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Removal of Potassium Alters b-Dimension of Muscovite

Abstract. *By treatment of muscovite with molten lithium nitrate at 300°C we have been able to remove a large portion of the interlayer potassium and observe a decrease in the apparent* b-*axis length as a function of potassium content over the range of 8.8 to 0.7 percent potassium. The* b-*axis length of Silversheen mica (a $2M_1$ muscovite) decreases from 9.024 to 8.988 Å as the potassium content decreases from 8.79 to 3.31 percent. The contraction of the* b-*dimension results in an effective decrease in the size of the ditrigonal opening in the planar surfaces with a consequent increase in the d_{001} upon re-saturation with potassium.*

The fact that structural cations significantly influence the unit cell dimensions in layer silicates has been appreciated for some time. The effect of the composition of the tetrahedral and octahedral layers on the *b*-dimension of clay minerals was discussed by Brindley and MacEwan (*1*). In a recent paper proposing modifications in the accepted muscovite structure, Radoslovich (*2*) showed that tetrahedral groups can rotate quite easily to allow a fit between the tetrahedral and octahedral layers, thus producing a ditrigonal configuration of surface oxygens into which the interlayer potassium ions fit. More recently, Radoslovich (*3, 4*) and Radoslovich and Norrish (*5*) have shown both theoretically and by multiple regression analyses that the *b*-dimension in most cases is unaffected by tetrahedral composition but that the composition of the octahedral layer, and, in the case of micas, the interlayer cations, play major roles in determining the length of the *b*-axis. It was shown for a restricted range of potassium contents that the amount of potassium present as the interlayer cation in muscovite was directly related to the length of the *b*-axis.

The molten lithium nitrate method employed by White (*6*) and Bronson *et al.* (*7*) to create a series of potassium-depleted, charge-reduced micaceous minerals offers an excellent possibility for studying the effect of gradual potassium removal from interlayer positions in a muscovite on the *b*-dimension. The migration of lithium into vacant octahedral sites (*8*) which accompanies this potassium removal should not in itself affect the *b*-dimension (*2, 5*).

The *b*-parameter is usually calculated from the (060) reflection which occurs in the region 1.50 to 1.54 Å. As noted by Brindley (*9*), however, caution should be exercised in this, since other reflections such as (331) and (332), which are often equally strong, may coincide or nearly coincide with the (060) and cause assignment of incorrect *b*-parameters. For the $2M_1$ muscovites used in this study it should be noted that the powder line inspected is a superposition of (060) and $(33\bar{1})$ (*10*) which are practical equals. They may be treated as one entity, however, because of the pseudohexagonal nature of the structure. The correct designation of the line is thus $(060, 33\bar{1})$ for the untreated muscovite; this becomes (06, 33) in the expanded mineral, since the structural layers become displaced randomly along the *a* and *b* directions (*9*).

Since the *a*-dimension is considered to be related to the *b*-dimension by the relationship $a = b/3^{1/2}$, it will be affected in the same manner as the *b*-dimension.

Two $2M_1$ muscovites, Delamica (*11*) and Silversheen mica (*12*), were treated with molten lithium nitrate for varying periods of time for the purpose of removing potassium. Figure 1*A* shows the 1.50 Å region (60 to 63 degrees 2θ Cu Kα) of the diffraction pattern of the 5 to 2 μ fraction of Delamica (*6*) for 0 and 409 hours of treatment with molten lithium nitrate (*7*). The d-spacing decreased from 1.506 to 1.500 Å as the potassium content decreased from 7.45 to 0.75 percent. The *b*-dimension was reduced from 9.038 to 9.000 Å. The latter value represents a maximum value for the reduced *b*-dimension; the presence of a very definite shoulder at about 62.2° 2θ (1.492 Å) indicates the minimum reduced *b*-dimension to be approximately 8.950 Å.

The effect of removal of potassium from the 2 to 1 μ fraction of Silversheen mica on the 1.50 Å region of the diffraction pattern is shown in Fig. 1*B* for treatment times of 0, 4, 8, 12, and 24 hours. The d-spacing decreased from 1.504 to 1.498 Å as the potassium content decreased from 8.79 to 3.31 percent; the *b*-dimension decreased from 9.024 to 8.988 Å.

The relationship between the *b*-dimension and potassium content is not a simple linear relationship as indicated by the regression analysis of Radoslovich (*4*). Our data indicate a curvilinear relationship with at least two distinct slope values.

Once the unit cell has contracted slightly, presumably by rotation of the tetrahedra, the size of the opening in the oxygen surface, initially occupied by potassium, decreases and potassium can-

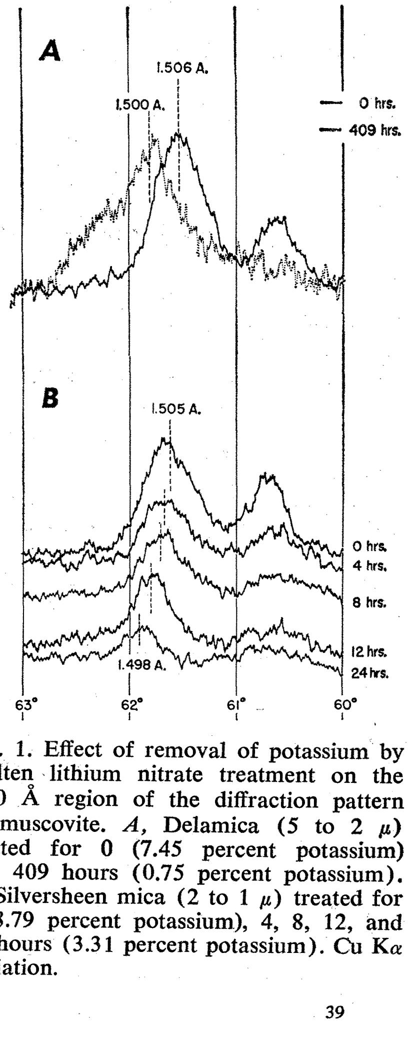

Fig. 1. Effect of removal of potassium by molten lithium nitrate treatment on the 1.50 Å region of the diffraction pattern of muscovite. *A*, Delamica (5 to 2 μ) treated for 0 (7.45 percent potassium) and 409 hours (0.75 percent potassium). *B*, Silversheen mica (2 to 1 μ) treated for 0 (8.79 percent potassium), 4, 8, 12, and 24 hours (3.31 percent potassium). Cu Kα radiation.

not fit down into the opening as far as it did initially. Thus, when potassium was added to the potassium-depleted mica and the mineral heated to 300°C to collapse the d_{001} to a minimum value, it was found that the d_{001} increased from 9.96 to 10.00 Å.

The implications of this relationship include the possibility of interpreting past history of micaceous minerals such as illite by careful measurements of the d_{001} values. For example, a value of 10.0 Å or greater for a mica might indicate that potassium had been removed to the point of producing a decrease in the *b*-dimension; subsequent resaturation with potassium in a new environment produces a mineral with a d_{001} value greater than that of the initial material (*13*).

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11. Delamica is a delaminated $2M_1$ muscovite obtained from English China Clays Lovering Pochin and Co., Ltd., St. Austell, Cornwall, England.
12. Silversheen mica is a $2M_1$ muscovite obtained from the Harwick Standard Chemical Co., Akron, Ohio.
13. This report is journal paper No. 2005 of the Purdue University Agricultural Experiment Station, Dept. of Agronomy, Lafayette, Ind. Supported by grant NSF G6063 from the National Science Foundation, made through the Purdue Research Foundation (PRF 2007).

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Lichens in a Greenhouse

Abstract. *The discovery of the first species of lichen capable of tolerating cultural conditions in greenhouses opens the possibility for conventional physiological experiments in this group of plants.*

In the temperate world greenhouses provide tropical habitats that are quickly infested with lower plants. Aside from the notorious cryptogamic pathogens that attack the greenhouse crops, an impressive array of saprophytic fungi, mosses, liverworts and algae of all sorts are the uninvited but usually harmless guests in all long-established greenhouses. Yet it has always been noteworthy that none of the some 20,000 known species of lichens seem to participate in this heterogeneous, synthetic flora. The lichen's apparent aversion for greenhouse life is doubly demonstrated by the regular failure of collected specimens to survive when brought inside for scientific or ornamental purposes. A vigorous and extensive growth in greenhouses—whether spontaneous or induced—has never been reported for any lichen species. Yet just such a development of one species can be seen in Paris.

This French lichen is crustose and grows over the plant debris used as a medium for culturing orchids in the two houses devoted to those plants in the Jardin des Plantes of the Muséum National d'Histoire Naturelle. It is always sterile and the thallus is whitish or pale green, disorganized in structure and mealy in texture, resembling coarse soredia. The hyphae are 2.5 to 4.0 μ in diameter. The algae are unicellular and globose; they measure 8 to 21 μ in diameter, and they belong to the genus *Trebouxia* (*1*). The general habit of the lichen resembles that of the imperfect species *Lepraria aeruginosa* (Wigg.) Sm., which is common in western Europe. But apparently the species in the greenhouse in Paris should neither be identified with this *Lepraria* nor indeed with any other of the common imperfect lichens of Europe. The notion that it might be one of these species can almost surely be ruled out, both because this lichen produces the depsides atranorin and stictic acid (*2*) and because it seems to be restricted to the greenhouses in Paris. The common European imperfect lichens have not been reported to elaborate these substances (although it must be admitted little at all is known of their chemistry). Furthermore, if it were simply a question of a local species that "came indoors," it should occur in greenhouses in many places in Europe, while in reality it appears to be unknown outside the conservatories of the Muséum National. A more plausible explanation is that it is a tropical imperfect species (or in any event a tropical species that does not fruit under these greenhouse conditions) that was accidentally introduced with the orchids themselves and that has since flourished in its new home (*3*).

Emile Manguin, director emeritus of the greenhouses of the Muséum National, told me that to his knowledge the lichen has been present there for at least 30 years. It grows in hundreds of pots over the mixture of polypody (*Polypodium vulgare*) fiber and various species of mosses used as a culture medium for the orchids. The growth rate is apparently rapid, at least from the lichenological point of view, since the lichen must be scraped off the surface of the medium about every 6 months. It is removed because it prevents the gardeners from telling when the plants need watering and not because it directly harms the orchids. And it might be added that the lichen also withstands both the extremely calcareous water of Paris as well as the badly contaminated atmosphere of the center of the city.

The real importance of the discovery of the spontaneous occurrence of lichens in glass houses, however, goes far beyond its mere immediate botanical curiosity. Experiments in the biology of the lichens have never progressed very far because most isolated fungal components are hard to culture and because attempts to grow the complete lichen in greenhouses and growth chambers have all failed. But it would appear that at last the perfect experimental subject has been found. And to increase the subject's attractiveness, it produces two substances, atranorin and stictic acid, which could well be called typical of that odd group of natural products—the extracellular, water-insoluble lichen constituents or "lichen acids"—that are almost entirely restricted to the lichens (*4*). In recent years the lichen substances have been used more and more as taxonomic criteria in the classification of this group of plants, and of course many critical questions about their suitability as such criteria have been raised (*5*). Lichenologists have regretted that they could not conduct experiments to determine the extent to which the environment affects (or does not affect) the qualitative and quantitative production of these unique compounds. But the substances produced by the modest lichen growing in Paris must surely be elaborated along the same biochemical pathways and subject