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Cell dimensions, polymorph type, and infrared spectra of synthetic white micas: the importance of ordering

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Abstract

Synthetic dioctahedral white micas (muscovite–phengite, margarite, and paragonite) were investigated by X-ray diffraction and infrared methods. Correlation of cell dimension (*b* dimension was the most useful) with infrared spectra suggests that the variations in size are due to ordering in the micas.

Potassic micas in the muscovite–celadonite series crystallized at pressures above 12 kbar show ordering in two sites, the octahedra in the case of celadonite-rich micas and the tetrahedra (Si–Al substitution) for muscovite. This results in a 0.27% change in the *b* dimension of muscovite. Synthesis pressure favors the ordered muscovite. Polymorphs are not affected by ordering.

Margarite and paragonite, Ca and Na micas, show a decrease in cell dimension with ordering. However it appears that the ordering is related to various polytypes (1Md, 1M, and $2M_1$), which show a decrease in cell size of 0.28% in the polytype sequence. In this case stacking of the mica sheets is the mode of ordering, while the relative positions of atoms in the sheets are invariable.

Paragonite appears to behave more like margarite than muscovite as far as ordering is concerned. This can be put in parallel with the fact that paragonite–margarite solid solution seems to be complete at moderate physical conditions while that of muscovite–paragonite is not.

Introduction

Numerous studies of the stability and physical properties of white micas have been published, and there will probably be more in the future (Yoder and Eugster, 1955; Crowley and Roy, 1964; Chatterjee, 1970, 1974a,b; Storre and Nitsch, 1974; Blencoe, 1977; Velde, 1965, 1966, 1971, 1978; and many others). Some of these studies were designed to determine the limits of mica stability in *P–T* space, others to determine physical properties. However, the stability studies have often been in disaccord. The assumption made in most cases was that a pure end-member mineral, one of a fixed composition, was the starting material and the same mineral was the final product. However, in most cases little attention was given to the structural state of the materials involved. Since polymorphism is common in micas and since polymorphism in other phases is known to change their thermodynamic properties significantly (*e.g.* consider the aluminum silicates kyanite, andalusite, and sillimanite) it might be wise to take the structural state into consideration as one tries to explain the dispersion of experimental results. There is no reason, *a priori*, to suspect the veracity of the experimental results published.

This paper deals with the variation in cell dimension of some synthetic micas and the possible cause of this variation as a function of the site ordering and layer ordering in the mica structure. The data are presented in graphical form. Some of the cell dimensions or determinations of diffraction reflections have already been reported (Chatterjee, 1970, 1974 a,b; Blencoe, 1977; Velde, 1971, 1978).

Cell dimensions are those of the *b* value, which is estimated as 6 × (060) (Cu*Kα* radiation and silicon metal as a standard). The diffractometer is a Siemens machine. The (331) reflection could be identified separately in most cases, and thus the *b* value should be near to a simple reflection. From published results, it is apparent that simple reflections give more consistent values than *b* values defined by least-squares refinements of diffractometer data [see Franz *et al.*

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(1977) and the data given here, for example]. It was found that (001) reflections gave less consistent results in most cases, and thus they are not cited here.

Infrared spectra were made on Beckman 4240 and Perkin Elmer 580 grating spectrometers,[1] with 0.2 mg of sample $<2\mu$ grain size in KBr pellets. The range between 1200 cm^{-1} and 200 cm^{-1} was investigated.

Samples of margarite–paragonite solid solution were kindly provided by G. Franz, Technische Universität, Berlin, West Germany, and some muscovites and paragonites were provided by J. Blencoe, Pennsylvania State University.

Cell dimensions

Muscovite-celadonite [$KAl_2(Si_3Al)O_{10}(OH)_2$–$KMgAlSi_4O_{10}(OH)_2$]

This material has been reported for the most part by Velde (1977). However, the pressures attained were 10 kbar or below. Subsequent syntheses at 13 kbar indicate that the trend for muscovite-rich phases is changed by pressure of synthesis to produce a sequence more or less continuous with the phengite–celadonite trend (Fig. 1). It was deduced that the 10-kbar synthesis produced an ordered mica where significant numbers (>50%) of Mg–Al ion pairs were present in the octahedral site of the mica. This ordering greatly affected the *b* dimension of the mica. 13-kbar muscovite has a much smaller *b* dimension than others synthesized at lower pressure. The (001) reflections do not give consistent results, nor do they seem to vary as much as (060) reflections. There is apparently a greater tendency to have smaller cell dimensions above 10 kbar than below.

Margarite-paragonite [$CaAl_2(Si_2Al_2)O_{10}(OH)_2$–$NaAl_2(Si_3Al)O_{10}(OH)_2$]

Figure 2 gives the *b* dimensions for various paragonites, margarites, and members of the intermediate compositions (samples from Franz *et al.*, 1977). Infrared spectra and the cell dimensions indicate that these samples which were crystallized at 2 kbar, 650°C, do in fact form a continuous structural series. Note that the more paragonitic micas tend to form a 2M polymorph while margarite is 1Md+1M (determinations made from published diffractograms).

If we join low-pressure (2-kbar) 1M polymorph values for Na and Ca micas, we find that the intermediate phases give for the most part smaller dimensions when 2M is present with 1M (Pa 70 to margarite). The pure margarite and paragonite mica polymorphs show significant variation (0.28%) in cell dimension. Margarites show a marked difference between stacking-disordered 1Md and the two-layer 2M$_1$ polymorph, as does paragonite. Pressure seems to affect cell dimension to a certain extent also (see 2–8-kbar 1M paragonite and 2–4-kbar 2M margarite), but the polytype seems to be much more important in determining the *b* dimension.

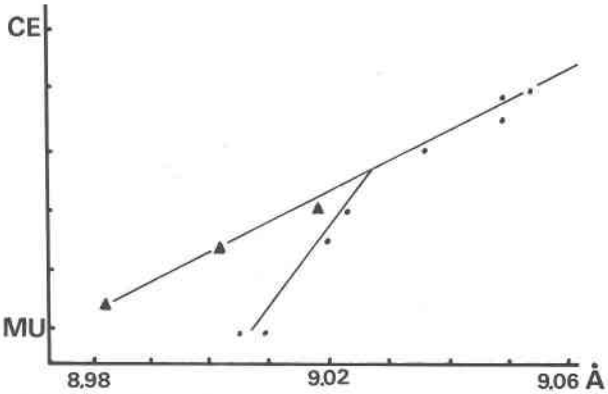

Fig. 1. *b* cell dimensions of synthetic potassic micas in the series muscovite–celadonite. Dots show values for 10-kbar synthetic products, triangles of those at 13-kbar. High-pressure low celadonite and high celadonite micas form a trend interpreted as being due to ordering in the octahedral site for celadonitic micas (Velde, 1978) and in the tetrahedral site for muscovite micas.

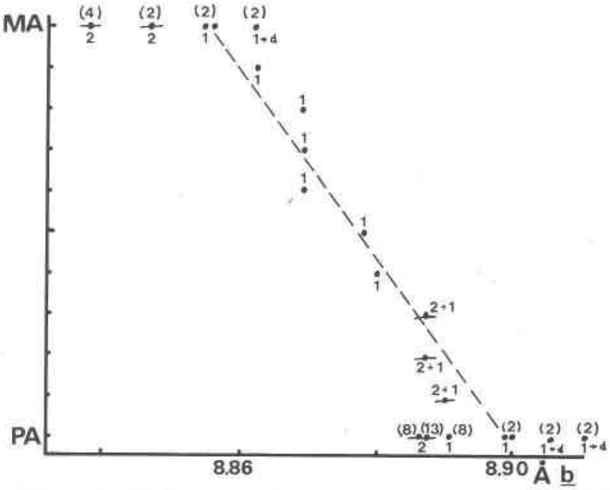

Fig. 2. *b* cell dimensions of margarite (MA)–paragonite (PA) synthetic micas. Numbers indicate polytype (1 = 1M, 2 = 2M, d = 1Md), and numbers in parentheses indicate pressure under which the synthesis were carried out. Dashed line joins predominantly 1M polytypes at 2kbar pressure for margarite and paragonite. Samples between margarite and paragonite were provided by G. Franz.

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[1] I would like to thank Prof. Mignac, Lab. de Chimie Organique, Univ. de Poitiers and Prof. Perchard, Lab. de Spectro-Chimie Moléculaire, Univ. Paris VI, for the use of their machines.

Infrared spectra

Muscovite

Figure 3 gives the infrared spectra for the synthetic muscovites of 1M and 2M polymorphs at various pressures in the range 900–600 cm^{-1}. In this region we find the Al–O tetrahedral bands at 802 cm^{-1} (Farmer and Velde, 1973; Farmer, 1974, p. 350) and 735–725 cm^{-1} Al–Si–O (Stubican and Roy, 1961; Farmer, 1974, p. 350), along with others of the Si–O polymer 748–640 cm^{-1}. The 828–830 cm^{-1} band has a dipole moment perpendicular to the (001) direction, as seen in oriented specimens of synthetic paragonite (Fig. 4). Deuterated paragonite and muscovite show a great loss in intensity of the band also (Fig. 5), which suggests an OH bending component. The figure shows that the high pressure (13-kbar) muscovite has neither the 802 nor the 737 cm^{-1} band. No other bands in the 1200–300 cm^{-1} region appear to be affected nor are any new bands apparent as a function of cell size or polymorph except the 643 cm^{-1} band, which appears to be associated with the large cell 1M polytype only.

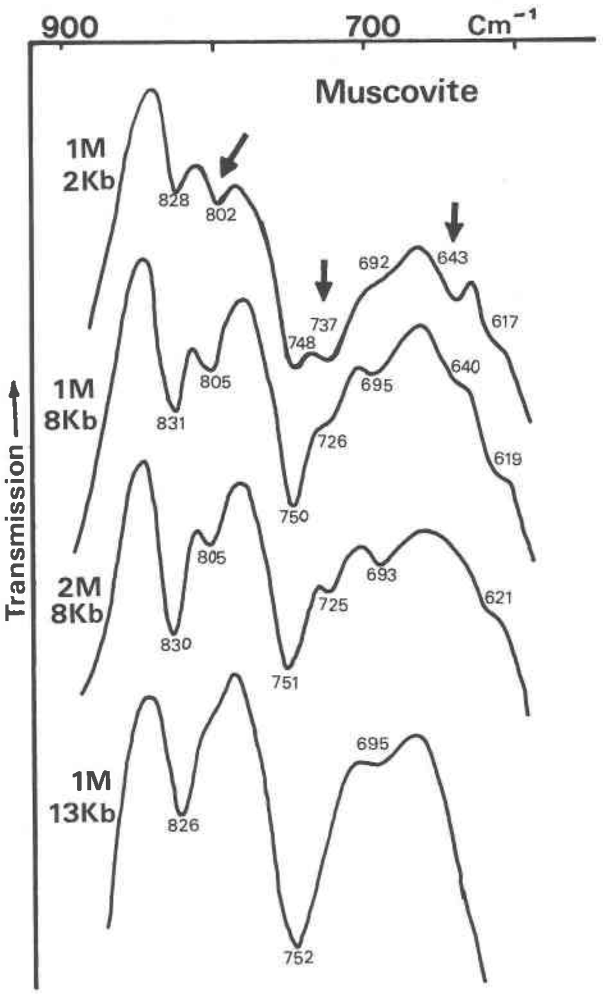

Fig. 3. Infrared spectra in the region 900–550 cm^{-1} for synthetic muscovites. Samples A, B, and C were provided by J. Blencoe. Samples D and E were prepared by the author. Arrows at 802, 737, and 643 cm^{-1} show bands affected by polytype.

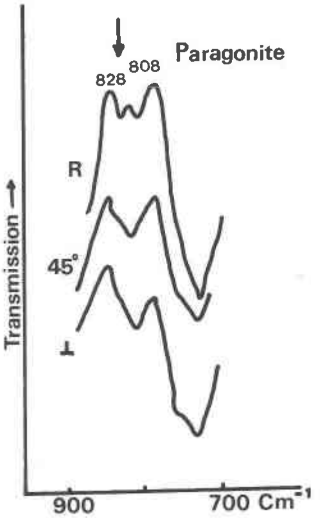

Fig. 4. Spectra of synthetic paragonite (1M polymorph) in randomly oriented preparations (R) and oriented preparations run at 45° angle to the beam (45°) and perpendicular (⊥) to the beam. Note loss of band at 830 cm^{-1} indicated.

Thus we see variation of the more "fundamental" Al^{IV}-related bands in muscovite as a function of cell size and not of polymorph.

Margarite

Figure 6 gives the spectra of the three polymorphs of margarite synthesized at 2 kbar. The spectra show variations only in the 725–400 cm^{-1} region. Four bands are decidedly sharpened and intensified as the polymorph changes from 1Md to 1M and then 2M. Bands at 510 and 725 cm^{-1} are lost in 1Md margarite. The 612 cm^{-1} band is greatly strengthened in 2M forms, as is the 446 cm^{-1} band. These bands are likely to be combinations of basic O–Si–O or Si–O polymer bending vibrations common to most dioctahedral white micas, as are those around 542, 492, 398 cm^{-1} (see Farmer, 1974, p. 350, for examples).

Note that no 802 cm^{-1} band is present. This is attributed to ordering of Al–Si tetrahedra which is most likely fundamental to the margarite structure with a tetrahedral Si–Al ratio of one (Farmer and Velde, 1973), and thus no Al–O–Al vibrations are possible due to this ordering.

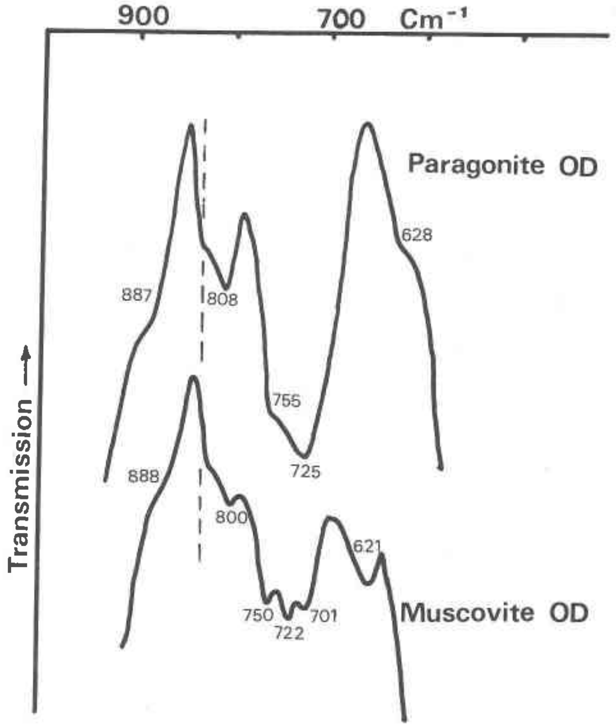

Fig. 5. Spectra of synthetic OD muscovite and paragonite. Note low intensity of the 830 cm^{-1} band.

Discussion

Given the above information, one can make several statements concerning muscovite: (1) cell dimensions in muscovite are not strongly related to polymorph type; (2) as cell dimensions change in muscovite of the 1M polymorph, two band vibrations involving Al atoms are affected; (3) high-pressure muscovites of small *b* cell dimension appear to follow the same trend as the ordered phengites in the muscovite–celadonite series.

These relations suggest that ordering can occur in muscovite and that it does not affect the polytype. The ordering probably involves the Al–Si tetrahedra, since all other sites contain identical ions (K in the larger interlayer position and only Al in the octahedral). The ordering then occurs within the basic 10Å unit and does not affect the stacking of these units (polymorphism).

If one considers the disposition of tetrahedral sites in mica silica polymers, it is apparent that ordering of one in four sites is not simple. The tetrahedra are arranged in hexagonal symmetry. The basic symmetry group of the mica is based upon a mirror plane. Further, most structural determinations of micas, at standard conditions, find that the hexagonal rings of tetrahedra are deformed into a ditrigonal symmetry. If ordering takes place respecting the mirror-plane symmetry element and the ditrigonal arrangement of tetrahedra, I can find no array which satisfies these conditions. However, if the mirror-plane element can be ignored, one can arrange the Si–Al atoms in several arrays, but they will necessarily be ones which

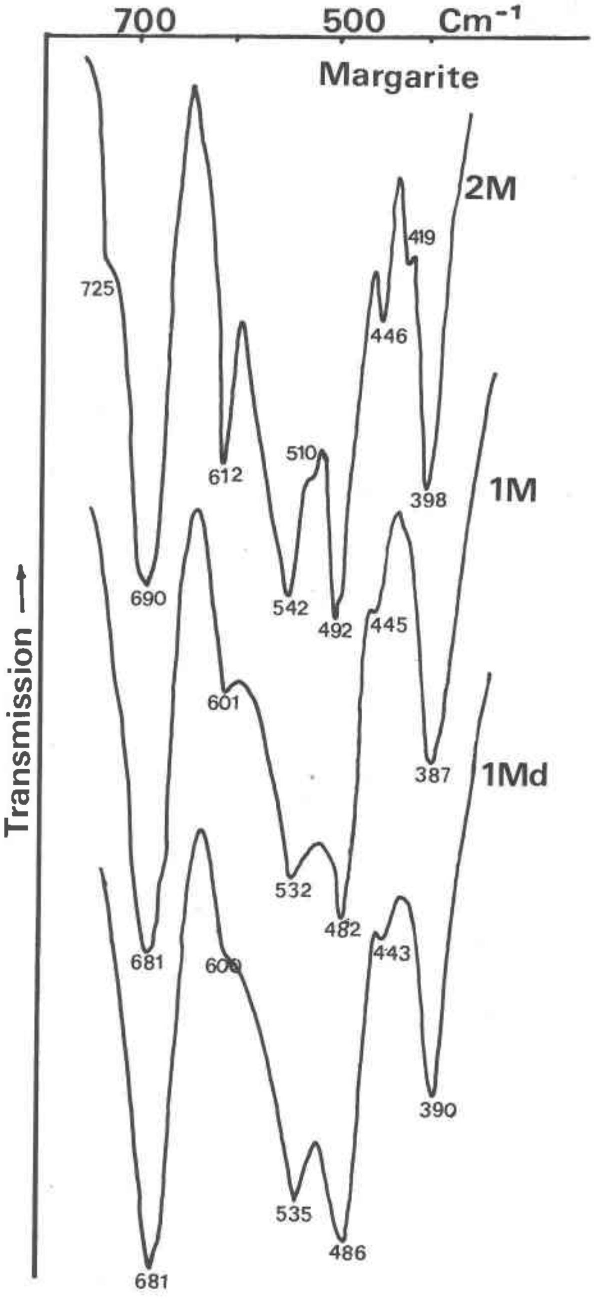

Fig. 6. Synthetic margarite infrared spectra in the region 750–350 cm^{-1}. Note loss of bands at 612, 510, and 446 cm^{-1} as polytype changes from 2M to 1M to 1Md.

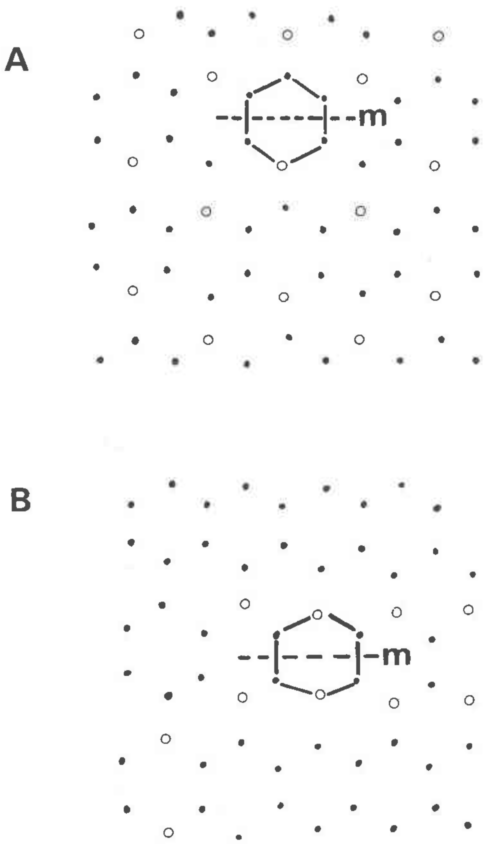

Fig. 7. Two possible arrays for Si–Al ordering (Si_3Al) in tetrahedral sites of micas. (A) shows an array where the mirror-plane symmetry element passing through coordinating oxygens (between symbols in the figure) is not respected. (B) shows a possible domain-type ordering of two Al atoms in a hexagonal ring, leaving other rings to contain only Si atoms. Circles represent Al atoms, dots represent Si atoms.

place Al ions at greatest distances from one another in order to avoid local stress due to the difference in size of Al^{3+} and Si^{4+} ions. Figure 7a gives a possible array. If the structure obeys the mirror-plane symmetry restriction, then a possibility for ordering would be on a domain basis, where some hexagonal rings of tetrahedra would contain more Al atoms than others (Fig. 7b). If we consider the infrared spectra we see that small cell dimension muscovite shows loss of two Al-related bands. This means that ordering, if this is the reason for diminishing the cell size, disrupts certain atomic arrangements in the silica polymer structure. No new bands seem to be added. Possibly a domain-type ordering (Fig. 7b) would produce the results observed in the infrared spectra.

The information concerning margarite–paragonites can be summarized as follows:

(1) Polytype is related to cell dimension and infrared spectrum.

(2) Pressure of synthesis has a relatively small effect on cell dimension.

(3) The infrared spectra indicate that band splitting of multi-atom vibrations is produced as polytype changes. This suggests "second-order" type ordering, which can be reconciled by stacking sequences in the 10Å layer structure which affect only lower energy vibrations of the Si–Al–O polymer structure.

(4) These relations occur for paragonite and margarite but not muscovite, despite the fact that the paragonite molecule is more similar to muscovite than to margarite:

$KAl_2(Si_3Al)O_{10}(OH)_2$, muscovite

$NaAl_2(Si_3Al)O_{10}(OH)_2$, paragonite

$CaAl_2(Si_2Al_2)O_{10}(OH)_2$, margarite

Concerning margarite, the infrared spectra and cell dimensions indicate that polytype (stacking of 10Å layers) produces the most efficient or ordered sequence. Absence of the 802 cm^{-1} Al–O–Al band in all polytypes suggests that the structure is "internally" ordered (within the 10Å sheet) in all polymorphs.

In summary, it appears that two types of site ordering occur in white micas, both resulting in smaller cell size. Muscovite and phengites order in the tetrahedral and octahedral sites respectively. This ordering occurs within the 10Å units only and does not affect the stacking or long-range order of the structure. Na–Ca micas (margarite–paragonite) show ordering in the stacking sequence of the 10Å units only. This ordering does however decrease cell dimension significantly.

If one accepts the arguments demonstrating ordering in these micas, it is apparent that any studies of the stability of such phases by laboratory methods must compare materials with the same structures. Not only does the ordering affect the statistical distribution contribution to the entropy of the mica, but it also affects the cell volume. Thus thermodynamic values for white micas will vary, depending upon their ordering state.

References

Blencoe, J. G. (1977) Molal volumes of synthetic paragonite–muscovite micas. *Am. Mineral.*, *62*, 1200–1215.

Chatterjee, N. D. (1970) Synthesis and upper stability of paragonite. *Contrib. Mineral. Petrol.*, *27*, 244–257.

——— (1974a) X-ray powder pattern and molar volume of synthetic 2M-paragonite: a refinement. *Contrib. Mineral. Petrol., 43,* 25–28.

——— (1974b) Synthesis and upper stability of 2M margarite. *Schweiz. Mineral.Petrogr. Mitt., 54,* 753–757.

Crowley, M. S. and R. Roy (1964) Crystalline solubility in muscovite and phlogopite groups. *Am. Mineral., 49,* 348–362.

Farmer, V. C. (1974) *The Infrared Spectra of Minerals.* Mineralogical Society Monograph, London.

——— and B. Velde (1973) Effects of structural order and disorder on the infrared spectra of brittle micas. *Mineral. Mag., 39,* 282–288.

Franz, G., T. Hinrichsen and E. Wannemascher (1977) Determination of the miscibility gap in the solid solution series paragonite–margarite by means of infrared spectroscopy. *Contrib. Mineral. Petrol., 59,* 307–316.

Storre, B. and K. H. Nitsch (1974) Zur Stabilität von Margarit im System $CaO-Al_2O_3-SiO_2-H_2O$. *Contrib. Mineral. Petrol., 43,* 1–24.

Stubican, V. and R. Roy (1961) Isomorphous substitutions and infrared spectra of layer silicates. *Am. Mineral., 46,* 32–51.

Velde, B. (1965) Phengitic micas: synthesis, stability and natural occurrence. *Am. J. Sci., 263,* 886–913.

——— (1966) Upper stability of muscovite. *Am. Mineral., 51,* 924–929.

——— (1971) The stability and natural occurrence of margarite. *Mineral. Mag., 38,* 317–323.

——— (1978) Infrared spectra of synthetic micas in the series muscovite–MgAl celadonite. *Am. Mineral., 63,* 343–349.

Yoder, H. S. and H. P. Eugster (1955) Synthetic and natural muscovite. *Geochim. Cosmochim. Acta, 8,* 225–250.

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