

## Relationships among 2:1 layer silicates

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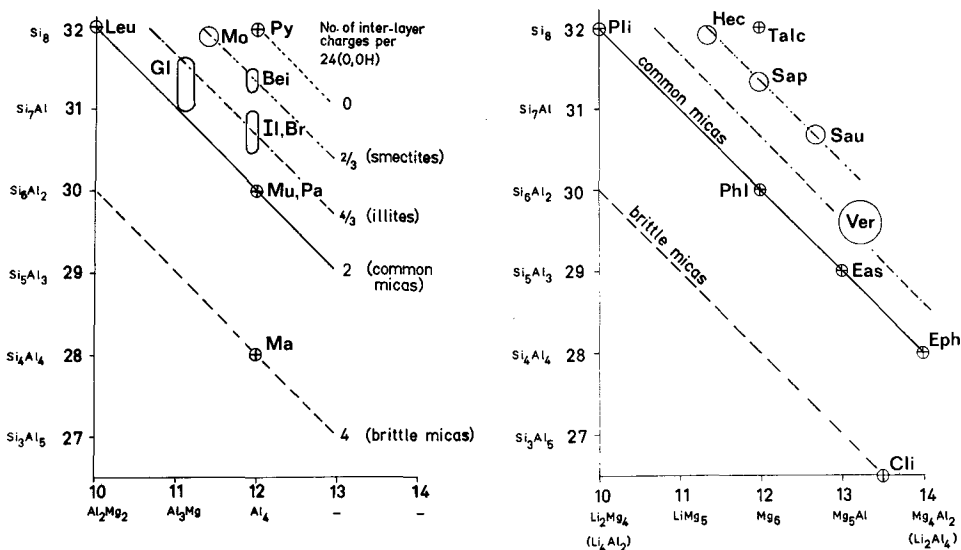
**SUMMARY.** The relationships between the 2:1 layer silicates are discussed in terms of the charge balance between the ions occupying *X*, *Y*, and *Z* sites. This brings out the relationship of glauconite to the illites, and clarifies the reason for the ideal occupancy of the *Y* sites in montmorillonite. It not only shows hectorite, saponite, and saucornite to be tri-octahedral smectites, but also shows vermiculite to be a tri-octahedral analogue of the illites. Apparently anomalous differences in permitted compositions of the di-octahedral and tri-octahedral micas are explained in terms of mismatch between the tetrahedral and octahedral layers, and it is shown that ephesite is to be regarded as a tri-octahedral common mica, not an analogue of margarite. Anandite is the nearest known naturally occurring equivalent to a tri-octahedral analogue of margarite, but the true analogue is a barium magnesium mica synthesized by Frondel and Ito.

WHEN one element (or more than one) in a mineral formula is replaced by another (or others) of the same valency, there is very little difficulty in visualizing unambiguously the relationships between the resulting mineral species. But when paired replacements of elements of differing valency can occur, it is often difficult to decide how best to view such inter-relationships; and this is a difficulty that becomes even more acute when some ionic sites may be left vacant. These problems have in the past caused some lack of clarity in the literature in connection with the 2:1 layer silicates, and it is the purpose of this paper to suggest that some of the inter-relationships of these minerals can be clarified if attention is directed to the total charges on the ions filling particular roles in the structure, regardless of their chemical nature.

Let *y* and *z* be the total charge on the *Y* and *Z* ions respectively in the formula  $X_n Y_4 Z_8 O_{20} (OH)_4$ —which includes all the di-octahedral common and brittle micas, the illites, the smectites, and pyrophyllite. Fig. 1 shows an approximate plot of the regions occupied by these minerals on the *yz* plane. Minerals with well-defined idealized formulae are plotted at points, without, of course, any implied denial of the possibility of solid solutions. The minerals of rather vaguer composition are shown as more extended areas, though again without implying any particular limits. The elements indicated alongside the axes are only illustrative examples of the common way in which the coordinates can be achieved. In this plot, the sum of the charges (*y*+*z*) on *Y* and *Z* ions is constant along lines sloping down to the right at 45°, and some lines of this type have been drawn in through the plotted points and regions. Since the total charge *x* required on the inter-layer (*X*) ions to achieve neutrality is given by 44−(*y*+*z*), these lines correspond to particular values of *x*, and these are indicated on the right-hand side of the diagram.

It may be regarded as natural that important compositions should lie at integral values of *y* and *z*, and of the values 0, 2, and 4 for *x*, which correspond respectively to total occupation of *X* sites by vacancies in pyrophyllite, by K or Na in the common

micas, and by Ca in the brittle micas. The values of  $4/3$  and  $2/3$  appear somewhat more surprising, but they correspond to the simplest regular ways in which the hexagonal arrays of interlayer sites can be left partially vacant. When  $x = 4/3$  (in the illites) every vacant site can be surrounded by filled sites, and when  $x = 2/3$  (in the smectites) every filled site can be surrounded by vacant sites.

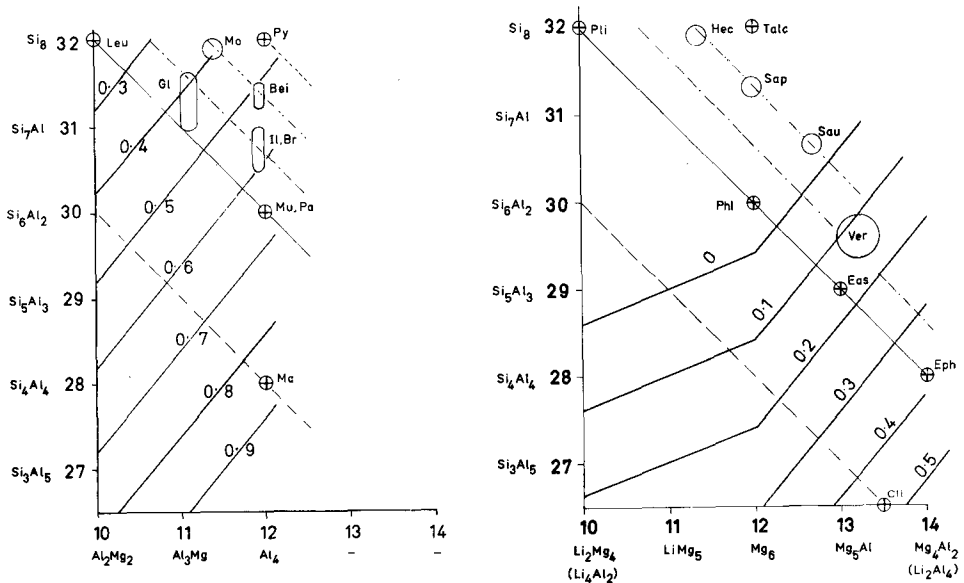


Figs. 1 and 2: Fig. 1 (left). Charge in Z sites plotted against charge in Y sites for dioctahedral 2:1 layer silicates. Leu = leucophyllite, Gl = glauconite, Mo = montmorillonite, Py = pyrophyllite, Bei = beidellite, Il = illite, Br = brammalite, Mu = muscovite, Pa = paragonite, Ma = margarite. Fig. 2 (right). Charge in Z sites plotted against charge in Y sites for trioctahedral 2:1 layer silicates. Pli = polyolithionite, Hec = hectorite, Sap = saponite, Sau = sauconite, Phl = phlogopite, Ver = vermiculite, Eas = eastonite, Eph = ephesite, Cli = clintonite.

Fig. 1 suggests two points of interest: from the point of view of charge balance glauconite is to be related to the illites. And secondly the ideal occupancy of the Y sites in montmorillonite is well known to be  $Al_{3.34}Mg_{0.66}$ ; this gives  $y = 11.33$ , and appears anomalous compared with the more usual integral values of  $y$ ; it is explicable from fig. 1, since this is the  $y$ -coordinate at which the line  $x = 2/3$  reaches the maximum possible value of  $z$  (namely 32).

A corresponding plot for the tri-octahedral layer silicates is shown in fig. 2. Whereas in the di-octahedral series  $y$  cannot normally exceed 12, in the tri-octahedral minerals it can rise to about 14 when some Al is present along with Mg in Y sites. Thus fig. 2 is more extensive than fig. 1. From fig. 2 one may draw the following four conclusions on the basis of charge balance: Hectorite and saponite plot as tri-octahedral smectites, and sauconite (with  $Y_6 = Zn_4Mg_{1.3}Al_{0.7}$ ) also belongs to this series. More surprisingly, vermiculite plots as a tri-octahedral analogue of the illites, not as a smectite as it is sometimes said to be; this is in line with its lower capacity for swelling by solvents.

Ephesite (recently shown by Schaller, Carron, and Fleischer (1967) to be  $\text{Na}_2\text{Li}_2\text{Al}_4\text{Si}_4\text{Al}_4\text{O}_{20}(\text{OH})_4$ ) plots as a common mica, not a brittle mica; this does not accord with their description of it as belonging to the margarite group. The only micas with predominant Na or Ca in *X* sites are confined to the region of very low *z*-values, i.e. high tetrahedral Al, with *Z* occupation ranging from  $\text{Si}_4\text{Al}_4$  to  $\text{Si}_{2.5}\text{Al}_{4.5}$ ; there is no tri-octahedral analogue of paragonite or of margarite; the tri-octahedral common mica containing Na at *X* (ephesite) and the tri-octahedral brittle mica containing Ca at *X* (clintonite) are a long way down the plot from the positions of paragonite and margarite.



FIGS. 3 (left) and 4 (right). As figs. 1 and 2, but showing lines of constant mismatch of the *b*-axis repeat of unconstrained tetrahedral and octahedral nets for the compositions indicated alongside the axes (but these are not quite correct for the alternative compositions in parentheses in fig. 4).

The reason for the lack of correspondence between the permitted compositions of the di-octahedral and tri-octahedral micas brought out above can be clarified if we consider the circumstances that affect the size of the inter-layer site. This depends on the extent to which the silicate nets are distorted from the ideal hexagonal arrangement to the di-trigonal arrangement by rotation of the  $\text{SiO}_4$  tetrahedra about axes perpendicular to the layer. As shown by Radoslovitch (1960), this depends on the degree of mismatch between the repeating unit in the unconstrained tetrahedral and octahedral layers, and this mismatch depends on the average sizes of the ions occupying the tetrahedral and octahedral sites.

Fig. 3 shows the essential features of fig. 1 with superimposed lines of constant mismatch in the unconstrained *b*-axis repeat distance of the two layers. In order to calculate the mismatch it is necessary to assume that the *Y* and *Z* sites are occupied

by particular ions of definite size, so that the contours given are correct only for the particular ions indicated, which are therefore no longer merely illustrative. It is to be noted that mismatch is substantial throughout the diagram, and this leads to substantial rotation of the  $\text{SiO}_4$  tetrahedra. As a result the inter-layer sites are small enough to be satisfactorily filled by ions as small as sodium or calcium, although larger ions like potassium can also be accommodated by pushing the layers apart.

On the corresponding plot for the tri-octahedral series (fig. 4) the mismatch is much smaller. This must lead to zero or small tetrahedral rotations over the upper part of the diagram, with the result that the interlayer sites in the micas will be too large to be satisfactorily filled by Na or Ca until we get down to the bottom right-hand corner, where at last the mismatch approaches that in paragonite. The situation in the illite and smectite series is less clear because of the complicating factor of hydration of the inter-layer ions, and for this reason attention is confined to the micas.

The mismatch in ephesite will probably be even higher than that shown by the contours, since it belongs to the Li,Al series and not to the Mg,Al series for which the contours in this part of the diagram were calculated. Thus ephesite appears to be best regarded not as a sodium brittle mica but as a common mica related to paragonite structurally in much the same way as clintonite is related to margarite.

As a further confirmation of this approach it is noteworthy that the tri-octahedral mica of the phlogopite-eastonite type that contains the highest (minor) Na content among those listed by Deer, Howie, and Zussman (1962) is one in which the mismatch is increased by the presence of tetrahedral Ti and Fe(III) (no. 3, p. 46).

In conclusion, it may be suggested that a tri-octahedral mica providing a true analogue to margarite (i.e. with  $z \sim 28$ ) requires a divalent inter-layer cation of the size of barium. Although the simple  $\text{Ba}_2\text{Mg}_6\text{Si}_4\text{Al}_4\text{O}_{20}(\text{OH})_4$  is not known to occur in nature, it has been synthesized by Frondel and Ito (1968). The closest analogue among natural minerals appears to be the high-iron species anandite described by Pattiaratchi, Saari, and Sahama (1967), although this mica is now known to have substantial substitution of hydroxyl by sulphur and chlorine (Lovering and Widdowson, 1968), and its coordinates on fig. 2 or 4 are  $y = 12$ ,  $z = 29.1-29.3$ . Thus it lies approximately half way between the common mica and brittle mica lines, but the significance of this with respect to the charge required on the inter-layer cations is diminished by the unusual substitution for hydroxyl.

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