larger dimensions could maintain a high SiOH to $(Mg)_3OH$ ratio if they had more irregular surface geometry or more imperfect crystallinity. Short crystals also would increase the proportion of SiOH because the terminal ends of each fiber unit offers sites for six additional SiOH; thus each time a crystal is broken in the 001 plane 12 additional SiOH sites are produced per fiber unit.

If the above model is correct then sepiolite with large perfect crystals will show few SiOH while shorter or more imperfect smaller crystals will show more. Cannings (1968) first suggested that the band he found above 3700 cm^{-1} could be an SiOH band. Assuming that this is correct, and assigning the band at 3680 cm^{-1} to $(Mg)_3OH$, since it is similar to that in talc, then comparison of band intensities in three commonly used sepiolites can be made. The highly crystalline Ampandrandava sepiolite with large crystals of a long fiberous character gave an absorbance ratio of SiOH to $(Mg)_3OH$ of 0·2. The Vallecas sepiolite of intermediate crystallinity with a powder character, although it appears as well crystallized short fibers under electron microscopy, gave a ratio of 0·5. The Salinelles sepiolite of lower crystallinity gave a ratio of 0·8. This is the order predicted by the model.

The SiOH should provide a distinct weight loss in T.G. (thermogravimetric) studies. The structural hydroxyls associated with magnesium were lost at temperatures around 750°C in T.G. studies, but most thermal studies reported stop at or below 1000°C. McDonald (1958) shows that hydroxyl associated with silica remain in silica gel and in silica powder at 940°C after 8 hr under vacuum. In T.G. studies up to 1200°C at atmospheric pressure we found an additional weight loss near 1100°C which equalled 1·8 per cent for the Salinelles and 0·6 per cent for the Vallecas based on the weight of the sample after loss of the zeolitic water. For these two sepiolites this is in general agreement with the band intensities observed for the 3720 cm^{-1} band assigned to SiOH in this study.

The absence of this 3720 cm^{-1} band in most sepiolite spectra in the literature proves to be an artifact of sample preparation technique. Figure 2(a) shows the i.r. spectra of the same Vallecas sepiolite sample prepared by two methods. The film was prepared as a self supporting film. Both the 3720 cm^{-1} and the 3680 cm^{-1} band are very intense. Note the complete absence of the 3720 cm^{-1} band in the KBr preparation of the same clay. Figure 2(b) shows spectra of clay films similar to the one in 2(a) but moments after coating with Nujol or fluorolube. Note that the 3720 cm^{-1} band disappears in both, however fluorolube produces a new shoulder at 3705 cm^{-1}. The shoulder at about 3705 cm^{-1} on the fluorolube treated sample supports the idea of a perturbation of the band by these compounds with the effect being greater with KBr and Nujol and less with fluorolube. Samples washed with dilute solutions of aluminum hydroxy material and Na acetate, also were found to perturb the band.

Since the dehydroxylation of the SiOH by T.G. is about 1100°C it should be possible to heat the

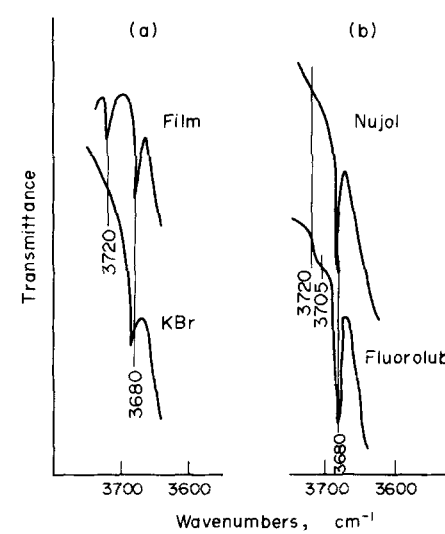

Fig. 2. Hydroxyl stretching bands of the Vallecas sepiolite in different sample preparations (self supporting film, KBr disc, Nujol over self supporting film, fluorolube over self supporting film).

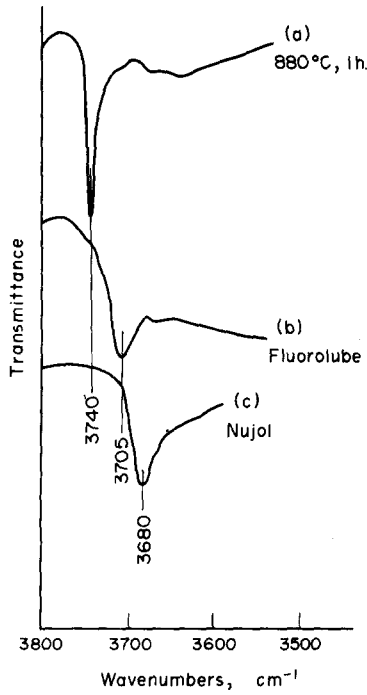

Fig. 3. Perturbation of the i.r. stretching frequency of the SiOH (a) film heated to 880°C during one hour, (b) the same film after coating with fluorolube and (c) an identical film coated with Nujol.

sample to a temperature below this but above the temperature of $(Mg)_3OH$ loss. Infrared spectra should then show only the spectral band of the SiOH at 3720 cm^{-1}. The perturbation of this band by Nujol and other compounds could then be measured. Heating up to 880°C over a period of 1 hr produced a spectra, Fig. 3, with only the high frequency SiOH remaining in the hydroxyl stretching region. Nujol treatment of the clay film was then observed to shift the band 60 cm^{-1} lower. Fluorolube produced a 35 cm^{-1} shift. It should be noted here that the heat treatment caused a shift of the SiOH from 3720 cm^{-1} to near 3740 cm^{-1} so the effect of the Nujol and fluorolube were measured from the latter position. This shift on heating is characteristic of sepiolite OH. It appears that in natural sepiolite where this band is at 3720 cm^{-1}, rather than the 3740 cm^{-1} of the heated sample it is partially perturbed by adsorbed water, or the 3740 cm^{-1} frequency may result from a different crystal environment resulting from the loss of $(Mg)_3OH$. In natural sepiolite the shift from fluorolube or other compounds may be less by the amount of perturbation which has already occurred. The fluorolube shift in Fig. 2 supports this idea since it appears to be only 15 cm^{-1} from 3720 to 3705 cm^{-1}. In the heated sample, Fig. 3, it shifts from 3740 to the same 3705 cm^{-1} position. The perturbation is to be expected even with Nujol and fluorolube. McDonald (1957) shows that the SiOH of silica surfaces are easily perturbed even by weakly adsorbed compounds. For example he reports that methane gas caused a shift of 32 cm^{-1}.

The band returns to its normal frequency when the Nujol or fluorolube is burned off of the film or when the $Al(OH)_2^+$ or Na acetate are washed out. However, the $Al(OH)_2^+$ does not readily wash off the sample and thus only partial return of the band was obtained with five washings in water.

Prost (1973) has suggested that this band is an artifact of the use of ultrasonic treatment to disperse the sample for film preparation. However, the ultrasonic used is very weak and appears to disperse crystals and to separate crystal groups but not to produce new fractures within crystals. Samples treated for up to 1 hr gave the same SiOH to $(Mg)_3OH$ intensity ratios as samples from natural sepiolite rock prepared by scraping gently with a knife to produce a small amount of powder and shaking this in water for a moment before depositing it on an IRTran-2 window.

The band is not from free silica compounds. Treatment with hot 0·5 N NaOH for 15 min as is used to remove free amorphous siliceous matter from soils and clays shows no effect on this band in sepiolite. Treatment with a hot base for longer periods gradually diminished both the 3720 cm^{-1} and the 3680 cm^{-1} band as the crystals degenerated but their intensity ratio stayed constant. Likewise, grinding the sepiolite gradually destroys the crystal as is evident with both X-ray and i.r. In the i.r. both bands may be made to disappear with sufficient grinding. The effect proceeds slightly more rapidly on the 3720 cm^{-1} band by broadening and shifting as in an amorphous silica. The loss of both bands is concurrent with the loss of crystallinity. It appears from the i.r. spectra that the crystal SiOH is partially destroyed in the first stages of grinding and the remaining part is perturbed by the products produced by the grinding.

Free $Mg(OH)_2$ could produce the band near 3720 cm^{-1}. HCl washing would eliminate it if this were the source. However, HCl treatment had no effect until it was strong enough to destroy the crystal of sepiolite, thus the band is not from $Mg(OH)_2$. Figure 4 shows that strong HCl treatment of sepiolite (from studies of Fernandez Alverez, 1972) decreases the 3720 cm^{-1} band only when the 3680 cm^{-1} is also decreasing due to crystal destruction. The HCl treatments produce a silica compound as an end product. This SiOH has a wide band in the same general frequency range and is easily removed with the hot NaOH treatment (Fig. 4). Samples from the last two, strongest HCl treatments dissolved too completely with NaOH to obtain a spectra. The above again supports the theory of the SiOH being part of the sepiolite crystal.

The high frequency of the SiOH and its easy perturbation are readily explained by its location at crystal edges in a very open, isolated site. Not only is it on a crystal edge but it is also separated from its nearest neighbor along the edge by the diameter of the ditrigonal silica ring since the edge bisects this ring. Thus, in a clean clay it is a very free OH and it vibrates at a high frequency. However, it is

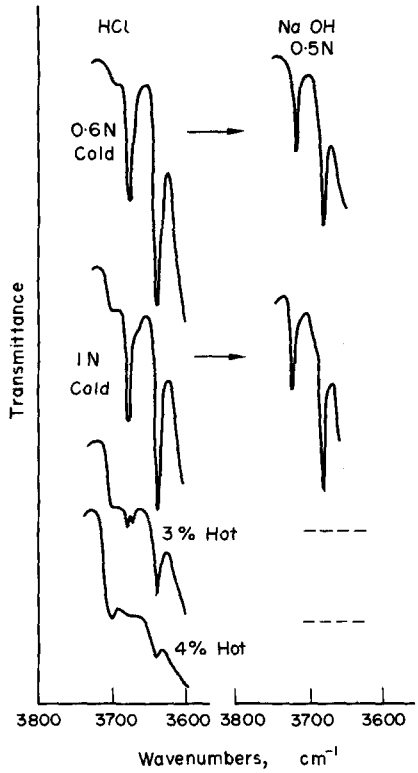

Fig. 4. Effect of HCl and NaOH on the Vallecas sepiolite OH stretching bands. Spectra on the left result from increasingly stronger HCl treatments. Spectra on the right are the same sample after 15 min hot NaOH treatment to remove free silica.

also a very exposed site and its vibrational frequency is easily affected even by rather non-polar compounds like Nujol and fluorolube. Because of its surface position, molecules of this type have no difficulty approaching and perturbing it.

Another indication of the external location of the SiOH is the ease of both deuteration and rehydrogenation of this group. Figures 5(a and b) shows that exposure to D_2O at ambient temperature under vacuum conditions immediately shifts the 3720 cm^{-1} band to 2740 cm^{-1} while the band at 3680 cm^{-1} from $(Mg)_3OH$ does not shift. At higher temperatures (480°C) both types of OH are deuterated (Fig. 5c). The 3680 cm^{-1} band appears at 2710 cm^{-1}. The SiOH readily rehydrogenates (Fig. 5d) upon exposure to moist air and reappears at 3720 cm^{-1}.

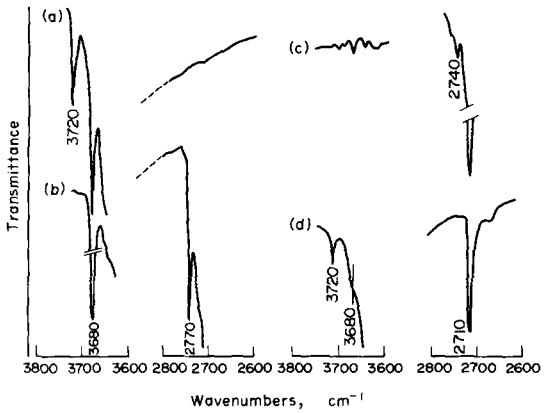

Fig. 5. Deuteration effects on OH spectra of the Vallecas sepiolite (a) natural sepiolite, (b) after deuteration at room temperature, (c) after deuteration at 480°C and (d) after rehydration of (c) at room temperature.

Hydroxyls from trioctahedral sites

All workers have correctly assigned the 3680 cm^{-1} band to $(Mg)_3OH$ and it agrees with a similar band in talc. Everything in this work supports this assignment. We also find its bending mode at 655 cm^{-1}. Talc also shows a small additional band at about 16 cm^{-1} lower frequency (Farmer and Russel, 1964). The persistent evidence for a small band near 3640 cm^{-1} in sepiolite encourages the suggestion of minor trioctahedral substitution for some Mg ions. This substitution logically would be Fe″ for Mg because Fe″ is the other ion available for octahedral occupancy according to X-ray fluorescence analysis. A chemical analysis of the same Vallecas sepiolite sample material, by Dr M. Robert of the C.N.R.S., Versailles, France, in other cooperative work produced a mineralogical formula that shows such substitution, $[Si_{11\cdot92}Al_{0\cdot08}][(Al_{0\cdot52}Fe''_{0\cdot02})(Mg_{6\cdot98}Fe''_{0\cdot08})]$. This band is small but most evident in the Vallecas and Salinelles materials with only nebulous evidence for such a band in that from Ampandrandava (Fig. 6). However, the Ampandrandava sample shows the most iron substitution as seen by the analysis of it in Rautureau *et al.* (1973), $[Si_{11\cdot6}Al_{0\cdot24}Fe'''_{0\cdot16}[(Fe'''_{0\cdot16})(Mg_{7\cdot55}Mn''_{0\cdot37}Fe''_{0\cdot11})]$. Therefore, while this band should be from trioctahedral substitutions because of its high frequency position, its near absence in the Ampandrandava sample does not support a Mg_2Fe'' assignment. The effect on the spectrum of the significant amount of Mn″ in the Ampandrandava sepiolite is unknown.

Hydroxyls from dioctahedral sites

In Fig. 6 the three sepiolites are shown after deuteration at temperatures below 140°C. There is a well defined 3620 cm^{-1} band in the Vallecas sample and an even stronger one in the Salinelles sepiolite, as well as a shoulder at 3585 cm^{-1}. The Ampandrandava sepiolite has only a 3560 cm^{-1} band which appears to be coordinated water and is similar to the slight shoulder seen at this frequency in the Salinelles sample. Because of the extremely long fibers of the Ampandrandava sepiolite the exchange of the last coordinated water from these films depended on very long diffusion paths in the small channels of this sepiolite and therefore the exchange was very slow. Exchange was completed very rapidly in the Salinelles sepiolite and was nearly completed in the Vallecas sample.

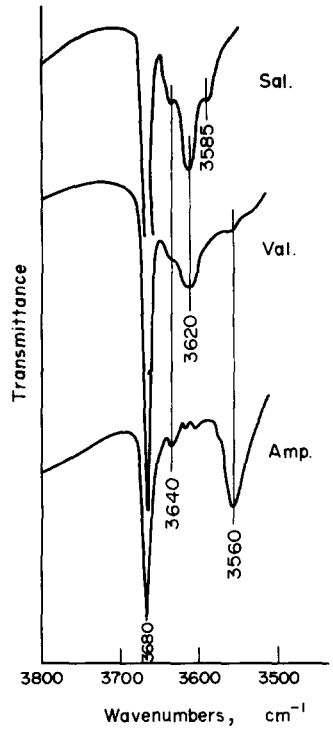

Fig. 6. Infra-red spectra of three sepiolites after deuteration at temperatures up to 140°C; Salinelles (Sal), Vallecas (Val), Ampandrandava (Amp).

These spectra indicate that the sepiolites from Salinelles and Vallecas are not pure sepiolites of the quality shown by that from Ampandrandava. The position of 3620 cm^{-1} is characteristic of dioctahedral systems. There must be either some inclusions of the dioctahedral type minerals, such as attapulgite, in the sepiolite or else a significant number of vacant sites in a regular sepiolite crystal. This low frequency dioctahedral region of the i.r. spectra is very similar to that of the Serradilla (Spain) attapulgite studied in this laboratory. It also has a strong band near 3620 cm^{-1} with a shoulder near 3640 cm^{-1} and another near 3580 cm^{-1}. Attapulgite crystals within the sepiolite in the quantity indicated by the intensity of the 3620 cm^{-1} band of the Salinelles sepiolite should be evident in the X-ray diffractograms. Since no evidence for the 10·5 Å spacing of attapulgite was found the theory of vacancy sites in these two sepiolites is preferred. Montmorillonite could also be a contaminant in sepiolite but the X-ray diffractograms of ethylene glycol treated sepiolites gave no evidence of an expanded phase. Only the sharp symmetric 12·5 Å peak characteristic of sepiolite appeared.

The mineralogical formula given for the Ampandrandava sepiolite by Rautureau *et al.* (1973) shows 8·16 cations for the 8·00 octahedral sites thus indicating no vacancies. This is in agreement with the i.r. spectra which indicate none. However, the Vallecas sepiolite formula given earlier shows only 7·60 cations for 8·00 sites leaving the definite possibility of a significant number of vacancy sites. The Vallecas sepiolite formula would indicate Mg–Al–vacancies as the most probable dioctahedral occupancy with either Al–Fe″–vacancies or Fe‴–Mg–vacancies producing the secondary dioctahedral band near 3585 cm^{-1}. This would agree in order with the work of Farmer *et al.* (1967) on celandonites and on the muscovite–phengite series.

Modification of the ratios of the SiOH *to* $(Mg)_3OH$ *intensity*

The hydroxyls of the octahedral sheet are not all associated with trioctahedral sites and even the trioctahedral sites are not all $(Mg)_3OH$ sites. Therefore it must be recognized that the comparison of the SiOH to $(Mg)_3OH$ intensities does not give a correct numerical relationship between the external OH and the internal OH of the crystal. The ratio of these two intensities gives too large a number whenever there is isomorphic substitution of other ions for Mg or when there are vacancies. This is because the $(Mg)_3OH$ represented at 3680 cm^{-1} is produced by only part of the octahedral OH in these cases, and thus it produces a too small absorbance. Thus, the absorbance ratio for SiOH to $(Mg)_3OH$ in the Salinelles sepiolite was 0·8. Actually even if the absorbance coefficients were equal for the two types of OH, the ratio of the SiOH to the octahedral OH must be considerably less than 0·8 because of the large amount of isomorphic substitution in this clay. A quantitative correction for this error cannot be made at present. A similar error of smaller magnitude is present in the Vallecas sample absorbance ratio figure of 0·5. The Ampandrandava sepiolite however, would appear to give a valid ratio because little evidence of vacancy bands or other significant substitution bands was found.

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