

# CELL DIMENSION STUDIES ON LAYER-LATTICE SILICATES: A SUMMARY

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## ABSTRACT

The statistical techniques of multiple regression analysis have been used to obtain more reliable formulae relating the cell dimensions (especially the *b*-axis) of layer-lattice silicates to their composition or structural formulae. This allowed the significance of each coefficient to be expressed precisely and so provided rigorous tests for certain structural concepts about the different factors affecting cell dimensions. More recently an explicit theory has been developed about the various forces controlling the layer-lattice silicate structures which (a) removes some anomalies, (b) explains many variations in accurate bond lengths and angles, and (c) has several interesting structural implications for properties such as polymorphism, composition limits, crystal morphology, and stability under weathering. This paper summarizes work now being published *in extenso* elsewhere.

## INTRODUCTION

The studies reviewed in this paper have been concerned with the cell dimensions of the layer lattice silicates mainly in the sense that these data provide readily available links between known properties and the known or supposed crystal structures of these minerals. Nevertheless it is expected that many of the arguments at present primarily based on cell dimensions will eventually be confirmed (or possibly refuted) by further accurate determinations of layer-lattice silicate structures.

The re-determination of the  $2M_1$  muscovite structure (Radoslovich, 1960) showed the ways by which this particular mica adjusts itself to reduce internal strains to a minimum. Some anomalies, such as the departure of the monoclinic angle from ideal, are thereby explained. In relation to other properties, however, the analysis merely revealed that this structure is suitably "distorted" from an ideal atomic arrangement, without (at that time) suggesting compelling explanations about why these "distortions" must of necessity occur.

From the clay mineral literature it seemed that any dimensional misfit between the tetrahedral and octahedral layers in muscovite should be an important key to this problem. Various formulae already existed which sought to relate the sheet dimensions (e.g. the *b*-axis) of layer-lattice silicates to their

isomorphous substitutions, both tetrahedrally and octahedrally. The most recent and comprehensive formulae were those due to Brindley and MacEwan (1953). These not only proved inadequate for the immediate muscovite problems but are not at all applicable to some layer lattice silicates of rather extreme composition. For example for the unusual brittle mica, xanthophyllite,  $\text{Ca}(\text{Mg}_2\text{Al})(\text{SiAl}_3)\text{O}_{10}(\text{OH})_2$ , the "unconstrained" tetrahedral and octahedral dimensions and the calculated  $b$ -axis *each* exceed  $b_{\text{obs}}$ ; i.e.

$$b_{\text{tetr}} = 9.84, \quad b_{\text{oct}} = 9.19, \quad b_{\text{calc}} = 9.49, \quad \text{but} \quad b_{\text{obs}} = 9.00 \text{ \AA}$$

### SURFACE SYMMETRY

Muscovite, in common with other layer-lattice silicate structures already published, proved to have a ditrigonal rather than hexagonal arrangement of surface oxygens. It was therefore suggested that the "ideal" mica structure should more properly allow a ditrigonal surface symmetry, and attention was drawn to this property in relation to mica polymorphism (Radoslovich, 1959). Smith and Yoder (1956) have proposed six simple polymorphs of micas on theoretical grounds, yet only three are at all commonly observed. These are based on  $120^\circ$  rotations between layers, and therefore permitted by ditrigonal surfaces on the layers. The rare or unobserved polymorphs depend on  $60^\circ$  interlayer rotations, which seem unlikely to occur with such surface symmetry.

In several mica structures now published (including muscovite) these ditrigonal surfaces ensure six- rather than twelve-fold co-ordination around the interlayer cation, e.g.  $\text{K}^+$ . Indeed a roughly octahedral arrangement around the cation of *six* closest surface oxygens with *direct* K-O (or Na-O or Ca-O) bonds may be expected as the normal interlayer configuration. In detail the structural and unit cell data for micas led to the hypothesis (Radoslovich and Norrish, 1962) that:

- (i) the  $b$ -axis is controlled mainly by the octahedral layers and
- (ii) the interlayer cations exert additional control through their *direct* bonds to surface oxygens, whereas
- (iii) the tetrahedral layers do not affect the cell dimensions significantly but do control the surface configuration, i.e. the degree of "twist".

### REGRESSION RELATIONS

Although satisfactory " $b$ -axis formulae" could have been derived empirically this would not have *convincingly* shown whether the interlayer cations and/or tetrahedral Al contribute to the sheet dimensions. A multiple regression analysis of the unit cell data against the compositional data of the micas, however, allowed the statistical significance of each coefficient to be tested rigorously (Radoslovich, 1962a). The coefficient for  $\text{K}^+$  was significant and large, but for tetrahedral Al it was non-significant—as predicted. In similar regression analyses of data for the kaolins and for the chlorites the coefficient

for tetrahedral Al was also non-significant; for the vermiculites and dioctahedral montmorillonites taken together it was significant but small. The new *b*-axis formulae not only can be applied to most minerals with rather extreme compositions but also provide a better fit for the more common minerals.

### GENERAL THEORY

Various data have already hinted that the octahedral cations in these minerals may tend to be partially ordered, and a careful comparison of the regression coefficients and ionic radii also pointed to this possibility. It appeared that cations with high valence either occupy two sites, leaving the third vacant, or else they occupy one site with the other two essentially filled with mono- and di-valent cations. An attempt to test this by more elaborate regression techniques only partly succeeded (Veitch and Radoslovich, 1962), but this study did lead to an explicit new geometrical model of these octahedral layers. This shows that the octahedral are not generally regular in shape, but compressed along *c*\*. The average effect of substituting larger cations is to increase the thickness three to four times as fast as the sheet dimensions.

The initial justification for the model physically has since been developed into a set of general principles about the forces which are thought to control the structures of the layer-lattice silicates (Radoslovich, 1962b; 1962c). The detailed and explicit statement of these principles, and of the restrictions and limitations in their applicability (Radoslovich, 1962c), cannot safely be condensed into this brief review. The individual concepts must, of course, be consistent with current structural inorganic chemistry. The innovation is the attempt to assess which stresses dominate and which stresses are unimportant throughout this group of structures. Despite the tentativeness of such an initial study this approach appears to have been notably successful both in removing certain previous anomalies and in explaining in considerable detail the individual variations in some precisely known bond lengths and angles, e.g. in dickite (Newnham, 1961) and in muscovite.

### SOME IMPLICATIONS

This general theory appears to be soundly based, but at this stage any interpretation of known physical properties in terms of these concepts must be viewed cautiously. Nevertheless, certain implications are highly interesting and merit attention in passing.

For example, the composition limits for natural micas (which have been extensively studied) are more restricted than any limits imposed solely to maintain electrical neutrality. But these observed limits are seen to be quite reasonable for natural specimens when the present principles are applied (Radoslovich, 1962d). Composition limits for the other clay mineral groups, which are of course less well defined, are also consistent in general.

The relative abundance of the different mica polymorphs is broadly known, but the reasons for the observed frequency distribution are hardly understood (Smith and Yoder, 1956). The dioctahedral nature of, and partial ordering of, tetrahedral cations in the  $2M_1$  muscovite polymorph is now clearly seen to cause a complex network of stresses and strains which must impose on this structure the observed pattern of layer stacking (Radoslovich, 1962c). Similar forces will be present in other micas and other polymorphs, and the main forms of structural control over mica polymorphism should become plain fairly soon.

The morphology of both kaolins and serpentines has been widely studied, both experimentally and theoretically. The tubular morphology of endellites is generally explained as due to the tendency of the tetrahedral layers to exceed the dimensions of the octahedral layers. Although this is no longer convincing to the author in the light of these studies, other asymmetric forces now may be postulated which could cause the layers to curl (Radoslovich, 1962e).

Finally, the relative stability under weathering of  $2M_1$  muscovite must be closely related to the almost unique way in which  $K^+$  is locked into the inter-layer positions in this particular mica (Radoslovich, 1962c). This suggests one direction in which future structures analyses may contribute to the study of the complex problems of clay mineral weathering and stability.

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