

INFRARED SPECTRA OF MUSCOVITES AS AFFECTED BY CHEMICAL COMPOSITION, HEATING AND PARTICLE SIZE

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ABSTRACT: Nine muscovite samples from different localities were analysed for all major chemical elements and examined by infrared spectroscopy in the range of 4000–250 cm^{-1} . Iron in the octahedral positions was found to cause an intensity decrease and shifting of some absorption bands. Other structural cations were found not to be effective in producing intensity and frequency changes due to the narrow variations in their amounts. Heating studies indicated that at about 800°C muscovite transforms into a dehydroxylated phase which is stable at least up to 1000°C. Particle size studies showed that 5 μm is the upper size limit for a representative spectrum.

The amount and type of structural cations have definite influence upon the appearance, position, and intensity of the absorption bands in the infrared spectra of minerals. In this connection, general infrared characteristics of layer silicates that occur naturally (Farmer & Russell, 1964), and that were produced synthetically (Stubičan & Roy, 1961a, b) have been studied in the past. Crystallochemical relationships have been sought for individual minerals such as lepidolite (Lyon, 1967), biotite (Liese, 1963), chlorite (Hayashi & Oinuma, 1965, 1967), montmorillonite and nontronite (Grman *et al.*, 1973), and celadonite (Farmer *et al.*, 1967). No correlative study between the infrared spectra and chemical composition of different muscovites has been carried out so far with the exception of the work of Arkhipenko *et al.* (1965). The calculation method used by these authors for the structural formula of muscovites is of dubious nature, and the infrared spectra presented are of poor quality. In the present study, the infrared spectra of nine chemically-analysed muscovite samples are presented with the idea in mind that this would contribute to the knowledge of the more complex soil-clay systems. The effect of heating and particle size on the absorption bands is also reported.

MATERIALS

All samples were obtained from F. Krantz Co. (Rheinisches Mineralien-Kontor KG, Bonn). The origins are as follows: Spittal and St Leonhard muscovite are from Kärnten, Austria; Gabel muscovite, Silesia, Poland; Lenkersmühle muscovite, Oberpfalz, W. Germany; Weissdorf muscovite, Oberfranken, W. Germany; Puy de Dôme muscovite, Auvergne, France; Ural muscovite, the Ural Mountains, USSR; Uluguru muscovite, the Uluguru Mountains, East Africa; Schwarzenbach muscovite, the Fichtel Mountains, W. Germany; Rozna lepidolite, Mähren, Czechoslovakia; and Hillsboro pyrophyllite, N. Carolina, U.S.A.

METHODS

Sample preparation

Clean muscovite flakes were wet ground by using a high speed Ultra-turrax homogenizer (Janke & Kunkel KG, Staufen, W. Germany), and separated to particle size fractions by sedimentation and centrifugation procedures (Tanner & Jackson, 1947).

Total chemical analysis

Duplicate samples of 5–20 μm size were analysed for chemical elements as follows: K, Na and Ca were determined by an Eppendorf flame photometer; Mg, Mn and Li by a Perkin-Elmer, Model 303 Atomic Absorption Spectrophotometer; total Fe (Yoe & Jones, 1944) and Ti (Yoe & Armstrong, 1947) by the colorimetric Tiron method; Fe^{2+} titrimetrically by the potassium dichromate method (Shapiro & Brannock, 1962); F electrometrically by an Orion fluoride electrode (Ingram, 1970); Si and Al after NaOH treatment, the former by the colorimetric molybdsilicate yellow method (Schwartz, 1942), the latter by the colorimetric alizarin S method (Shapiro & Brannock, 1962). Adsorbed water (H_2O^-) was determined by heating the samples for 10 h at 110°C , and structural water (H_2O^+) for 2 h at 900°C .

Infrared spectroscopy

0.8 mg of sample of 2–5 μm size was mixed with 400 mg of infrared-grade KBr powder in a Beckman Vibromill for $\frac{1}{2}$ min to obtain a good sample distribution. This mixing step was found to be important to obtain a reproducible and representative spectrum. A mixture of 300 mg sample was then pressed in an evacuable die by a Beckman 25 Ton Ring Press for 4 min (pre-evacuation: 2 min; pressure: 10 ton cm^{-2}). A 2 mg sample was used in recording the OH stretching region in order to obtain stronger bands. To drive off the adsorbed water, disks were heated overnight at 220°C and re-pressed to recover transparency. This heating procedure did not affect the lattice vibrations. The infrared spectra were recorded on a Beckman Model 4220 IR Spectrophotometer over the range $4000\text{--}250\text{ cm}^{-1}$ using the slow scan speed ($30\text{ cm}^{-1}/\text{min}$) for the OH stretching region and the normal scan speed ($300\text{ cm}^{-1}/\text{min}$) for the region of lattice vibrations. The accuracy of the absorption bands were checked by the use of a Beckman Polystyrene film. Wavenumber accuracy of the instrument is better than 4 cm^{-1} from 4000 to 2000 cm^{-1} and 2 cm^{-1} from 2000 to 250 cm^{-1} .

X-ray diffraction

X-ray diffractograms were recorded by a Seifert diffractometer using Ni-filtered Cu K_α radiation. d spacings were calculated from the third order reflections. For the b cell-dimension measurements from the 060 reflections, water-suspended samples were settled down on to Mylar films and supported films were exposed to X-ray beam at an angle of 90° to the normal sample holder position.

RESULTS AND DISCUSSION

Chemical composition

The chemical analyses of the muscovite samples on oxide basis are presented in Table 1, and the structural formulae on unit-cell basis together with the charge distribution in

TABLE 1. Chemical composition of muscovites

	1	2	3	4	5	6	7	8	9
SiO ₂	45.20	44.28	44.71	45.41	44.79	44.15	45.43	44.02	43.98
Al ₂ O ₃	35.63	36.67	33.55	33.55	36.17	36.55	33.93	34.93	37.72
TiO ₂	0.10	0.27	0.20	0.68	0.00	0.13	0.30	0.47	0.32
Fe ₂ O ₃	1.07	0.47	1.76	2.33	0.74	0.84	2.43	2.04	0.61
FeO	1.00	0.89	1.21	1.67	0.95	0.75	1.38	1.40	0.99
MgO	0.33	0.98	0.73	1.76	0.05	0.41	1.41	1.33	1.01
MnO	0.05	0.04	0.05	0.04	0.03	0.01	0.04	0.04	0.05
Li ₂ O	0.13	0.06	0.06	0.13	0.00	0.06	0.06	0.09	0.04
CaO	0.06	0.04	0.03	0.03	0.04	0.04	0.03	0.03	0.01
Na ₂ O	0.82	0.90	0.78	0.70	0.89	0.82	0.80	0.75	0.86
K ₂ O	9.94	10.17	10.33	9.42	10.27	9.99	10.15	10.00	9.92
F	0.58	0.24	0.46	0.07	0.20	0.12	0.25	0.31	0.26
H ₂ O ⁺	4.88	4.59	4.60	4.48	4.79	4.51	4.69	4.42	4.36
H ₂ O ⁻	0.79	0.50	0.50	0.80	0.30	0.29	0.28	0.10	0.19
	100.58	100.10	100.97	101.09	99.22	98.63	101.18	99.91	100.30
O≡F	0.24	0.10	0.19	0.03	0.08	0.05	0.11	0.13	0.11
Total	100.34	100.00	100.78	101.06	99.14	98.58	101.07	99.78	100.19

1, Gabel; 2, Lenkersmühle; 3, Puy de Dôme; 4, Schwarzenbach; 5, Spittal; 6, St Leonhard; 7, Uluguru; 8, Ural; 9, Weissdorf.

Table 2. In the calculation of structural formulae, the following assumptions were made: Cationic or anionic charge per unit-cell is equal to 44, and OH plus F equal to 4; only Si and Al are present in the tetrahedral sheet and all tetrahedral positions are occupied; ions like Al, Ti, Fe³⁺, Fe²⁺, Mg, Mn and Li occur in the octahedral sheet, and K, Na and Ca in the interlayer. The use of H₂O⁺ as structural OH was not preferred due to the inaccuracies involved in its determination. Arkhipenko *et al.* (1965) have found the structural OH content of muscovites mostly around and above 5% on the basis of 1000°C heating. Although there has been no experimental evidence on the presence of H₃O⁺ in muscovites, these authors have used the formula of Brown and Norrish which includes the hydronium ion as an interlayer cation in the calculation of structural formula. In the literature, reports of structural OH content much above the theoretical amount of 4.52% is not uncommon, and yet an OH determination on a mere heating is a delicate matter. For example, failure to heat the empty crucible at the same temperature gives higher H₂O⁺ values. Incomplete removal of adsorbed water, presence of impurities and volatile constituents such as fluoride, amount of sample and moisture conditions are also operative. The inclusion of structural OH so determined in the calculation of

TABLE 2. Numbers of ions on the basis of forty-four negative charges and the charge distribution in muscovites

	1	2	3	4	5	6	7	8	9
Si	6.08	5.95	5.99	6.08	6.06	5.98	6.08	5.93	5.85
Al(IV)	1.92	2.05	2.01	1.92	1.94	2.02	1.92	2.07	2.15
Sum	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Al(VI)	3.73	3.73	3.60	3.34	3.82	3.80	3.41	3.47	3.76
Ti	0.01	0.03	0.02	0.07	0.00	0.01	0.03	0.05	0.03
Fe ³⁺	0.11	0.05	0.18	0.23	0.08	0.09	0.24	0.21	0.06
Fe ²⁺	0.11	0.10	0.14	0.19	0.11	0.08	0.15	0.16	0.11
Mg	0.07	0.19	0.14	0.35	0.01	0.08	0.28	0.27	0.20
Mn	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01
Li	0.07	0.03	0.03	0.07	0.00	0.03	0.03	0.05	0.02
Sum	4.11	4.13	4.12	4.25	4.02	4.09	4.14	4.21	4.19
Ca	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.00
Na	0.21	0.23	0.20	0.18	0.23	0.22	0.21	0.19	0.22
K	1.70	1.73	1.76	1.60	1.77	1.72	1.73	1.72	1.68
Sum	1.92	1.97	1.96	1.78	2.01	1.95	1.94	1.91	1.90
F	0.25	0.11	0.20	0.03	0.09	0.04	0.11	0.13	0.10
OH	3.75	3.89	3.80	3.97	3.91	3.96	3.89	3.87	3.90
O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Tetra. charge	-1.92	-2.05	-2.01	-1.92	-1.94	-2.02	-1.92	-2.07	-2.15
Octa. charge	+0.01	+0.07	+0.03	+0.14	-0.06	+0.06	-0.04	+0.15	+0.24
Layer charge	-1.91	-1.98	-1.98	+1.78	-2.00	-1.96	-1.96	-1.92	-1.91

Sample numbers as in Table 1.

structural formulae can lead to serious errors. If the amount of H_2O^+ deviates appreciably from the theoretical, calculated amounts of the most abundant cations, particularly those in octahedral positions, are affected, and the charge distribution in the tetrahedral and octahedral sheets is varied. Therefore, it is not advisable to calculate the structural formula of sheet silicates by the method that uses H_2O^+ and twenty-four or forty-eight negative charges unless a reliable technique is employed in the determination of structural OH.

The muscovite samples under study have an appreciable amount of Na in the inter-layers (Tables 1 and 2). In general, there is an increase in Mg and Ti contents with increasing amount of Fe. Association with mica of anatase and rutile as crystalline and leucoxene as X-ray amorphous forms of Ti is well known and therefore at least some of this element which was allocated entirely to the structural sites may occur as separate oxide phases. Nevertheless, its exclusion in the calculation has caused no important changes in the structural formulae. For example, with Schwarzenbach muscovite which has the highest amount of Ti (0.41%) among the samples, no change was seen in tetrahedral and octahedral occupancies and layer charge (net negative charge) increased only from -1.78 to -1.81.

The octahedral occupancies in the samples are always over 4 and layer charges under 2 except Spittal muscovite which has the closest composition to ideal muscovite (Table 2).

Schwarzenbach muscovite being the 'most impure' sample has a considerably lower charge (-1.78) than the rest. K amounts in the equilibrium solutions after K–Ba exchange were also found to be the lowest in this particular sample (Sayin & Graf von Reichenbach, in manuscript).

Infrared spectra

The absorption band due to the stretching motion of OH groups was found between 3638 cm^{-1} and 3631 cm^{-1} as illustrated in Fig. 1. Its intensity seems to be affected by

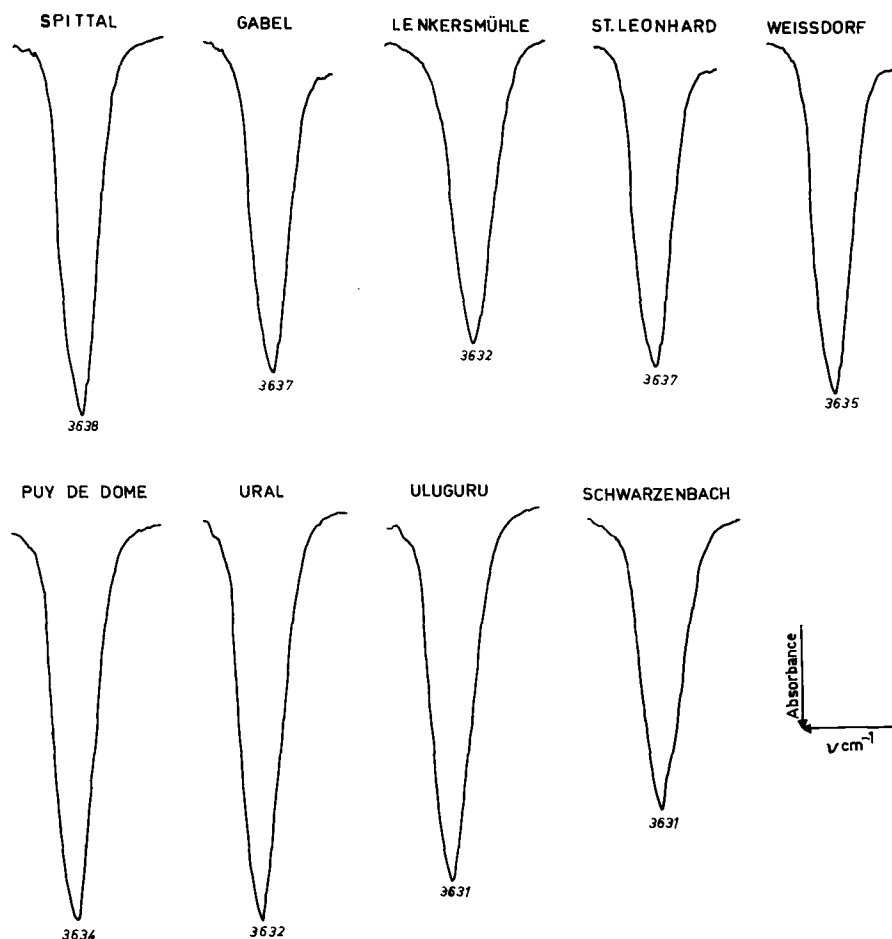


FIG. 1. OH stretching vibration of muscovites.

octahedral iron which decreases the absorption frequency with the exception of one sample (Lenkersmühle). Hence, the band appears at 3638 cm^{-1} in Spittal muscovite (1.26% Fe) and 3637 cm^{-1} in Gabel muscovite (1.53% Fe) but at 3631 cm^{-1} in Uluguru (2.77% Fe) and Schwarzenbach (2.93% Fe) muscovite. The broad half bandwidth of

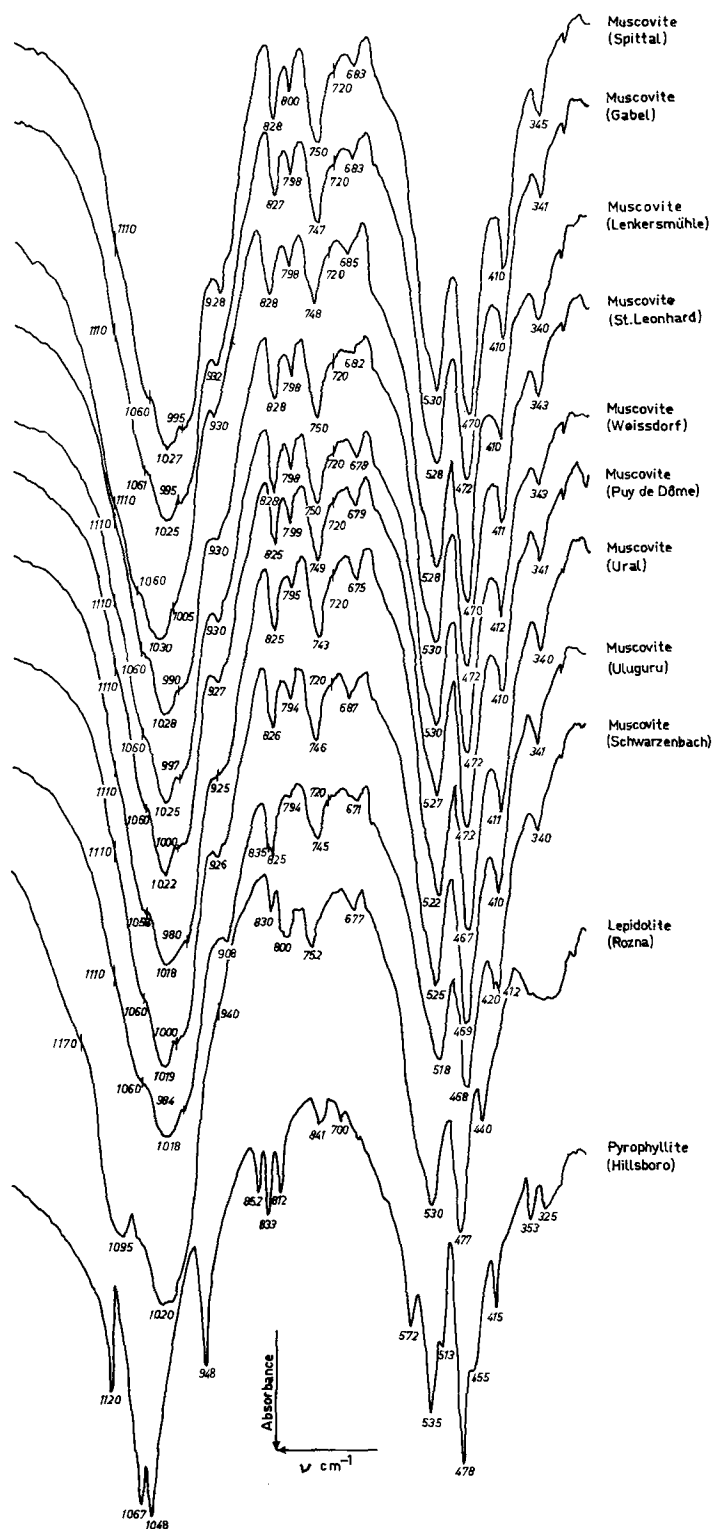


FIG. 2. Lattice vibrations of muscovites, lepidolite and pyrophyllite.

the absorption maxima is $67 \pm 3 \text{ cm}^{-1}$. A slight shoulder appears at $3650\text{--}3660 \text{ cm}^{-1}$ and even a slighter one at $3620\text{--}3625 \text{ cm}^{-1}$. These features may represent (1) combination vibrations, (2) vibrations of different OH groups, and (3) vibrations due to coupling between identical OH groups. Partial deuteration of OH groups is needed to differentiate the possible causes of these satellites. No relationship was found between the band intensity and tetrahedral Al, octahedral Al, total Al, and F contents. Low F amounts apparently did not affect the band intensities.

Vibrations below 1200 cm^{-1} in sheet silicates are not isolated vibrations of certain groups but represent cooperative motions of structural ionic groups. They involve vibrational, rotational and translational motions of anion-cation associations. Although the proportion of each factor in the production of vibrations is difficult to evaluate at the present time, comparative spectral studies have already revealed the general characteristics of these lattice vibrations. Hence, the stretching vibrations of SiO_4 tetrahedra produce a very strong and broad band centering at about 1025 cm^{-1} with two shoulders at the high frequency side and one shoulder at the low frequency side (Fig. 2). The highest frequency band occurs at 1110 cm^{-1} . It is very weak and can be easily missed. The analogue of this band appears at 1120 cm^{-1} in Wyoming montmorillonite and at 1091 cm^{-1} in nontronite (Farmer & Russell, 1964). The next band appears at 1060 cm^{-1} and its intensity is negatively affected by tetrahedral Al as demonstrated by the spectrum of lepidolite which has lower tetrahedral Al than muscovite (Fig. 2). The effect was clearly shown by Lyon (1967) in a series of lepidolites with varying Al content. The dickite and montmorillonite analogue of this Al^{IV} -sensitive band is perpendicularly polarized and was therefore assigned to $\text{Si-O-Al}^{\text{VI}}$ vibrations (Farmer & Russell, 1964). The strongest Si-O stretching band at about 1025 cm^{-1} moves toward lower frequencies with increasing octahedral substitution. The behaviour of the band near 980 cm^{-1} is unpredictable. Since octahedral substitutions change the *b*-cell-dimension, the tetrahedral rotation angle as well as the $\text{O}_{\text{apical}}\text{--Si--O}_{\text{basal}}$ angle, one would expect a correlation between these parameters and the different modes of Si-O absorption bands.

The band at about 930 cm^{-1} is a result of the bending motion of OH coordinated to the octahedral AlAl pair (Stubičan & Roy, 1961a, b). Concurrently its intensity decreases with decreasing Al and OH content. The spectra of OH- and Al^{VI} -poor lepidolite versus Al^{VI} -rich pyrophyllite illustrate this fact well (Fig. 2). In muscovites, Al variation is not wide (from 3.34 to 3.82 per unit-cell) and therefore cation effect is not noticeable. Nevertheless, with Schwarzenbach muscovite the $\text{Al}_2\text{-OH}$ band appears at appreciably lower frequency (908 cm^{-1}) with respect to others reflecting the influence of octahedral Fe and Mg on the spectrum.

The band at about 826 cm^{-1} has been assigned to Al-O (apical) stretching vibrations due to its perpendicular polarization and intensity increase with increasing tetrahedral Al (Farmer & Russell, 1964; Serratos & Hidalgo, 1964). However, it has been proposed that both SiO_4 bending and AlO_4 stretching may involve in the band formation (Vedder & Wilkins, 1969). The persistence of this band after dehydroxylation (see later) indicates a non-involvement of OH. The band moves slightly to lower frequencies and decreases in intensity with increasing octahedral substitution. No correlation was found between the band intensity and tetrahedral Al content probably because of the narrow variation of Al among the samples.

The band at about 798 cm^{-1} seems to be sensitive to octahedral Fe content. When K-depleted Spittal muscovite was treated with a reducing agent, sodium dithionite, it

became a shoulder. Its analogue appears at 889 cm^{-1} in Wyoming montmorillonite (Farmer *et al.*, 1967), at 880 nm^{-1} in Woburn Fuller's Earth (Heller *et al.*, 1962), at 848 cm^{-1} in Garfield nontronite (Stucki & Roth, 1976), at about 855 cm^{-1} in Nová Ves nontronite (Grman *et al.*, 1973), at 820 cm^{-1} in synthetic trioctahedral chlorite and synthetic ferrous phlogopite (Farmer, 1974). Stucki & Roth (1976) remark on the occurrence of a band at about 870 cm^{-1} in Nová Ves nontronite in the study of Grman *et al.* (1973). However, measurement from the peak position in Fig. 1 of the cited authors gives a value of $11.7\text{ }\mu\text{m}$ or 855 cm^{-1} . The shift toward lower frequencies probably increases with increasing tetrahedral Al content. Al^{3+} ($r = 0.50\text{ }\text{\AA}$) is a bigger cation than Si^{4+} ($r = 0.41\text{ }\text{\AA}$), and Al-O distance ($1.77\text{ }\text{\AA}$) is greater than Si-O distance ($1.62\text{ }\text{\AA}$) (Smith & Bailey, 1963). Therefore, an increase in bond strength and a decrease in vibrational frequency are expected as the tetrahedral Al substitution increases. This is also the case with tetrahedral Fe^{3+} . The libration of OH coordinated to AlFe^{3+} pairs was held responsible for this absorption in montmorillonite (Heller *et al.*, 1962), but in nontronite it was interpreted as a Fe-OH libration where OH moves as a unit (Stucki & Roth, 1976). Nevertheless the observations indicate that Fe^{3+} , octahedral Al or OH are not involved in the band formation. First, chemical analyses in this study indicate that the Fe-sensitive 798 cm^{-1} band cannot be associated with octahedral Fe^{3+} since it appears as the smallest peak in Schwarzenbach muscovite which has the second largest Fe^{3+} amount among the samples. Secondly, Nová Ves nontronite has no octahedral Al and Garfield nontronite has little. Thirdly, by heating up to 450°C , the intensity of this band in nontronite does not decrease appreciably whereas the 820 cm^{-1} band of Fe_2^{3+} -OH libration is lost (Grim & Kulbicki, 1961). No change in band intensity was observed in Spittal muscovite at temperatures as high as 700°C (see later). Fourthly, the band is resistant to deuteration in Wyoming montmorillonite (Russell *et al.*, 1970) and in nontronite (Stucki & Roth, 1976). Hence, the most probable candidates for this absorption are tetrahedral Si-O-Al librations that are negatively affected by octahedral Fe^{2+} and Mg.

An interesting alternative assignment for the Fe-sensitive band in montmorillonite and nontronite could be tetrahedral Si-O- Fe^{3+} vibrations. In line with this contention, both Heller *et al.* (1962) and Grman *et al.* (1973) have reported tetrahedral Fe which can be more easily reduced and re-oxidized than its octahedral counterpart due to locational accessibility. This could also explain why the 848 cm^{-1} band was eliminated but the 818 cm^{-1} band of Fe_2^{3+} -OH was scarcely affected when nontronite was treated with hydrazine vapour in Farmer & Russell's experiments (1964). The existence of Fe in tetrahedral sites has been in fact shown by selective dissolution analysis (Osthaus, 1954), and by Mössbauer spectral studies (Goodman *et al.*, 1976). The recognition of tetrahedral Fe^{3+} in sheet silicate would necessitate a reconsideration of the related spectral interpretations.

The band at about 748 cm^{-1} , like the one near 826 cm^{-1} , shifts slightly to lower frequencies and decreases in intensity with decreasing amount of octahedral Al. It has been assigned to in-plane Si-O-Al vibrations (Farmer, 1974). A shoulder at 720 cm^{-1} has been found to be perpendicularly polarized and assigned to a tetrahedral vibration (Serratosa & Hidalgo, 1964). The band near 680 cm^{-1} , as the one at 798 cm^{-1} , is dithionite-sensitive and probably represents another tetrahedral vibration.

The band at about 528 cm^{-1} which has been assigned to Si-O- Al^{VI} vibrations (Stubičan & Roy, 1961a, b) moves toward lower frequencies by increasing octahedral substitution

as in 14 Å chlorites (Hayashi & Oinuma, 1965). Some correlation has been found between the position of this absorption and octahedral Mg content in synthetic (Stubičan & Roy, 1961a) and natural (Arkhipenko *et al.*, 1965) muscovites. Since the Fe content is not constant but increases with increasing Mg, the share of each ion in frequency changes is not distinguishable in the present study. Nevertheless, both Mg and Fe^{2+} are expected to have an effect on the Si-O bending vibrations in the same direction.

The strong band at about 470 cm^{-1} corresponds to the bending equivalent of the Si-O vibration at 1025 cm^{-1} . A weak band near 410 cm^{-1} has been ascribed to out-of-plane OH librations (Vedder & McDonald, 1963). Although perpendicular character of this vibration has been questioned (Russell *et al.*, 1970), its weakening after partial deuteration indicates that it is an OH libration of which OD equivalent probably occurs below 300 cm^{-1} (Vedder & McDonald, 1963). The band near 340 cm^{-1} may be a mixed libration-translation motion. Its persistence after deuteration in muscovite (Vedder & McDonald, 1963) and in Wyoming montmorillonite (Russell *et al.*, 1970) speaks for a non-involvement of OH groups.

From the observations it is clear that the effects of the tetrahedral and octahedral cationic variations on the lattice vibrations can only be followed when these variations occur in a fairly large scale. On the other hand, the contribution of the octahedral cations to the production of the bands over the range $950\text{--}700\text{ cm}^{-1}$ reveals the cooperative (librational) character of the absorptions.

Effect of heating on muscovite

Spittal muscovite of 2–5 μm size was heated for 1 h from 300°C at 100°C intervals up to 1000°C in order to evaluate structural changes by infrared spectroscopy and X-ray diffraction. The lattice vibrations are presented in Fig. 3. The structure of muscovite starts losing OH ions at 500°C as evidenced by an intensity decrease of the OH stretching vibration at 3638 cm^{-1} (not shown) and the OH libration motion at 928 cm^{-1} . At 600°C the Si-O-Al^{VI} band at 530 cm^{-1} broadens toward higher frequencies. At 600°C the OH libration disappears but the OH stretch still persists in the spectrum. The 530 cm^{-1} band moves completely to 550 cm^{-1} and new bands appear at 1068, 1040, 857, 708, 648 and 306 cm^{-1} . In addition, the Si-O stretching vibration at 1027 cm^{-1} shifts to lower frequencies and the Si-O bending motions are intensified. At 800°C the OH stretching vibration disappears. The bands show almost no further changes at higher temperatures. The same trends were also observed with substitution-rich Schwarzenbach muscovite except the fact that the new bands in the Si-O stretching region are not apparent.

The results can be interpreted as follows: At about 800°C muscovite transforms into a dehydroxylated phase which is stable at least up to 1000°C . In the dehydroxylation process, water molecules form by the reaction of two adjacent OH ions and diffuse out of the structure. Al assumes a five-fold coordination by slight structural adjustments in the octahedral sheet. Al-O distances become shorter than in original six-fold coordination as evidenced by the high frequency shift of the 530 cm^{-1} band. Meanwhile Si-O distances become larger contributing to an increase in d spacing and b cell-dimension. This fact was substantiated by low frequency shift of the Si-O stretching band and X-ray observations. d spacing of the sample increased from $9.99 \pm 0.1\text{ Å}$ to $10.08 \pm 0.01\text{ Å}$ in the 700°C -product and remained constant at higher temperatures. However, the high order 001

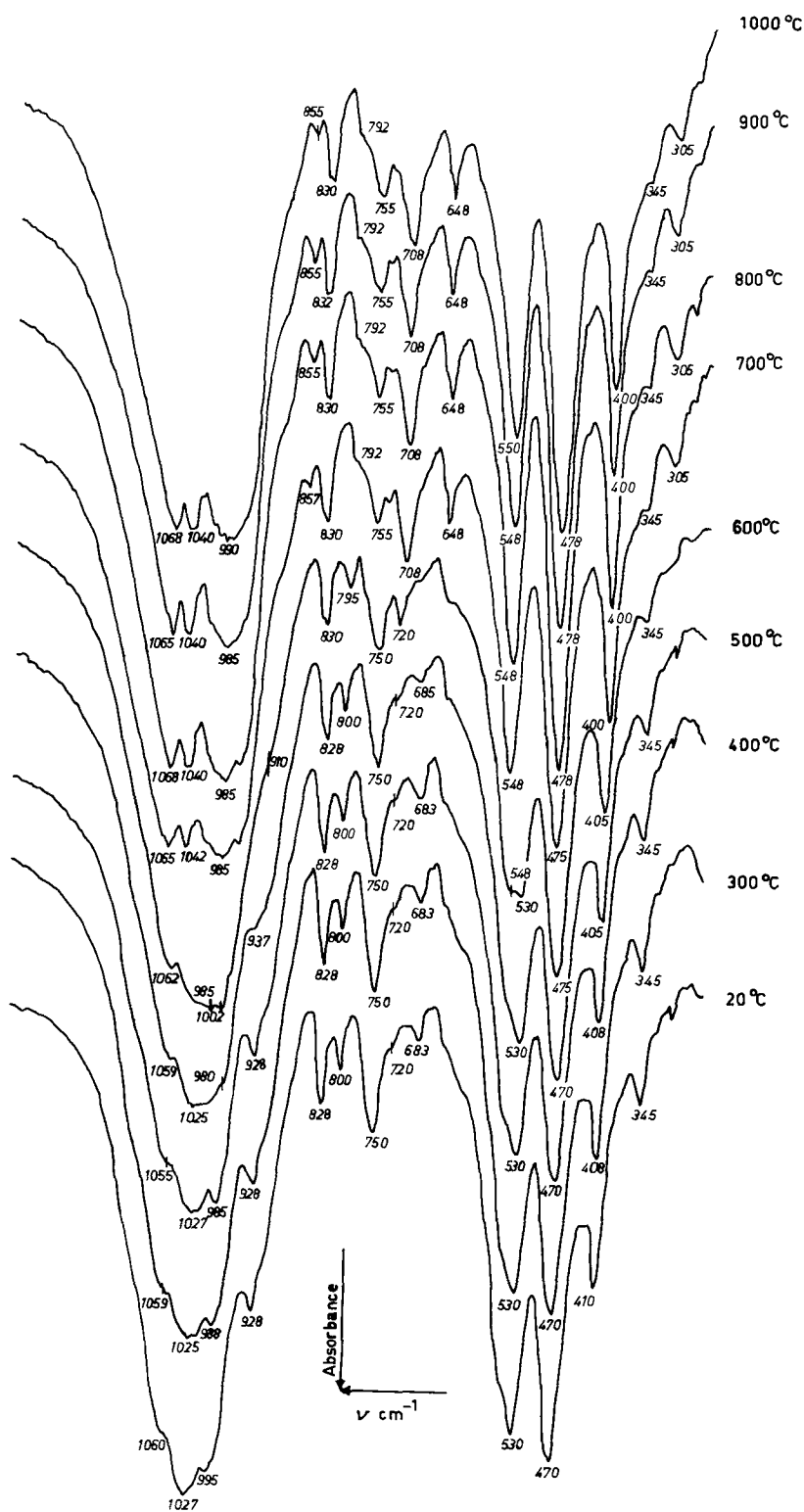


FIG. 3. Lattice vibrations of Spittal muscovite heated for 1 h at progressively increasing temperatures.

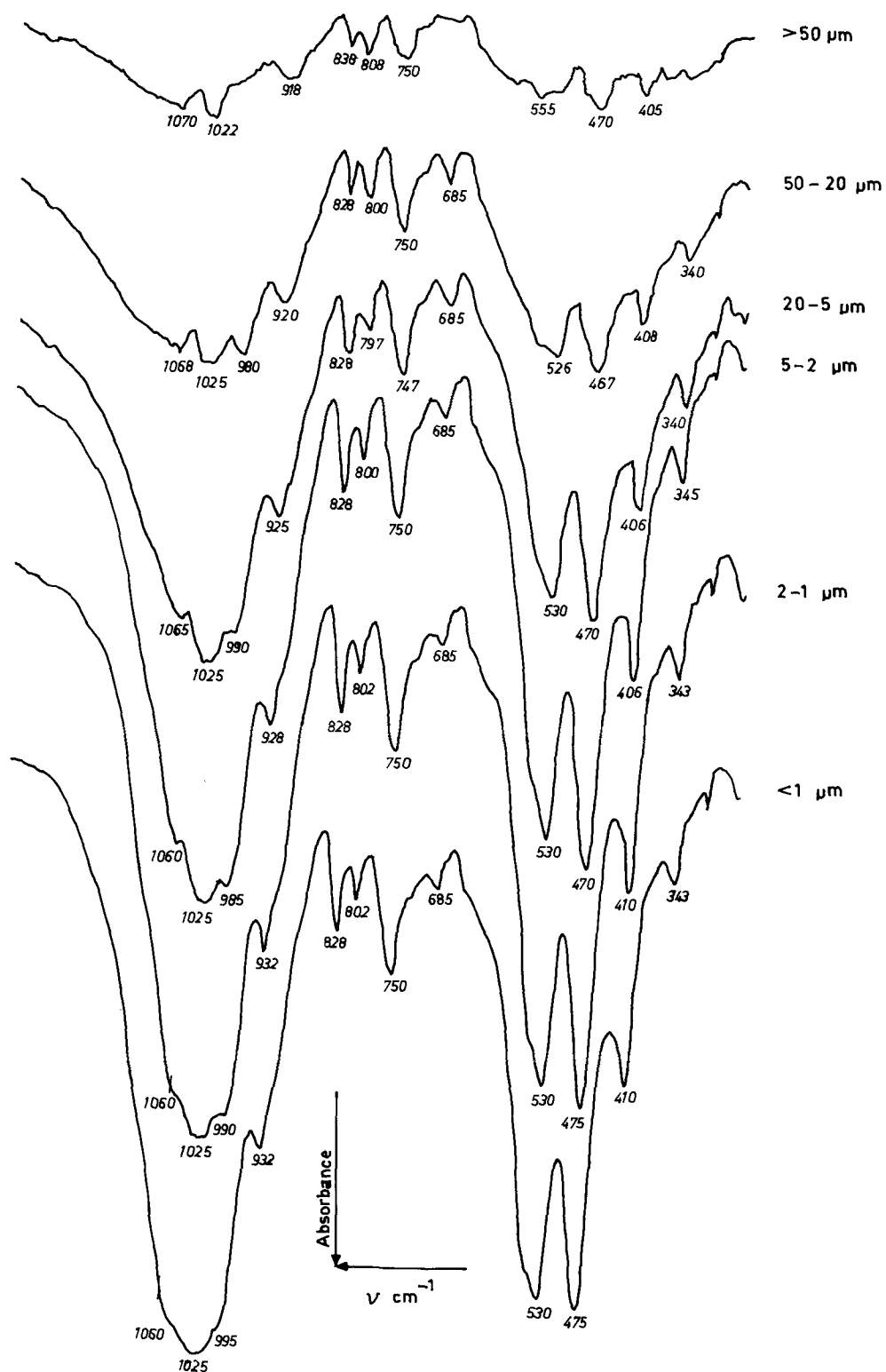


FIG. 4. Lattice vibrations of Spittal muscovite in different particle size fractions.

reflections increased in intensity progressively, particularly the third order reflection at the expense of the first order reflection. *b* cell-dimension increased from 8.98 ± 0.02 Å in original muscovite to 9.09 ± 0.02 Å in 600°C-product and remained the same at higher temperatures.

By using the one-dimensional Fourier synthesis, Eberhart (1963) in muscovite, and Wardle & Brindley (1972) in pyrophyllite, have shown that the electron densities of the Al plane are higher in the dehydroxylated phases than those in the original minerals. The opposite case has been observed for the O-OH plane. The authors have interpreted these changes as a movement of residual O ions to the level of Al ions but differed in the final form of the structure. Eberhart has assumed a chain-like structure in which Al is in six-fold coordination, an adaptation of the montmorillonite dehydroxylate model of Bradley & Grim (1951) to muscovite. Wardle & Brindley (1972) supporting with X-ray fluorescence data have proposed a five-fold coordination of Al ions with little structural re-arrangement. In Eberhart's model the Al-O distances are too large to be realistic. The shift of the Si-O-Al^{VI} band to higher frequencies in the present study indicates that a five-fold coordination with shorter Al-O distances proposed by Wardle & Brindley (1972) for pyrophyllite dehydroxylate could also be valid for muscovite dehydroxylate. Montmorillonite behaves differently from muscovite and pyrophyllite, the Si-O-Al^{VI} band decreases in intensity as temperature increases indicating a different reaction mechanism (Sayin, Zimmerman & Graf von Reichenbach, in manuscript).

The bands of 855, 710 and 647 cm⁻¹ may be libration motions of newly organized cation-anion associations. Furthermore, some of the new bands may represent modes which are activated by heat. Among them the 306 cm⁻¹ band is probably a shifted equivalent of the 340 cm⁻¹ band in the original mineral since the band intensities are very similar. The persistence of the bands at 830, 800 and 750 cm⁻¹ indicated that OH ions are not involved in the band formation. The strong band at 400 cm⁻¹ is entirely new as previously reported (Vedder & Wilkins, 1969).

Effect of particle size

Although the effect of particle size on the infrared spectra of minerals is well known, this has not been shown using a series of particle size fractions in sheet silicates. To serve this purpose, infrared spectra of Spittal muscovite using different size fractions of the same amount of sample (0.6 mg) were recorded and illustrated in Fig. 4. Above 5 µm the spectra become increasingly poorer, i.e. the absorption bands decrease in intensity and become broader; the band contours are distorted; the band positions change especially above 20 µm. An intensity decrease and a broadening toward higher frequencies are observed with OH stretching vibrations (spectra not shown). Below 5 µm, the bands are not only improved but also remain about the same, particularly below 2 µm. This means that the light loss by reflection and scattering is decreased to a minimum and the particles show their real absorption. The small variations in band characteristics should be interpreted with caution, since besides the particle size, other sample-related factors such as particle shape (Farmer & Russell, 1966), structural irregularities (Saksena, 1964), homogeneity in the pressed disk (Osipova *et al.*, 1976), differences in refractive indices (Duyckaerts, 1959) and even particle orientation in the pressed disk could contribute to the formation of bands.

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RÉSUMÉ : Neuf échantillons de muscovite de différentes localités ont été analysés pour déterminer tous les principaux éléments chimiques et examinés par spectroscopie infrarouge dans la gamme de 4000–250 cm⁻¹. On a constaté que du fer situé aux positions octaédriques causait une diminution d'intensité et un déplacement de certaines bandes d'absorption. On a trouvé que d'autres cations de structure ne produisaient pas de modifications d'intensité et de fréquence en raison des étroites variations de leurs quantités. Des études par chauffage ont indiqué qu'à environ 800°C, la muscovite se transforme en une phase déshydroxylée qui est stable jusqu'à au moins 1000°C. Des études de la taille des particules ont montré que 5 µm est la limite supérieure pour un spectre représentatif.

KURZREFERAT : Neun Muskovitproben unterschiedlicher Herkunft wurden auf die Hauptelemente analysiert und im Bereich von 4000–250 cm⁻¹ I R-spektrometrisch untersucht. Oktaedrisch koordiniertes Fe verursacht eine Verminderung und Verschiebung einiger Absorptionsbanden. Für andere Kationen waren keine Intensitäts- und Frequenz-

änderungen nachzuweisen, was in den geringen Schwankungen ihres Anteils zu suchen ist. Erhitzungsversuche ergaben, dass sich Muskovit bei etwa 800°C in eine dehydroxylierte Phase umwandelt, welche bis wenigstens 1000°C stabil ist. Untersuchungen hinsichtlich des Einflusses der Korngrösse zeigten, dass 5 μm die obere Grenze für ein representatives Spektrum sind.

RESUMEN: Se han analizado nueve muestras de muscovita de distintas localidades para constatar todos los principales elementos químicos y se han examinado mediante espectroscopia por rayos infrarrojos en la gama de 4000–250 cm^{-1} . Se halló que el hierro en las posiciones octaédricas causaba una disminución de intensidad y un desplazamiento de algunas bandas de absorción. Otros cationes estructurales resultó que no eran eficaces en la producción de cambios de la intensidad y la frecuencia debido a las pequeñas variaciones de sus cantidades. Los estudios realizados calentando las muestras han indicado que a alrededor de 800°C la muscovita se transforma en una fase deshidroxilada que es estable por lo menos hasta 1000°C. Los estudios del tamaño de las partículas han mostrado que 5 μm es el límite superior de tamaños para un espectro representativo.