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Infrared OH-stretch bands in potassic micas, talcs and saponites; influence of electronic configuration and site of charge compensation

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Abstract

Correlation of octahedral ion electronegativity with band frequency appears to best account for observed OH-stretch frequencies in the di- and trioctahedral minerals potassic mica, talc and saponite. The site of charge substitution in the octahedral layer or in the tetrahedral layer affects the band frequencies also. Band displacements are the same in di- and trioctahedral micas when charge increases in the tetrahedral layer. Substitution of ions of the same charge in the tetrahedral site does not change vibration frequencies as a function of the electronegativity of the ion substituted but there is a correlation between unit cell size and frequency shift. This is attributed to hydrogen–oxygen repulsion between ions in octahedral and tetrahedral layers. Electronic configuration of the ions bonded and involved in the bonding of the oxygen of the OH units seems to be the major factor in determining the OH-stretch band frequency.

Introduction

A summary and explanation of infrared spectra of OH-stretch bands in phyllosilicates can be found in Farmer *et al.* (1967) and in Farmer (1974). Attribution of vibration function for the various bands observed will be based on those of the above papers. The data presented and discussed in the present paper deals only with the OH stretch bands of di- and trioctahedral micas as well as saponites and talcs. As one can see in the literature, attribution of the various bands to specific atomic groupings around the OH site is well known. The reason for the frequency of these vibrations is not commonly given. The following discussion is made in hopes of clarifying this problem.

Several authors have felt that electronegativity of the ions surrounding the OH site can be used to explain the band positions observed in hydrous silicates. Wilkins and Ito (1967) have used this for talcs and Strens (in Farmer, 1974, Chapter 14) for amphiboles. Another possibility is a coupling between OH and octahedral ions in the octahedral layer. Since atomic mass and electronegativity are roughly correlated (see Pauling, 1947, for example), it is difficult to distinguish, initially, between the two factors. Electronegativity is related to ionic radius which depends upon the electronic levels and number of ions present in the coordination environment. Hazen and Wones (1972) have shown that the cell dimensions of trioctahedral micas are closely related to the ionic radii of substituting ions as calculated by Shannon and Prewitt (1970). These cell dimensions are not however a direct function of atomic number. Electronic configuration must then be important in determining the role of the ions in the phyllosilicate structure.

Concerning the possibility that coupling is the factor which determines the OH vibrational frequency, the study by Tarte (1965) on the effect of ionic substitution in olivines where there is a metal cation interaction with Si–O stretching modes shows that there is a better correlation between electronegativity of the ions and band frequency than with mass of the ions alone. We will look at band positions in a series of phyllosilicates in order to see which types of correlations best fit the infrared data.

It might be useful here to indicate briefly where the ionic substitutions will occur in the minerals studied here and which mineral names will be used to designate the different forms. First, the minerals are composed of two types of cationic layers in the silicate framework—the octahedrally and the tetrahedrally coordinated layers. The tetrahedral layer, in the minerals considered, is normally composed of silicon ions but there can be a limited substitution of trivalent ions in the place of quadrivalent silicon. Charge compensation can occur by inserting an ion between two tetrahedrally coordinated layers or by a substitution of an ion of greater charge in the adjacent octahedrally coordinated layer. The effect of substitution of the latter type is of great importance in the present study.

In the minerals considered here, the site occupation of the octahedral layer can be either three ions (trioctahedral) or two ions (dioctahedral). These two basic configurations are indicated in Figure 1 as they are spacially related to the OH group in the mineral structure. The total charge on these cations is six, ideally, which can be

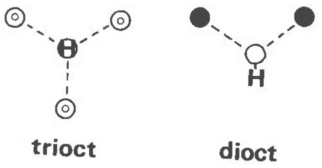

Fig. 1. Schematic drawing of the ionic configuration of cations around the OH units in the phyllosilicates discussed. Projection is on the *a–b* plane. The trioctahedral ions (double circles) can have different occupancy configurations (ex. in an Fe–Mg containing phase there will be Fe^{2+}_3, Fe^{2+}_2Mg Mg_2Fe^{2+}, and Mg_3 occupancies) which each give separate, distinct OH-stretch frequency bands.

indicated by the symbols R^{2+}_3 or R^{3+}_2. Substitutions of different charged ions in the tetrahedral site compensated by changing the charge in the octahedral site will change the overall charge on the octahedral layer, and will also create different ionic groupings in these sites such as $R^{3+}R^{2+}$ in the case of a dioctahedral mica and $R^{2+}_2R^{3+}$ or $R^{2+}R^{3+}_2$ in the trioctahedral form. Table 1 indicates the sites of charge substitutions and the mineral names which will be used to indicate each form.

The interpretation of the infrared spectra (Farmer, 1974, Chapter 15) indicates that each ionic configuration around an OH site gives a distinct vibrational band. In general, the frequency of these bands is affected by the species of the ions present and the overall charge on the octahedral layer of the mineral. This second observation leads one to consider the possibility of "molecular" bonding of the ions in the octahedral site of the mica structure in that a single ionic charge substitution could not affect other distant sites unless the charge were distributed over many ionic positions. Wilkins and Ito (1972) have shown that when ions of the same charge are substituted in the octahedral site the frequency of a given vibration is not affected. That is, if nickel is substituted for magnesium in a limited amount, the band position of the Mg_3 configuration is not affected. There is thus no coupling between the different octahedral groupings.

Table 1. Synopsis of substitutions in the various structural sites of the phyllosilicates considered. Cation layers are octahedral and tetrahedrally coordinated sites and interlayer sites.

		charge imbalance			
Mineral	oct. ions	tet.	oct.		interlayer ion
talc	3	0	0	0	0
saponite	2.85	0	0.3	0.3	0.3
phlogopite	3	-1	0	-1	1
eastonite	3	+1	-2	-1	1
muscovite	2	-1	0	-1	1
celadonite	2	0	-1	-1	1

Experimental

Much of the data used in the present study was taken from the literature. Band positions for talc are from Wilkins and Ito (1972), for ferrous, aluminous biotites (eastonites) from Levillain and Maurel (1980), for various magnesian, and magnesio-aluminous biotites (phlogopites and eastonites) from Robert (1981) and for celadonites (dioctahedral micas) from Farmer *et al.* (1967). Some new spectra were made using aluminous saponites provided and described by Decarreau (1980) and some new micas were synthesized using starting materials and methods described by Hazen and Wones (1972). The infrared spectra were made on a Perkin-Elmer 580 machine using KBr pellets (0.2 mg of sample in a 6 mm diameter disk) which were heated to 300°C overnight. Cell dimensions of the micas synthesized were essentially those reported by Hazen and Wones (1972).

The following mineral types were studied:

talc $R^{2+}_3Si_4O_{10}(OH)_2$
celadonite and muscovite $K(R^{3+}R^{2+})(Si_3R^{3+})\ O_{10}(OH)_2$
phlogopite $K\ R^{2+}_3\ (R^{3+}Si_3)O_{10}(OH)_2$
eastonites $K\ (R^{2+}_2R^{3+})(Si_2R^{3+}_2)O_{10}(OH)_2$
saponites $R^{2+}_{0.2}\ (R^{2+}_{2.8})Si_4O_{10}(OH)_2 \cdot nH_2O$

where the cations R^{2+} = Mg,Fe^{2+},Ni,Co,Zn, Cu and where R^{3+} = Al,Fe^{3+}, Ga.

Electronegativity values are those of Allred and Rochow (1958) and Allred (1961) which were derived from calculations using ionic radii as well as sequences based upon thermochemical data. When OH-stretch band frequency is plotted against atomic weight, the relation is in most cases less well defined than when electronegativity is used.

Correlations

Electronegativity (EN) and octahedral ion species. The effect of substitutions of ions of equal charge on the frequency of OH-stretch vibration is shown in Figure 2. Here we plot the average electronegativity of the three ions found in the tri-octahedral minerals investigated; talc, saponite and mica. For example, when nickel is substituted for magnesium in these minerals there will be a Mg_3, Mg_2Ni, Ni_2Mg and Ni_3 configuration and a specific OH-stretch band for each. Thus there will be four points on each curve representing these substitutions in the series where intermediate composition minerals were studied. In the figure three mineral series are shown, the talc–saponites which are much the same and the micas. There are two of this latter type, those where aluminum is the substituting element in the tetrahedral site, denoted by Si_3Al, and those where Fe^{3+} is the substituting element, denoted by Si_3Fe^{3+} in the figure. If one uses average atomic mass for the correlation factor, one finds

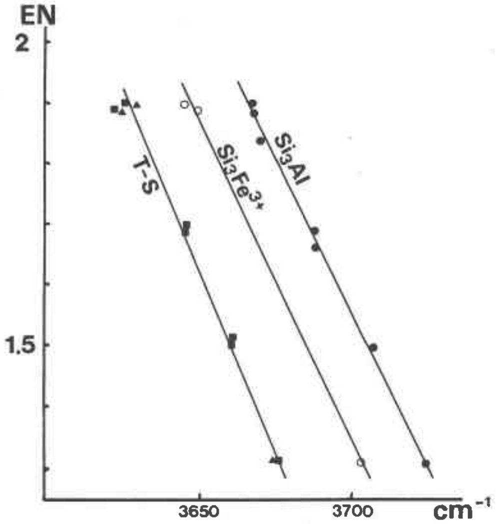

Fig. 2. Average electronegativity of octahedral R_3^{2+} site configuration versus frequency of vibration plot. The various experimental points show band positions attributed to different combinations of atoms present in the octahedral site of the minerals according to the assignments found in Farmer (1974,Ch.15). The highest frequency in each sequence represents three magnesium ion groups while the lowest frequency band represents an all transition metal ion grouping. Squares show Ni, Co, Mg talc (T) bands, triangles show those of saponites (S), circles show those of ferri-biotites with a tetrahedral configuration of Si_3Fe^{3+} and dots show aluminous biotites which have Si_3Al in the tetrahedral layer.

a slightly curved relationship using the ion combinations of Mg,Ni,Fe^{2+} and Co. Figure 3 shows the electronegativity–band frequency relations for the talc and saponites when the ions Zn and Cu are substituted in the structures. It is evident that these elements do not affect the infrared vibrations in the same way as the previous set of elements.

Figure 4 shows the data for the dioctahedral minerals. One can see that the slope of the relationship is different for the two phyllosilicate mineral types. In the case of the dioctahedral minerals it must be remembered that there are only two ions present and the average electronegativity difference is spread over only two sites rather than three as the case for the trioctahedral minerals. In comparing the four trioctahedral mineral series those of R_3^{2+} and $R_2^{2+}R^{3+}$ ion groups in the phlogopites and in the eastonites one sees that the effect of average electronegativity on the three sites is similar in both series. The difference between the two mineral series is that in phlogopites the average charge on the octahedral site is near six (the frequencies for the R R ionic groupings are extrapolated to charge six from slightly substituted minerals) and in the eastonites the average charge on the octahedral site is seven, as indicated in the figure. The effect of change in the average electronegativity is 82 cm^{-1} per EN unit for the talc–saponites, 96 cm^{-1} per EN unit in the trioctahedral micas and 170 cm^{-1} per EN unit for the dioctahedral micas.

Charge substitutions in the octahedral site. A second type of substitution which one can make is that of an increase in the total cationic charge in the ionic groups of the octahedral site. This is accompanied by a corresponding change in the charge of the ions in the tetrahedral sites. In a phase of intermediate composition, say with an overall octahedral charge of 6.5, one can still identify the band positions of the different octahedral ion configurations such as Mg_3^{2+}, Mg_2Fe^{2+} and so forth. In following these same bands as charge changes, it is possible to see the effect of charge which is compensated in both the octahedral sites. It can be seen in Figure 4 that the trioctahedral micas eastonite and phlogopite give two sequences of OH vibration band relations depending upon whether the overall charge on the octahedral sites is six or seven. The bands form parallel series on the electronegativity versus frequency plot. Both R_3^{2+} and $R_2^{2+}R^{3+}$–OH band configurations form series for each type of mineral. Using these four lines one can observe two effects, first by changing the charge on an octahedral grouping there is a shift in frequency of 30 cm^{-1} in phlogopites but only a shift of 20 cm^{-1} for the eastonites. The effect of changing the charge on the octahedral grouping while maintaining the same overall charge on the octahedral site and also maintaining the same electronegativity on the octahedral grouping shifts the band frequency more in the low charge mineral (phlogopite) than in the high charge mineral (eastonite). The same effect can be seen in another way by considering the shift in band position for the same type of octahedral group, R_3^{2+} or $R_2^{2+}R^{3+}$, in going from one mineral type to the

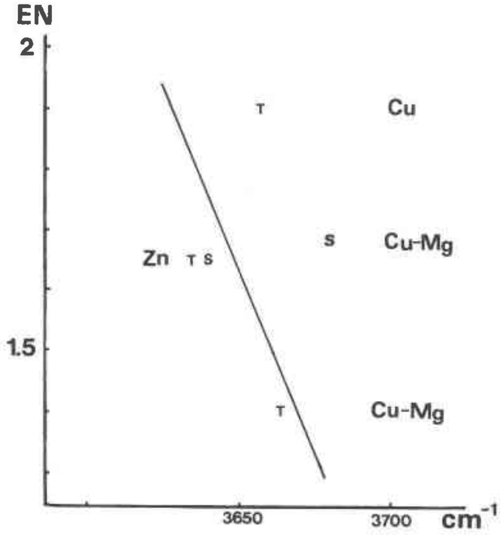

Fig. 3. Average electronegativity versus frequency plot for talcs Zn–Mg and Cu–Mg saponites. The letters T and S show values for each mineral type. Line shows values for Mg–Co and Mg–Ni minerals of Fig. 2.

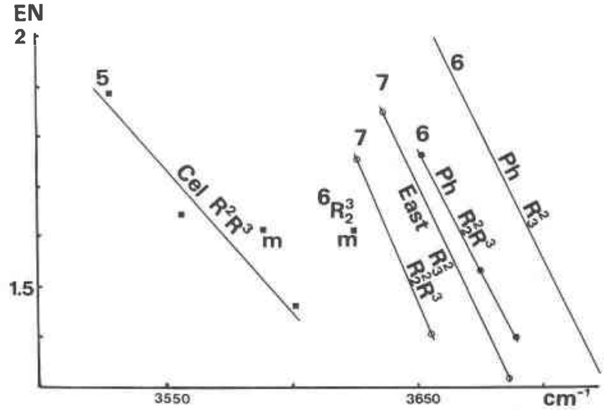

Fig. 4. Average electronegativity *vs.* frequency plots for micas with different overall charges on the octahedral site configuration shown as 5, 6, or 7. Cel = celadonite micas where the average charge is five. m = muscovite with an average of near six. Trioctahedral micas with average charge of six are phlogopites (Ph) and those with near seven are eastonites (East). The band frequencies for the $R_2^{2+}R^{3+}$ groups in phlogopite are extrapolated to values corresponding to a charge six octahedral layer by using band positions from micas of compositions intermediate between phlogopite and eastonite. The line for R_3^{2+} phlogopite bands is that of Fig. 2.

other. There is a shift of 37 cm^{-1} between the R_3^{2+} groupings and only 30 cm^{-1} between the $R_2^{2+}R^{3+}$ groups. This suggests two things; First, not only electronegativity is the factor in determining the band position but the charge on the octahedral grouping is important. Second, it seems apparent that the site of charge in the structure is important also. When one increases the overall charge on the octahedral site there is a correlative shift in the vibration of OH bands due to the different octahedral site groups.

It is possible to obtain the same type of charge site shift in the dioctahedral mineral series (celadonite–muscovite). Here we do not have the possibility of observing several bands in two different configurations but we can follow the Al_2 band in the substitutional series between the two mica types. In Figure 4 the celadonite series is indicated by Cel where the octahedral configuration is $R^{2+}R^{3+}$. Using the data for the substitutional series between celadonite and muscovite ($R^{2+}R^{3+}$–R_2^{3+}) one can see that the shift in the band position of the Al_2 band in muscovite is 38 cm^{-1} when one changes the overall charge on the octahedral site from six to five. This is the same value which is observed in changing the overall charge on the octahedral site in the trioctahedral micas. Now if we change both the overall charge and the charge on the site grouping in the dioctahedral minerals, going from muscovite to the celadonte series, the shift in frequency is 56 cm^{-1} which is the same as that found in the trioctahedral mineral series when a similar change in site and overall charge is effected. We see then that the change in the site and overall charge on the micas effects the same frequency shift for both di- and trioctahedral micas.

Charge substitution in the tetrahedral site. It is useful now to consider the sequence of band positions for equivalent electronegativity of octahedral configurations as a function of the charge on the tetrahedral layer. In the trioctahedral minerals, the talc–saponites are minerals with low charge (near zero) in the tetrahedral layer. By increasing this charge to one, (phlogopite micas) there is an increase in the band frequency of an equivalent site groups, *i.e.*, the octahedral ion group with the same electronegativity. In increasing the charge in the tetrahedral site of dioctahedral micas, *i.e.*, in going from celadonite to muscovite, the same type of band displacement is observed. In both cases the change is from about zero charge in the tetrahedral site to one charge unit which is not compensated in the octahedral site but which is compensated by the substitution of an ion in an interlayer position. When the increase in charge in the tetrahedral site is compensated in the octahedral site, as is the case in going from phlogopite to eastonite, the effect on OH vibrations due to octahedral site groupings of the same average electronegativity is to a decrease in frequency. This is the reverse effect to that observed where the charge is compensated outside of the tetrahedral–octahedral complex. Compensation site of charge substitution is thus important in determining the frequency of vibration of the OH-stretch bands.

Tetrahedral site substitutions of equal charge. It is possible to place various ions in the tetrahedral site of micas which vary the type of R^{3+} ions substituting there. Three ions have been used in this study; Al^{3+}, Fe^{3+}, and Ga^{3+}. It was found that the best relation between frequency of vibration (the Mg_3 configuration in all the cases studied) is one based upon the c sin β cell dimension. Thus neither mass nor electronegativity seem to be directly implicated in the effect. The results are shown in Figure 5. One can interpret this effect as being due to a change in the average distance of the apical oxygens of the silica tetrahedral sheet to the hydrogen ion in the OH groups which are found in the octahedral layer. Since the ions substituted in the tetrahedral layer represent only

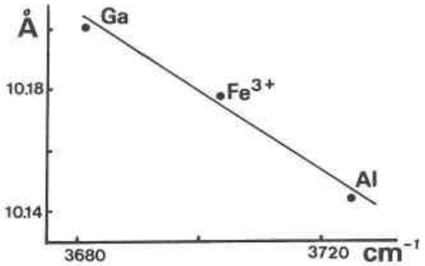

Fig. 5. Correlation of c sin β cell dimension and band frequency of the Mg_3 OH-stretch bands for various phlogopites where the ions Al, Fe^{3+} and Ga are present in the tetrahedral site.

one in four sites, one must imagine that the substitution must be spread over the entire layer in order to affect all of the OH vibrations in the octahedral layer in the same manner. This must be the case because it has already been noted by Wilkins and Ito (1972) that there is no coupling interaction between the different octahedral site groupings which could transfer and average an effect which was localized in only a few sites of these groupings in the structure.

An increase in cell dimension decreases the frequency of vibration of the Mg OH vibrations. The value is about 7 cm^{-1} per 0.01Å change in the cell dimension. It might be possible to compare this effect to that observed for kaolinite which has been submitted to hydrostatic pressure (Velde and Martinez, 1981). These authors found that a change in cell dimension effected by pressure increased the band frequencies of OH-stretch vibrations as the pressure increased. In this process cell dimensions decrease. One can attribute this effect to a repulsion between apical oxygens of tetrahedra and the hydrogen of the OH unit as the two approach one another. This repulsion then changes the frequency at which the OH stretch vibrates. This is true, according to these authors, when little or no hydrogen bonding occurs. When hydrogen bonding does occur, the effect is the reverse. In phlogopites, one can expect little or no hydrogen bonding because the charge imbalance in the tetrahedral layer is compensated in the interlayer site. We see then that the effect of electronegativity change is valid only for substitutions in the octahedral layer.

Summary

It should be possible now to correlate average site group electronegativity of octahedral ions with OH-stretch band frequency for the different structures; 82 cm^{-1} per EN unit for talc and saponites, 96 cm^{-1} for trioctahedral micas and 170 cm^{-1} for dioctahedral micas.

It is also possible to estimate the band shift which will occur when the overall charge on the octahedral layer changes. This is about 35 cm^{-1} per charge for trioctahedral minerals as well as for dioctahedral minerals. Such information should help one to assign bands found in complex samples of unknown or of poorly known composition.

In considering the various plots of the data presented here, it can be seen that there is a definite correlation between electronegativity and frequency shift for Mg, Ni, Co, Fe and Al. These ions are concerned with effects in the 3*s* and 3*d* electronic levels only. When the 3*d* shell is filled, as in the case of copper and zinc ions, the pattern no longer holds. This suggests that the electronic nature and the type of bonds between these ions and the oxygen of the OH group is important in determining the force constant of the OH bond. In these cases there is no clear relation between mass of the ions and the frequency of vibration. Coupling should play a minor role if any.

Also it was seen that the site of charge imbalance and the type of compensation (within the tetrahedral–octahedral layer complex or in the interlayer position) influences the band shift due to charge imbalance on the octahedral layer. This indicates again that the electronic configuration of the bonding in the octahedral layer is important in determining the OH vibration frequency. Substitutions in the octahedral site which do not implicate charge compensation in tetrahedral sites do not seem to affect the OH vibrations as a function of electronic configuration but do modify the relative positions of the apical oxygens of the tetrahedral units and then the OH vibrational frequencies.

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