

INFRARED ABSORPTION OF O—H BONDS IN SOME MICAS AND OTHER PHYLLOSILICATES

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ABSTRACT

THE FREQUENCIES, relative intensities and pleochroism of OH stretching bands in some micas and chlorites were studied, and the following conclusions are drawn:

Trioctahedral 2:1 and 2:1:1 phyllosilicates, where all octahedral positions are filled with Mg, will have an absorption band about 3700 cm^{-1} . These OH-groups have their axes normal to the mineral's cleavage.

Substitution of Fe^{2+} for Mg results in a band about 3665 cm^{-1} . Intensity ratios indicate that two Fe^{2+} most commonly substitute for two Mg in the same polyhedral group (pyramid).

Decreasing octahedral occupancy in the phlogopite-lepidomelane group, with increasing substitution of R^{3+} for Mg, causes bands with lower frequencies. These are not very sensitive to the incident angle for the infrared beam. In Li-micas where less than 50 per cent of the octahedral positions are filled with Li, and the rest of the positions are filled with Al and Fe^{2+} , it seems probable that OH-groups residing in a pyramid with two Li and one Al cause a band about 3580 cm^{-1} . Combinations of two Al and one Li or one Li, one Al and one Fe^{2+} cause absorption about 3480 cm^{-1} .

Dioctahedral 2:1 phyllosilicates having Al or Fe^{3+} in octahedral positions cause absorption about 3620 cm^{-1} .

EXPERIMENTAL

Methods

THE SPECTRA of mineral flakes were recorded on a Perkin-Elmer Spectrophotometer (Model 21) having a CaF_2 prism. For most of the minerals two curves are given, one in which the mineral flake was oriented normal to the infrared beam (0°) and one in which the mineral had been tilted out of this position.

Foster (1956, 1960a, b and c) has discussed the composition of the following mica groups: trioctahedral micas, lithium micas and dioctahedral micas. The same procedure is followed here for a description of the infrared absorption of O—H bonds in some micas and other phyllosilicates.

TRIOCTAHEDRAL MINERALS

The Phlogopite-Lepidomelane System

Foster (1960a) calculated the formulae for more than 200 analyses of

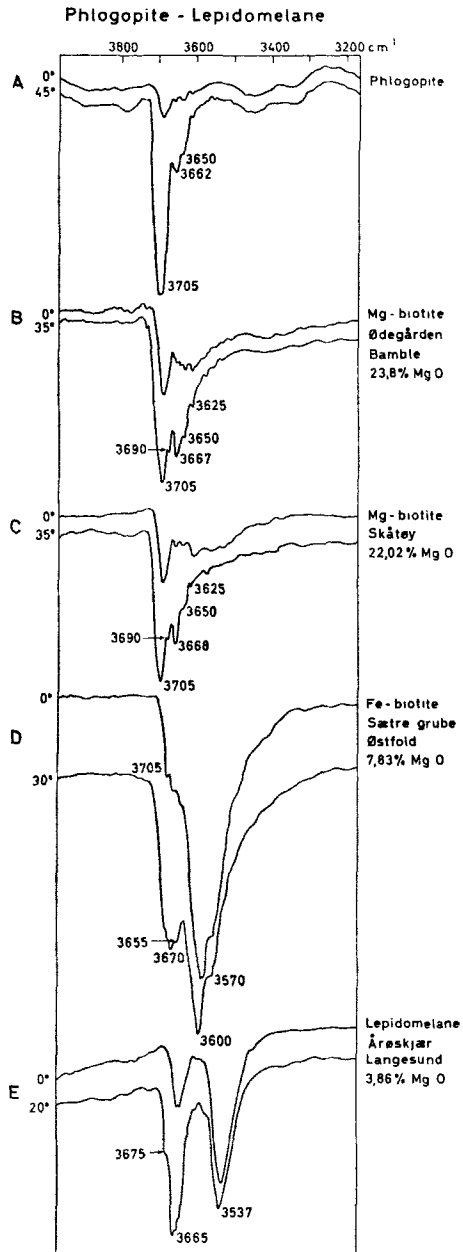


FIG. 1. Infrared curves for five samples from the phlogopite-lepidomelane system.

phlogopites, biotites, siderophyllites and lepidomelanes. She found that, in order of decreasing Mg content, these trioctahedral micas form a complete system, from full octahedral occupancy by Mg at one end to zero Mg occupancy at the other end.

Five different samples with varying Mg content were selected from this system, the infrared curves for which are shown in Fig. 1.

Results

Curve A (Fig. 1) shows that a phlogopite with a small iron content has two different major absorption bands caused by the activation of O—H groups in the mineral. The position of the strongest band is at 3705 cm^{-1} and of the weaker, at 3662 cm^{-1} .

The tilting of the mineral shows, as previously demonstrated by Serratosa and Bradley (1958) and Bassett (1960), that both types of O—H bonds are directed approximately normal to the cleavage plane.

The positions of the bands caused by absorption in an Mg-biotite are the same as for the phlogopite (curve B, Fig. 1), but the intensities of the bands are changed so that the intensity of the band at 3667 cm^{-1} is increased relative to the band at 3705 cm^{-1} . The intensities of these bands are not so sensitive to tilting in the infrared beam, indicating that the O—H bonds in these minerals are not oriented strictly normal to the cleavage plane, as in the case of phlogopite.

Fe-biotite (curve D, Fig. 1) has two distinct bands about 3665 and 3600 cm^{-1} . The latter band has a marked shoulder about 3570 cm^{-1} . It is clear that the intensity of one band (3665 cm^{-1}) varies with different angles of incidence for the infrared beam, while no such changes in intensity can be observed for the band at 3600 cm^{-1} .

Lepidomelane (curve E, Fig. 1) also has one band at 3665 cm^{-1} that is sensitive to changes in angles of incidence, while the other band at 3537 cm^{-1} is not.

This indicates, as previously stated by Bassett (1960), that lepidomelane and Fe-biotite both have one type of OH-group that is oriented approximately normal to the mineral's cleavage plane, and one group that is not.

Discussion in light of the mica structure

The ideal end-member phlogopite $\text{K Mg}^{\text{IV}}(\text{AlSi}_3)^{\text{VI}}\text{O}_{10}(\text{OH})_2$ has all octahedral positions filled with Mg ions. These Mg ions are the nearest cation neighbors to the OH-group. Figs. 2 and 3 show the orientation of these ions relative to the OH-group.

The cation-oxygen distance is about 2 \AA , while the distance between oxygen and the second nearest cation, Al or Si in tetrahedral co-ordination, is about 3.3 \AA . These polyhedral groups (Fig. 2) henceforth will be referred to as a pyramid. The cation plane in these pyramids is parallel to the mineral's cleavage plane (001).

The infrared curves for trioctahedral micas (Fig. 1) vary with changing

amounts of isomorphous substitution. Stubičan and Roy (1961) and Tuddenham and Lyon (1960) found bands at lower frequencies whose positions were gradually varying with increasing isomorphous substitution.

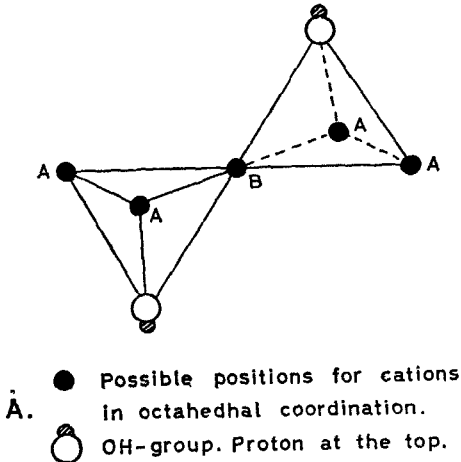


FIG. 2. The orientation of cations in octahedral positions relative to the OH-group.

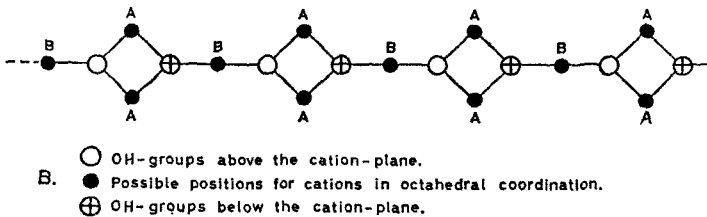
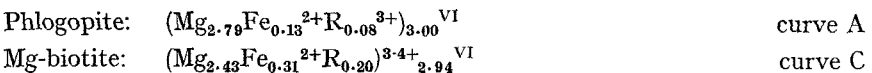


FIG. 3. The orientation of cations in octahedral positions relative to the OH-group. Looking along the *c*-axis.

The OH-bonds studied showed a change in frequency that was distinct rather than gradual. This indicates that each OH-group is mainly influenced by the nearest ions in octahedral positions.

Pure phlogopite has one absorption band at 3710 cm^{-1} , as was described by Bradley and Serratos (1960).

It is, therefore, natural (Bassett, 1960) to assign the band at 3710 cm^{-1} to an OH-group residing in a pyramid with three Mg in the nearest octahedral positions. The simplified composition of the octahedral layer for the minerals investigated is:



Fe-biotite:	$(\text{Mg}_{0.89}\text{Fe}_{1.50}^{2+}\text{R}_{0.20}^{3-4+})_{2.69}$	curve D
Lepidomelane:	$(\text{Mg}_{0.60}\text{Fe}_{1.45}^{2+}\text{R}_{0.70}^{3-4+})_{2.75}$	curve E

Since the only difference between a pure phlogopite and the phlogopite and Mg-biotite investigated is a small isomorphous substitution of Fe^{2+} and R^{3+} for Mg^{2+} , it is probable that the band at 3665 cm^{-1} is caused by OH-groups contained in pyramids in which the octahedral positions are filled by Mg and Fe^{2+} (or R^{3+}). These OH-groups are oriented approximately normal to the cleavage plane. Since this band is found for all minerals from this group, except pure phlogopite, the question was whether there exist zero, one or two Mg in the pyramids that cause the band at 3665 cm^{-1} .

The pyramids are linked together as shown in Figs. 2 and 3. Two of the three cation positions in a pyramid are symmetry-related (A positions), while the third is at a center of symmetry (B positions) (Radoslovich, 1963). A cation in one of these positions will influence the two nearest OH-groups, while two cations in two symmetrically related positions will influence the same two OH-groups.

The intensity ratios for the bands at 3705 and 3665 cm^{-1} are: phlogopite, 5 : 1; Mg-biotite, 2.5 : 1; Fe-biotite, 1 : 20; lepidomelane, no band observed at 3705 cm^{-1} .

For the phlogopite, less than each tenth position in the octahedral layer is not filled with Mg, but with Fe^{2+} or R^{3-4+} . According to Radoslovich (1963) it is probable that the R^{3-4+} cations are in unique positions. If the Fe^{2+} ions were completely randomly distributed in the octahedral layer, the ratio between pyramids with three Mg, pyramids with two Mg and one R^{3-4+} and pyramids with two Mg and one Fe^{2+} would be 13 : 1 : 2. Consequently, the ratio between pyramids with three Mg and pyramids with other combinations would be 13 : 3 (4.33 : 1). If two Fe^{2+} cations were in the same pyramid, the ratio would be about 7 : 1.

For the Mg-biotite, about each sixth cation position in the octahedral layer is not filled with Mg, but with Fe^{2+} or R^{3-4+} . Again assuming a random distribution of all cations in the octahedral layer, the ratio between pyramids with three Mg and pyramids with 2 Mg and another cation will be 1 : 1 (8 : 8).

The other possibility, that two Fe^{2+} ions are present in the same pyramid and R^{3-4+} is in a unique position, produces ratios between 3 : 1 and 8 : 3. For the Fe-biotite, about 30 per cent of the pyramids will have one vacant position. Where there is full octahedral occupancy the pyramids generally will have (2Fe^{2+} and Mg) or (Fe^{2+} , Mg and R^{3+}) in octahedral positions.

These three examples indicate that the band about 3665 cm^{-1} is mainly caused by OH-groups occurring in pyramids with two Fe^{2+} and one Mg in the octahedral positions.

Since this band is also present in phlogopite and Mg-biotite, it indicates that isomorphous substitution of Fe^{2+} for Mg is not randomly cation for cation, but that two Fe^{2+} ions substitute for two Mg.

The OH-groups causing the band at 3665 cm^{-1} (Fig. 1) are not oriented strictly perpendicular to the cleavage of the minerals, as are the OH-groups in phlogopite.

There is almost no change in the distribution of charge in the octahedral positions of phlogopite and Mg-biotite, but there are at least two other possible explanations for the varying bond frequencies and orientations. Because different cations in the octahedral positions will have a different influence on the electrons in the OH-group:

1. The strength of the O—H bond will vary with different cations (vacancies) in the octahedral positions.

2. The orientation of the O—H bond will vary with different cations (vacancies) in the octahedral positions, giving different possibilities of forming weak hydrogen bonds to oxygen in the tetrahedral layer.

Both Fe-biotite and lepidomelane have a band that is not influenced by tilting in the infrared beam. It is known that dioctahedral muscovite has one band like this (Bradley and Serratosa, 1960; Bassett, 1960; Vedder and McDonald, 1963), and it is probable that the bands at 3600 cm^{-1} (Fe-biotite) and 3537 cm^{-1} (lepidomelane) arise from OH-groups in pyramids having one vacant position. According to Radoslovich (1963), most biotites high in R^{3+} are likely to be somewhat deficient in all octahedral positions.

As previously mentioned, about 30 per cent of the pyramids in Fe-biotite will have one vacant position, and in the lepidomelane this will be true for about 25 per cent. That these bands are found only for the Mg-poor members is in agreement with the findings of Foster (1960a), who discovered that there was a decrease in octahedral occupancy with decreasing Mg content.

Other Trioctahedral Phyllosilicates

The curves F and G (Fig. 4) demonstrate that Mg-rich chlorites have two bands about 3700 and 3650 cm^{-1} (the latter band probably is composed of two bands about 3640 and 3660 cm^{-1}).

Hayashi and Oinuma (1963) found that Fe-rich chlorites have one band at 3674 cm^{-1} (and another band at 3412 cm^{-1}), while Kodama and Oinuma (1962) found bands at 3664 , 3574 and 3412 cm^{-1} for leuchtenbergite.

Bradley and Serratosa (1960) reported that a vermiculite with mainly Mg in octahedral positions (Llano vermiculite) had one adsorption band at about 3700 cm^{-1} and that the OH-groups had their axes normal to the flakes.

Grim and Kulbicki (1961) found that hectorite (montmorillonite with mainly Mg in octahedral positions) had an absorption at 3700 cm^{-1} , and the OH-groups had their axes normal to the flakes.

Roy and Roy (1957) stated that talc had one OH-band at 3705 cm^{-1} (2.71μ), while Hayashi and Oinuma found a band at 3685 cm^{-1} . The following conclusions are drawn from these data:

1. In trioctahedral 2:1 and 2:1:1 phyllosilicates, in which all the

octahedral positions are filled with Mg, the band at about 3700 cm^{-1} is caused by OH-groups occurring in these pyramids. The OH-groups have their axes normal to the flakes.

2. The substitution of Fe^{2+} for Mg produces a new band about 3665 cm^{-1} . These OH-groups have their axes only approximately normal to the flakes. The ratios between the intensities of the bands at 3705 and 3665 cm^{-1} indicate that most commonly 2 Fe^{2+} substitute for 2 Mg^{2+} in the same pyramid.

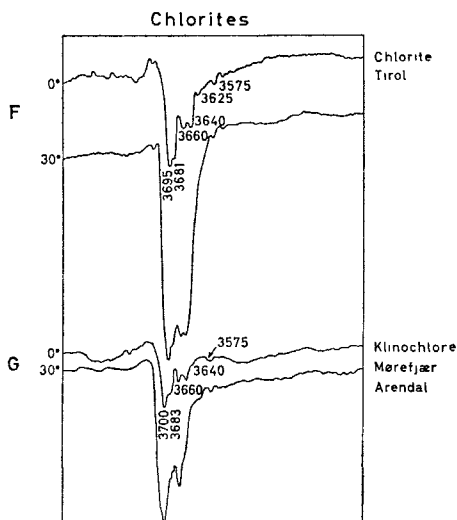


FIG. 4. Infrared curves for two Mg-rich chlorites.

3. Decreasing octahedral occupancy in the phlogopite–lepidomelane group with increasing substitution of R^{3+} for Mg causes bands that are not very sensitive to the incident angle for the infrared beam. This finding previously was stated by Bassett (1960).

Li-Micas

Lepidolite, zinnvaldite and polyolithionite

The simplified chemical composition of the octahedral layer of lepidolite zinnvaldite and polyolithionite is:

Lepidolite: $(\text{Al}_{1.4}\text{Li}_{1.4}\text{R}_{0.1}^{2+})_{2.90}^{\text{IV}}$ Curves J and K, (Fig. 5)

Zinnvaldite: $(\text{Al}_{1.2}\text{Fe}_{0.5}^{2+}\text{Li}_{1.2})_{2.90}$ Curve H (Fig. 5)

Polyolithionite (not analyzed): $(\text{AlLi}_2)_{3.00}$ Curve L (Fig. 5)

Polyolithionite has one very strong and broad band at 3535 cm^{-1} and two distinct bands at 3730 and 3710 cm^{-1} . Lepidolites have their strongest band about 3588 cm^{-1} , and two weaker bands at 3485 and 3680 cm^{-1} . A lithian

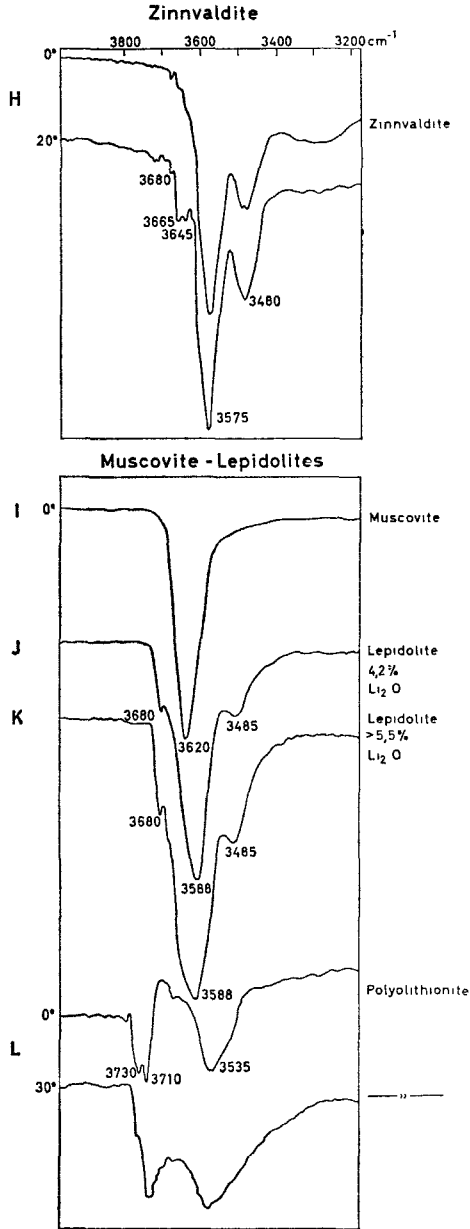


FIG. 5. Infrared curves for muscovite and some lithium-micas.

muscovite from Tørdal, Telemark county, Norway, caused absorptions at the same frequencies and with approximately the same intensities as the lepidolite.

Zinnvaldite has its strongest band at about 3575 cm^{-1} , a weaker band at 3480 cm^{-1} and two bands at 3665 and 3645 cm^{-1} that are very sensitive to the angle of incidence of the infrared beam.

According to Radoslovich (1963), these minerals probably will contain highly ordered octahedral layers having R^{3+} in the unique site, and the other cations in symmetry-related positions.

This means that pyramids will occur in polyolithionite having two Li and one Al. Pyramids having one Li and two Al or three Li also will probably occur. Because polyolithionite yields only one very broad band between 3650 and 3450 cm^{-1} , it is difficult to say anything further about the OH-groups causing this band, except that they are generally in pyramids having two Li and one Al. A probable reason for this is that more than each second position is filled with F instead of OH. In this mineral, a probable combination would be three Li in octahedral positions in one pyramid. Because of this uniform distribution of cations, the OH-group will probably not be able to establish hydrogen bonds. It is, therefore, natural to assign the bands about 3720 cm^{-1} to OH-groups of this kind.

The two most common pyramids in lepidolite will probably have two Li and one Al or two Al and one Li in the nearest octahedral sites, while pyramids in zinnvaldite will most probably have two Li and one Al, one Li, one Al and one Fe^{2+} or one Al and 2 Fe^{2+} in these positions. For lepidolite, the ratio between OH-groups in pyramids having two Li and one Al or having one Li and two Al will be 2 : 1 to 3 : 1. Pyramids having two Li and one Al will be more common in zinnvaldite than pyramids having one Li, one Al and one Fe^{2+} .

It appears probable, therefore, that in lepidolite and zinnvaldite the absorption from an OH-group in a pyramid having two Li and one Al causes a band at approximately 3580 cm^{-1} , while the combinations of two Al and one Li or one Al, one Li and one Fe^{2+} cause bands about 3485 and 3480 cm^{-1} . If these assumptions are true, this is a possible explanation of the absorption at 3472 cm^{-1} , found by White and Burns (1963), in muscovite after treatment with molten lithium nitrate.

These minerals demonstrate that even if almost all octahedral cation positions are filled, the O—H bond will not always be perpendicular to the cleavage plane. This again indicates that the different cations in octahedral positions will have different influences on the orientation of this bond.

DIOCTAHEDRAL MINERALS

Muscovite

Muscovite (Curve I, Fig. 5) has one type of OH-groups that are not very sensitive to the angle of incidence for the infrared beam. This was demon-

strated by Serratosa and Bradley (1958), Bassett (1960) and Vedder and McDonald (1963). Serratosa and Bradley thought that the O—H bonds were directed toward the vacant octahedral position, but this view was not shared by Vedder and McDonald, who found that the directions of the OH-transition moments were tilted 16° away from the octahedral layer. The Serratosa and Bradley position is about 20° into the octahedral layer.

The composition of the octahedral layer in the mineral investigated was:

Muscovite: $(Al_{1.83}Fe_{0.16}^{3+})^{VI}$ Curve I

The band at 3620 cm^{-1} can be associated with OH-groups in pyramids in which the unique positions are empty and the other two positions are filled with Al or Fe^{3+} .

It is probable that Al and Fe^{3+} will have about the same influence on the absorption frequencies for dioctahedral micas, because only one band is found. This view is further supported by the findings of Grim and Kulbicki (1961) and Serratosa (1962) who found that nontronite (a montmorillonite with Fe^{3+} in octahedral positions) has an absorption at about 3610 cm^{-1} while montmorillonite (Al in octahedral positions) has a band at about 3630 cm^{-1} .

Other Dioctahedral Minerals

Kodama and Oinuma (1962) and Hayashi and Oinuma (1963) found that dioctahedral illites have an absorption band at about 3620 cm^{-1} , and this was also true for montmorillonite.

This leads to the conclusion that in dioctahedral 2:1 phyllosilicates having Al and Fe^{3+} in octahedral positions, the OH-groups will have an absorption at about 3620 cm^{-1} .

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