

Effect of pressure on OH-stretching frequencies in kaolinite and ordered aluminous serpentine

B. VELDE

*Laboratoire de Pétrographie, Université de Paris VI
4 Place Jussieu, 75230 Paris Cedex 05, France*

AND G. MARTINEZ

*Laboratoire Physique des Solides associé au C.N.R.S.
Université de Paris VI
4 Place Jussieu, 75230 Paris Cedex 05, France*

Abstract

Infrared spectra of the OH stretching region for natural kaolinite and synthetic ordered aluminous serpentine were recorded between 100 and 9400 bars helium pressure at room temperature. Kaolinite showed an increase of about $+0.5 \text{ cm}^{-1}/\text{kbar}$ for two major stretch frequencies while the aluminous serpentine indicated almost constant energy of vibration for the inner and a $-1.7 \text{ cm}^{-1}/\text{kbar}$ value for the surface hydroxyl vibration. We suggest that this negative shift with pressure is due to an increase in hydrogen bonding between the layers of the structure and thus an increase in O-H distance of the outer hydroxyl groups.

Experimental

Spectra were made using a Coderg single-beam spectrometer with a quartz-iodine lamp source and a cooled PbS detector. About 0.5 mg sample was dispersed in KBr which was compacted into a glassy state, as is usual for analysis of silicate minerals. A sapphire-window pressure cell (Besson *et al.*, 1974) was pressurized with helium gas. Estimation of the pressure error is ± 25 bar.

The initial recorded transmission spectra were measured and corrected for background variation. Absorption was then calculated and plotted to give the spectra presented here. A comparison of spectra made at 100 bar pressure using the single-beam instrument and those made at one atmosphere using a Perkin Elmer 180 double-beam spectrometer are in agreement to $\pm 5 \text{ cm}^{-1}$ for the band studied.

The spectra were made at several pressures between 100 and 9400 bar, half on pressure increase and half on pressure decrease. One duplicate pressure run at 1500 bar was made, with the result that the positions estimated for the absorption maximum were identical. Some slight variations in absorption intensity were seen for the serpentine sample at dif-

ferent pressures but almost none between pressure increase or decrease spectra for the kaolinite sample.

Estimation of the absorption maxima was made largely upon the position of the band flank, which is a curve usually based upon five to ten measured points. We felt that use of the smoothed curve of the maxima would not give reliable results as they are based upon too few points—usually five or six making up two different slopes and the maximum—and the bands are not perfectly symmetrical. Estimated errors due to measuring are shown in Figure 1. Total error is assumed to be $\pm 1.5 \text{ cm}^{-1}$ approximately. Given the rather small variations in frequency as pressure changes, the frequency shift estimated here should be considered to be approximate. However the relative shift for the different vibrations observed is certainly correct, *i.e.* positive and negative, and the relative magnitudes of shifts for the different bands are probably correct.

The samples used were a natural kaolinite from Georgia which showed a fairly well ordered structure similar to that shown in Farmer (1974, p. 335) for the same type of sample, and a synthetic aluminous serpentine near the amesite composition $[\text{Mg}_{4.25}\text{Al}_{1.75}(\text{Si}_{2.25}\text{Al}_{1.75})\text{O}_{10}(\text{OH})_8]$ which was highly ordered

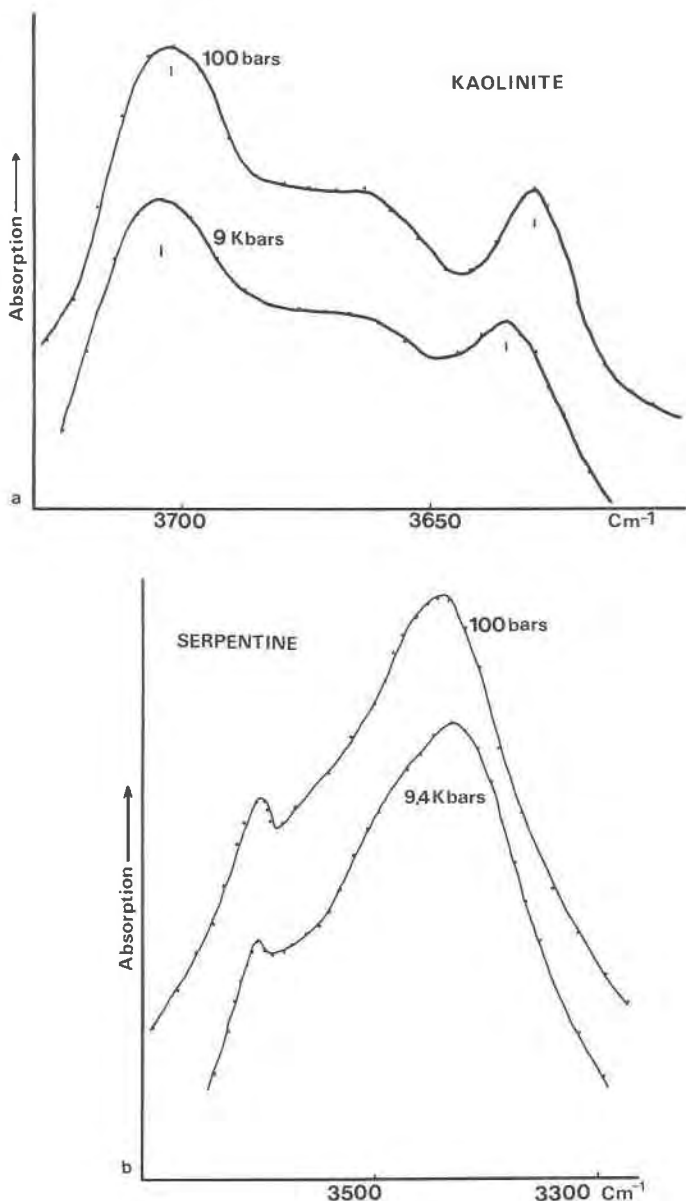


Fig. 1. (a) Absorption spectra of kaolinite showing the experimentally determined points and estimated curve. (b) Absorption spectra for serpentine.

in the octahedral and tetrahedral sites (Serna *et al.*, 1977). Grain size of the minerals was well below 2 microns for both samples.

Results of the measurements as a function of pressure are shown in Figure 2. The error bars are estimates of measurement errors and errors in positioning the maxima. Reference should be made to the calculated spectra in Figure 1 to assess the accuracy of this operation.

In the kaolinite sample there are in fact four OH stretch bands; the two intermediate bands were rather poorly defined in this study. In order to observe their variations more carefully, subtraction spectra were made by taking out the band intensities of the highest and lowest frequency bands. This was done by estimating a smooth curve for the outside flank of each band and assuming a symmetric form. Then the "outside" band intensity was subtracted

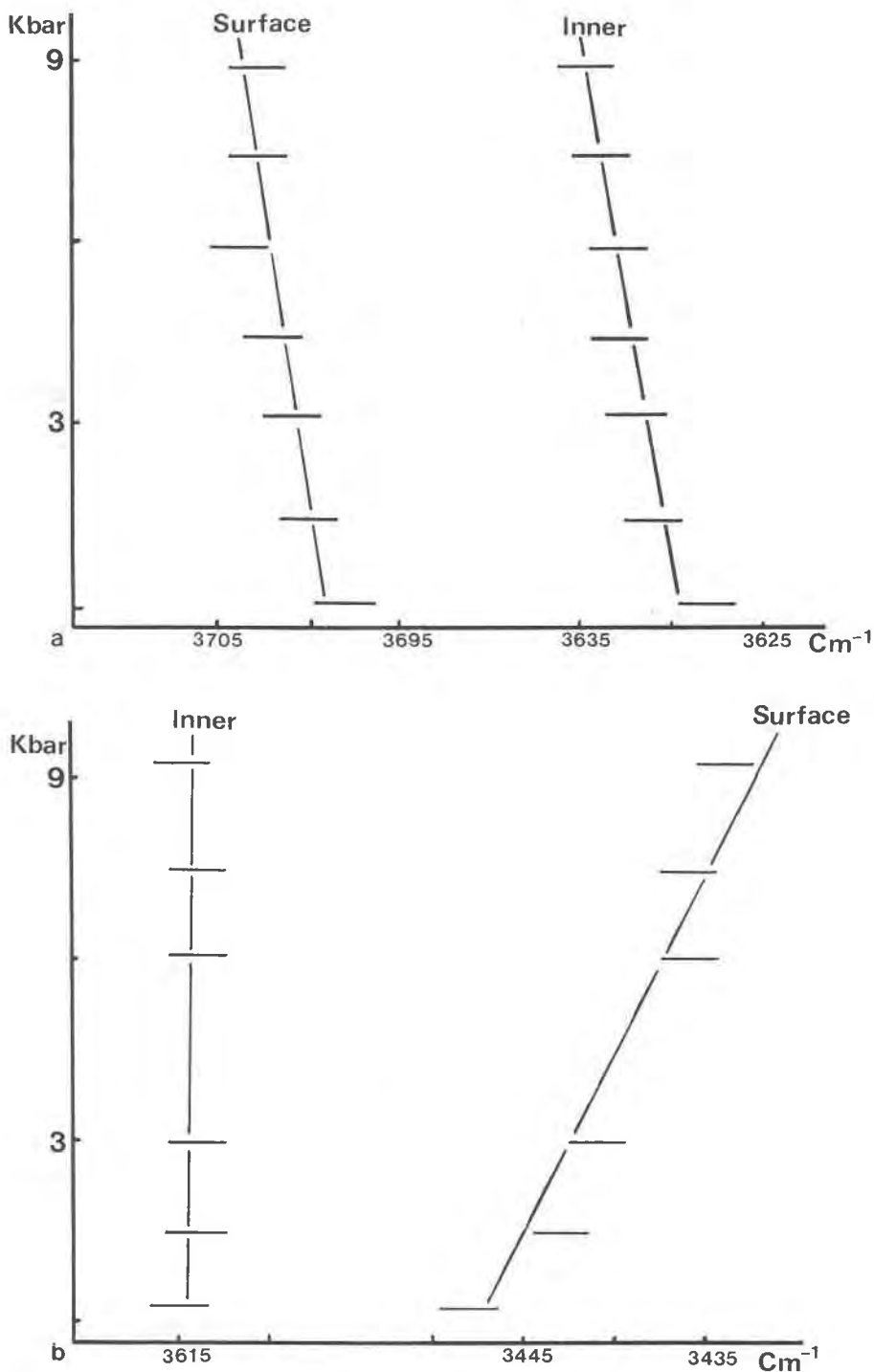


Fig. 2. Pressure-temperature plots for estimated absorption maxima of major intensity OH stretch vibrations for inner and surface hydroxyls of kaolinite (a) and aluminous serpentine (b).

from the total observed intensity leaving only the two inner bands. Figure 3 presents these results. Two bands are identifiable at low pressure and only one is obvious at high pressure.

Observations

Given the problems of experimental measurements, the estimated positions of the major OH

stretching bands seem to vary coherently as pressure varies in the two sequences of experiments. Kaolinite OH stretch bands at the highest and lowest frequency both increase in frequency as pressure increases by about the same amount: $0.5 \text{ cm}^{-1}/\text{kbar}$. This shows that the inner hydroxyl and surface hydroxyls behave in the same way or that structural deformations of the configuration of atoms around them vary in the same way (the significance of inner and surface sites will be discussed directly). In the aluminous serpentine sample, the higher frequency inner OH stretch band shows little or no variation with pressure, while the surface OH stretch band found at lower frequency decreases in energy as pressure increases. Thus the behavior of hydroxyl stretching is quite different for the two minerals. The explanation can only lie in the difference in atomic substitutions and electronic configuration between the two minerals since both structures are crystallographically very similar (7\AA , 1:1 phyllosilicates). Note also that the effect of pressure on the frequency of the surface OH stretch in the serpentine is roughly three times as important as that for the kaolinite.

Discussion

One should first recall the principal similarities and differences between the kaolinite and ordered

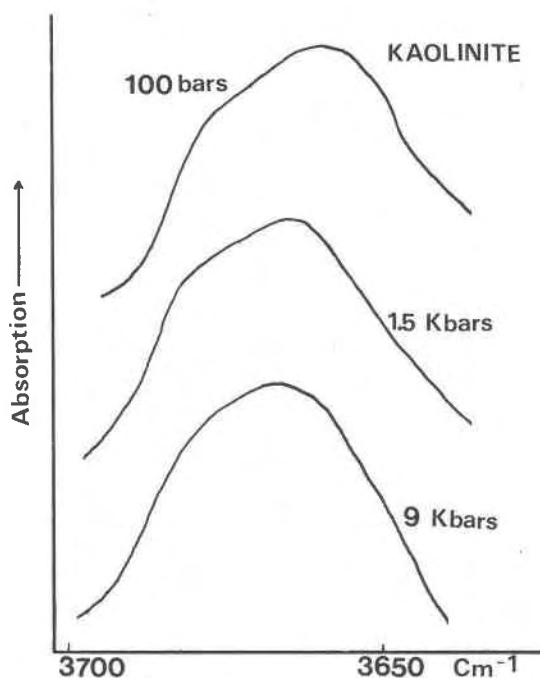


Fig. 3. Three spectra indicating the evolution of the two surface hydroxyl vibrations which appear to merge into one as pressure increases.

aluminous serpentine structures: kaolinite is dioctahedral, *i.e.* in the octahedrally-coordinated cation sites, there are two Al atoms present for three possible sites. In the serpentine, all three sites are filled by cations but they are of two species—2 Mg and 1 Al—and the mineral is trioctahedral. In an ordered serpentine near the amesite composition, most of the sites are filled in fact by Mg_2Al , and few if any by other combinations (Velde, 1980; Serna *et al.*, 1977). In the tetrahedrally-coordinated sites, kaolinite contains only one species (Si), while the serpentine shows Si-Al occupancy. The valence of Al^{3+} in the two sites of the serpentine structure is compensatory as far as total 7\AA structural unit is concerned: $\text{Al}^{3+}\text{Al}^{3+} \rightleftharpoons \text{Si}^{4+}\text{Mg}^{2+}$.

Concerning the OH molecules, there are two sites in the structure, inner and surface (see Brown, 1961, p. 59 for a general discussion). In the first instance the OH unit is clearly "within" the unit layer of the sheet structure whereas the surface OH position has the hydrogen opposed to the oxygen layer of the tetrahedral units belonging to an adjacent 7\AA sheet in the mineral structure. Theoretically, each sheet in the structure (7\AA in dimensions in both kaolinite and serpentine) is neutral in total electrostatic charge, *i.e.* no charge transfer or compensating ions between the sheets are necessary for electrostatic balance as is the case for micas. However, the relative frequency of inner and surface OH stretch vibrations is reversed in the two minerals, surface being of higher frequency in kaolinite and lower in aluminous serpentine compared to the vibration of the inner OH unit (see Farmer, 1974, p. 340–343 for further discussion). This difference is considered to be the result of interaction between the outer hydrogen ions and the oxygen atoms of the adjacent tetrahedra which have a higher net charge in the substituted serpentine structure, which gives a hydrogen bonded structure. As Al substitution increases in the serpentine structure, the frequency of the outer OH band decreases, due apparently to the increased hydrogen bonding of the outer OH hydrogen with the high charge oxygen layer of the adjacent tetrahedral unit (Fig. 4). The same effect is possibly present for the inner hydroxyls but it is much less important.

The two structures differ basically in that for kaolinite little influence is present between the layers in the sheet structure. However, in aluminous serpentine there is an interaction in the form of hydrogen bonding. It might be noted that the thermal stability of kaolinite at pressure is several hundred degrees centigrade below that of aluminous serpentine (about 250°C at 1 kbar). Since the thermal effect is initially

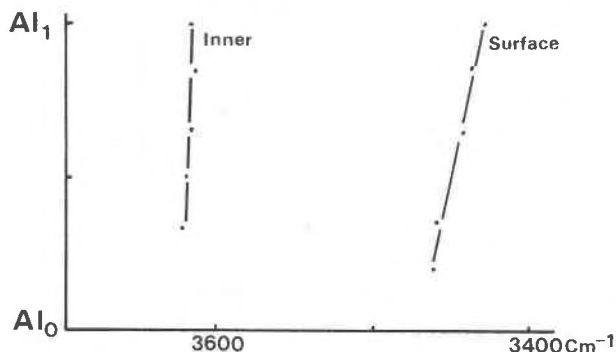


Fig. 4. Surface and inner hydroxyl vibration frequencies for serpentines of different alumina content. Al_{0-1} indicates alumina content of tetrahedral site ($Al \rightleftharpoons Si$). The aluminous serpentine studied is found near the Al_1 composition.

that of dehydration (see Brown, 1961, p. 62 and 97), the bonding of the hydrogen atoms in the structures could well explain this difference.

Our experimental results show that the greatest difference in the effect of pressure on OH stretch frequency is that found for the surface hydroxyls in serpentine. The lowering of frequency in the aluminous serpentine is analogous to the effect of increasing alumina content of the mineral, which is interpreted as an increase in hydrogen bonding. Next, we know that pressure effects a highly anisotropic compression on the chlorite structure, one very analogous to that of serpentine (Hazen and Finger, 1978). The greatest dimension change is perpendicular to the basic 7\AA sheets in the structure. This would tend to decrease the distance between the outer hydrogen atoms and the oxygens to which they are hydrogen-bonded more than deformations in other directions, which would affect the inner OH units. Since the stretch frequency for surface hydroxyls decreases with pressure, one can assume a greater distance between oxygen and hydrogen in the OH couple. Increased hydrogen bonding between the 7\AA layers could explain this effect. This being the case, and if one can attribute high thermal stability due to hydrogen bonding, one can suppose that an increase in pressure will increase the stability of aluminous serpentine. However, in the case of kaolinite, the effect of an increase in hydrogen bonding with pressure is not evident and its thermal stability as a function of pressure is less affected than that of aluminous serpentine (Velde and Kornprobst, 1969; Fawcett and Yoder, 1966).

Now, turning to the two intermediate frequency vibrations in kaolinite, Farmer and Russell (1964) have attributed these bands to a surface hydroxyl vi-

bration within the plane of the layer structure whereas the highest frequency band is assigned to a perpendicular vibration of surface hydroxyls (see Farmer, 1974, p. 340–343 for a discussion of this and other interpretations). The doublet of in-plane vibrations is due to asymmetry of the oxygen ion positions in the next layer. We see that pressure seems to make one band out of two. It is possible to assume a more symmetric configuration of the atoms in a high-pressure kaolinite structure, at least as far as the basal oxygens in the silica tetrahedra are concerned, which would explain a unique band for the in-plane OH stretch of the surface hydroxyls.

Conclusions

We conclude that increase in pressure applied to kaolinite and aluminous serpentine affects the OH stretch bands of the latter more than the former. In kaolinite, pressure increases OH stretch frequencies in much the same way for both inner and surface hydroxyls, indicating that the atoms approach each other in much the same manner as compression is greater. This is a rather normal result. However, the effect of pressure on ordered aluminous serpentine is to decrease the surface hydroxyl frequency and not change that of the inner hydroxyl. This suggests a change in the bonding character of the OH pair in the surface hydroxyl site.

References

- Besson, J. M., Pinceaux, J. O. and Piotrkowski, T. (1974) Optics under pressure to 25 kilobars. *High Temperatures and High Pressures*, 6, 101–106.
- Brown, G. (Ed.) (1961) *The X-ray Identification and Crystal Structure of Clay Minerals*. Mineralogical Society, London.
- Farmer, V. C. (1974) *The Infrared Spectra of Minerals*. Mineralogical Society Monograph, London.
- Farmer, V. C. and Russell, J. D. (1964) The infrared spectra of layer silicates. *Spectrochimica Acta*, 20, 1149–1173.
- Fawcett, J. J. and Yoder, H. S. (1966) Phase relations of chlorites in the system $MgO-Al_2O_3-SiO_2-H_2O$. *American Mineralogist*, 51, 353–380.
- Hazen, R. M. and Finger, L. W. (1978) The crystal structures and compressibilities of layer minerals at high pressure. II. Phlogopite and chlorite. *American Mineralogist*, 63, 293–296.
- Serna, C. J., Velde, B. D. and White, J. L. (1977) Infrared evidence of order-disorder in amesites. *American Mineralogist*, 62, 296–303.
- Velde, B. (1980) Ordering in synthetic serpentines: infrared spectra and cell dimensions. *Physics and Chemistry of Minerals*, in press.
- Velde, B. and Kornprobst, J. (1969) Stabilité des silicates d'alumine hydratés. *Contributions to Mineralogy and Petrology*, 21, 63–74.