Computer simulation of cation distribution in the octahedral layers of micas

W. J. KRZANOWSKI AND A. C. D. NEWMAN

Rothamsted Experimental Station, Harpenden, Herts.

SUMMARY. Without direct evidence that cations favour particular sites in the octahedral layers of phlogopite–biotite micas, it is usually assumed that the cations are distributed randomly. Such a distribution, however, implies appreciable populations of cation combinations that seem electrostatically improbable. A computer program was written that rearranges a random distribution so that the improbable combinations of cations are eliminated by predetermined restrictions. Its use shows that conditions deduced from Pauling's electrostatic valence rule lead to grouping of trivalent cations around vacancies; for some chemical compositions, chains of alternate trivalent cations and vacancies extend through the structure.

WITHIN the structural framework of the 2:1 layer silicate minerals many cation substitutions are possible: Al is the usual substituent for Si in the tetrahedral layers, but the octahedral layers tolerate a more varied range of cations. In the natural micas, for instance, the octahedral layers usually accommodate Mg, Fe^{2+}, Fe^{3+}, Al, and lesser amounts of Ti, Mn, and Li, in such proportions that the average cation charge is about 6 per 3 sites. Only one kind of ordering of cations in the octahedral layer has been established with certainty: if only 2/3 of the sites are occupied, as for example in muscovite, the cations are situated in those octahedra that have OH groups at adjacent vertices ('cis' configuration) and the octahedra with OH groups at opposite corners ('trans' configuration) are unoccupied. However, if all or nearly all the octahedral sites are occupied, as in the phlogopite–biotite micas, X-ray diffraction studies show the average octahedra to be very nearly equal in size, suggesting that the various cations can occupy any site without restriction. Therefore for purposes in which the cation distribution is required, such as the interpretation of OH spectra, it has usually been assumed that the cations occupy the octahedral sites randomly.

Each O of (OH) lies above or below the centre of an equilateral triangle of octahedral cations and the frequency of the OH-stretching vibration is influenced by these three cations. For instance, in talcs the fine structure of the OH absorption in the region 3630–3680 cm^{-1} has been attributed to replacement of Mg by Fe^{2+}, a different absorption frequency being assigned to each of the combinations Mg_3OH, $Mg_2Fe^{2+}OH$, and $MgFe_2^{2+}OH$. For a random arrangement of Mg and Fe^{2+} the relative intensities of the components in the spectrum are consistent with the frequency of occurrence of each combination calculated from the terms in the expansion of $(a+b)^3$, where a is the fraction of the sites occupied by Mg and b is the fraction occupied by Fe^{2+} $(a+b = 1$ in talc) (Vedder, 1964; Wilkins and Ito, 1967).

Micas, however, have wider ranging substitutions than talc, so that their OH spectra are more complex, and correspondingly more difficult to interpret unequivocally. If it is assumed that the atoms are randomly distributed in the octahedral sites, the proportion of each combination can be calculated from the terms of a polynomial of the form $(a+b+c+...)^3$, but with many trioctahedral micas this predicts significant proportions of combinations such as $R^{2+}R^{3+}R^{3+}OH$, $R^{3+}R^{3+}R^{3+}OH$, and $R \square \square OH$, $\square$ representing a vacant site; such combinations seem improbable from a consideration of structural chemistry. We have overcome this defect of the random model by using a computer to synthesize a random net representing the octahedral cations, which are subsequently rearranged so that the minimum number of improbable combinations remain.

The computer program calculates the proportions of each combination of atoms after rearrangement, and also prints out the net of octahedral cations produced; by introducing different restrictions the effect of removing different types of improbable combinations can also be studied.

The model. In setting up a model for simulating the distribution of cations in the octahedral layer, we used the structure of trioctahedral micas discussed by Donnay, Donnay, and Takeda (1964); for our immediate purpose it was not necessary to include displacements of the anions from octahedral symmetry in the model, though exact interpretation of spectra may eventually require this further information. The octahedral cations lie on a triangular net, and to avoid any undue restriction at this stage we have assumed in the first instance that all the octahedral sites are equivalent. The cations were grouped by charge: the divalent cations Mg^{2+}, Mn^{2+}, and Fe^{2+}, represented by R^{2+}, and the trivalent cations and Ti by R^{3+}, together with vacant sites as the third category. In the actual program, the R^{2+} cations were further subdivided into $(Mg^{2+}+Mn^{2+})$ and Fe^{2+}; this was done to study the distribution of Fe^{2+}, but this aspect of the synthesis is not discussed further in the present paper.

Let the proportion in each category be a, b, and c respectively, so that $(a+b+c) = 1$. The atoms are allocated to sites as follows. The number of sites to be considered, k, is stipulated; sites are then labelled from 1 to k, and k random numbers lying in the range 0 to 1 are generated, using the congruential generation method given in the Scientific Subroutine Package for the IBM/360 machine. The occupant of the jth site is determined by the jth random number; if it lies between 0 and a, the site is occupied by R^{2+}, between a and $a+b$, the site is occupied by R^{3+}, and so on. The overall structure considered is that of a triangular network and the sites are filled sequentially line by line from the apex of a triangle, each line containing one more site than the previous line (see fig. 4); except at the edges each new letter forms two new combinations, which are inspected and recorded. When the network is complete, the program prints out the numbers and proportion of each possible combination of three letters. Each computer simulation was replicated with a different set of random numbers, usually four times, and the mean probabilities calculated from the replicates. The coefficients of variation of four replicates were about 3 % for combinations with large probabilities, increasing to about 12 % for some combinations with much smaller probabilities.

The proportions of cation combinations were also calculated directly; for the random distribution, the probability of each combination of three cations is the appropriate term in the expansion of $(a+b+c)^3$, e.g. the probability of $R^{2+}R^{3+}\square$ is $6abc$, of $R^{2+}R^{2+}\square$ is $3a^2c$, etc. The proportions of combinations so calculated were very close to the mean proportions from four replicates generated by computer simulation using 5050 sites (Table I, columns 3 and 4).

TABLE I. *Proportions of cation combinations in biotite 3a from random and restricted distributions*

Octahedral cations: $Mg_{3.89}$ $Fe^{2+}_{0.98}$ $Al_{0.48}$ $Fe^{3+}_{0.25}$ $Ti_{0.17}$ $Mn_{0.08}$ per 6 sites; $R^{2+} = 0.825$; $R^{3+} = 0.150$; $\square = 0.025$

Cation combination	V score	Polynomial calculation	Random number generation	Restriction $4 \leqslant V \leqslant 8$	Restriction $4 \leqslant V \leqslant 7$	Restriction $5 \leqslant V \leqslant 8$	Restriction $5 \leqslant V \leqslant 7$
R_3^{2+}	6	0.559	0.566	0.555	0.506	0.597	0.578
$R_2^{2+}R^{3+}$	7	0.306	0.304	0.313	0.424	0.291	0.346
$R^{2+}R_2^{3+}$	8	0.055	0.056	0.060	0.000*	0.045	0.001*
R_3^{3+}	9	0.003	0.003	0.000*	0.000*	0.000*	0.000*
$R_2^{2+}\square$	4	0.050	0.049	0.048	0.040	0.000*	0.000*
$R^{2+}R^{3+}\square$	5	0.017	0.018	0.021	0.027	0.059	0.053
$R_2^{3+}\square$	6	0.001	0.002	0.002	0.003	0.008	0.022
$R^{2+}\square_2$	2	0.001	0.002	0.000*	0.000*	0.000*	0.000*
$R^{3+}\square_2$	3	0.000	0.000	0.000*	0.000*	0.000*	0.000*
$\square_3$	0	0.000	0.000	0.000*	0.000*	0.000*	0.000*

* Indicates combination forbidden by restriction on V.

Examination of these probabilities shows that in a random arrangement of cations, combinations such as $R^{2+}\square_2$, $R^{3+}\square_2$ and $\square_3$ have an appreciable chance of occurring; in mica B6 for example (Table II; for the full structural formulae of the micas, see Newman, 1969), the combined probability of these combinations is 2.7 %. Although these probabilities are small relative to the total, their exclusion would increase the populations of combinations such as $R^{2+}R^{2+}\square$ and $R^{2+}R^{3+}\square$. To lessen the proportion of improbable combinations, criteria were formulated for deciding whether a particular combination was allowed or forbidden.

Criteria for forbidden combinations

The rules of Radoslovich. From his study of mica structures, Radoslovich (1963) concluded that vacancies in the octahedral layer are likely to occur at the trans–OH sites, which are vacant in muscovite, and that cations form regular hexagonal arrangements around vacancies. Divalent cations tend to be disposed hexagonally around trivalent cations, separating adjacent R^{3+} as much as possible.

These assumptions however, tend to be too restrictive on the cation arrangements, and an approach based on Pauling's rules was preferred.

The electrostatic valence rule of Pauling (1960). According to this rule, the valence of each anion is exactly or nearly equal to the sum of the strengths of the electrostatic bonds between it and the adjacent cations; the strength of the electrostatic bond is

defined as the electric charge of the cation divided by the number of co-ordinated anions. This rule is satisfied nearly completely by most silicate mineral structures, deviations of $\pm\frac{1}{6}$ being rare; when applied to mica structures, the rule has some useful implications.

Because cation ordering in trioctahedral micas is not yet proved, and one object of the present work was to find out what ordering is possible, we have assumed that the electrostatic valence rule may also be used for the 'average' occupant of a polyhedron. For example, if the tetrahedral cations have the average composition Si_3Al per 4 tetrahedra, we suppose that each tetrahedral site is occupied by $\frac{3}{4}Si$ and $\frac{1}{4}Al$, so that the strength of the electrostatic bond to each tetrahedral oxygen is $\frac{1}{4}(\frac{3}{4}\times4+\frac{1}{4}\times3) = \frac{15}{16}$.

Any individual site is of course occupied by either Si or Al; the above assumption applies only to the average effect of Al for Si substitution over a large volume of the structure and has the merit that it leaves open the actual arrangement of cations. In the following discussion, the general mica formula unit is expressed by the formula $K_2(Si_nAl_{1-n})_8(R^{2+}_m \; R^{3+}_l)_6O_{20}$ (OH, F)$_4$. In dioctahedral micas, $m+l \sim 2/3$ and in trioctahedral micas, $m+l \leqslant 1$.

This discussion is primarily concerned with the octahedral layer; however, the anions of the octahedral layer consist of hydroxyl and oxygen ions shared between tetrahedral and octahedral cations, so that it is first necessary to calculate the contribution to the oxygen ions from the tetrahedral layer.

FIG. I. Tetrahedral charge and frequency distribution of trioctahedral micas (data from Foster, 1960).

The average electrostatic bond strength between each tetrahedral oxygen and (Si, Al) is $\frac{1}{4}[4n+3(1-n)]$ or $\frac{1}{4}(n+3)$ and the bond strength from interlayer K, which is co-ordinated to 12 oxygen atoms, is $\frac{1}{12}$ towards the basal oxygen atoms. The total contribution to each basal oxygen from 2(Si, Al) and 2K is therefore $2[\frac{1}{4}(n+3)+\frac{1}{12}]$ or $\frac{1}{2}(n+10/3)$, which should be nearly equal to the valency of oxygen, 2. For the total electrostatic bond strength to equal 2 exactly, n must equal 2/3, that is, the tetrahedral cation composition is $(Si_{5.33}Al_{2.67})$ per unit formula; this is the condition for the charge of the interlayer K to be balanced by the (Si, Al) contribution to the basal oxygen atoms, and substitution of Al for Si in excess of 2·67 leads to a net negative charge on the basal oxygens that cannot be balanced by monovalent interlayer cations. Therefore $n = 2/3$ should be the upper limit for tetrahedral substitution of Al in the common micas. The formulae of 135 trioctahedral micas listed by Foster (1960), accord with this conclusion: Al for Si substitution lies between 2 and 3 per (Si, Al)$_8$, with a frequency maximum for the group 2·6 < Al < 2·7 (fig. 1). This limit is evidence in support of the application of Pauling's rule in the way described above. Its corollary is that trivalent cations may substitute for divalent cations in the octahedral layer, up
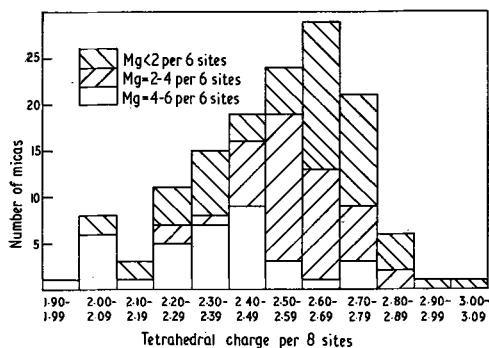
to about 0·67 per 6 octahedral cation, without vacancies being necessary for overall charge balance; further substitution of trivalent cations requires that an appropriate proportion of octahedral sites become vacant to balance the excess positive charge. Foster noted this tendency in her discussion (see fig. 8 in Foster, 1960).

In the octahedral layer, the proportion of hydroxyl anions to oxygen ions shared between tetrahedral and octahedral cations ('apical' oxygen ions, O_{ap}) is 1:2. The electrostatic bond strength between the tetrahedral cations and the apical oxygens is $(n+3)/4$ as before, and between H and O in the hydroxyl anions is 1; each oxygen is adjacent to three octahedral cation sites, so the average electrostatic bond strength to each oxygen is $V_1/6+V_2/6+V_3/6$, where V_1, V_2 and V_3 are the charges on the octahedral cations. The electrostatic bond strength sum to the 'average' oxygen $(2O_{ap}+1OH)/3$ is therefore $(V_1+V_2+V_3)/6+[2(n+3)/4+1]/3$ = valency of oxygen $\pm\frac{1}{6}$; this equation simplifies to

$$V_1+V_2+V_3+n = 7\pm1. \tag{1}$$

The substitution of Al for Si in trioctahedral micas (fig. 1) lies within the range $\frac{2}{3} < n < \frac{3}{4}$, so that the most probable values for V ($= V_1+V_2+V_3$) are 6 or 7, with a lesser probability of $V = 5$ or 8.

Rules can now be formulated to select the allowed combinations of cations. Of the ten possible combinations of divalent and trivalent cations and vacancies, $R^{2+}R^{2+}R^{2+}$, $R^{2+}R^{2+}R^{3+}$, and $R^{3+}R^{3+}\square$ are allowed, with a lesser probability of $R^{2+}R^{3+}\square$ and $R^{2+}R^{3+}R^{3+}$, but $R^{3+}R^{3+}R^{3+}$, $R^{2+}R^{2+}\square$, and combinations of two or more vacancies are prohibited. These restrictions were introduced into the computer program in the following way. R^{2+} cations were given a score of 2, R^{3+} cations a score of 3 and vacancies a score of zero. The network of randomly distributed cations generated on the first pass is scanned and the total score V ($= V_1+V_2+V_3$) of each triplet combination inspected. If V falls within the set limits, the scan is continued, but if V is outside the limits, the scan is stopped and the cation giving rise to impermissible score is interchanged with a cation later in the network that gives permitted scores in the two combinations being considered. Should no cation be found that will give a permitted combination, the original cation is left in place. The scan now continues and where necessary further rearrangements of cations are made in the same way until the whole network has been traversed. During the development of the program, three rearrangement scans were done, but it was found that scans after the first did not further decrease the small numbers of impermissible combinations that still remained, so that only one scan was used in production work.

The program allows the total score parameter V to be varied between limits preset before each synthesis, in accordance with the conditions of equation 1.

Results

The effectiveness of the program in eliminating the prohibited cation combinations is illustrated for a magnesium biotite (Table II). In the random distribution of cations, the combinations $R^{3+}R^{3+}R^{3+}$, $R^{2+}R^{3+}R^{3+}$, $R^{2+}R^{2+}\square$, $R^{2+}\square\ \square$, and $R^{3+}\square\ \square$ account for just over 10 % of the total, whereas the restriction $5 \leqslant V \leqslant 7$, which should eliminate these combinations, decreases their proportion of the total to 0·4 %.

TABLE II. *Proportions of different cation combinations in biotites from random and restricted distributions*

Mica Octahedral cations	B1 Mg$_{2.97}$ Mn$_{0.12}$ Fe$^{2+}_{2.11}$ Al$_{0.0}$ Ti$_{0.24}$ Fe$^{3+}_{0.46}$			B6 Mg$_{1.80}$ Mn$_{0.08}$ Fe$^{2+}_{2.12}$ Al$_{0.84}$ Ti$_{0.21}$ Fe$^{3+}_{0.34}$			L1 Mg$_{1.87}$ Mn$_{0.06}$ Fe$^{2+}_{3.02}$ Al$_{0.20}$ Ti$_{0.33}$ Fe$^{3+}_{0.19}$		
Cation combination	Random distribution	Restriction $4 \leqslant V \leqslant 7$	Restriction $5 \leqslant V \leqslant 7$	Random distribution	Restriction $4 \leqslant V \leqslant 7$	Restriction $5 \leqslant V \leqslant 7$	Random distribution	Restriction $4 \leqslant V \leqslant 7$	Restriction $5 \leqslant V \leqslant 7$
R^{2+}_3	0·644	0·648	0·745	0·295	0·234	0·371	0·561	0·522	0·662
$R^{2+}_2 R^{3+}$	0·212	0·234	0·140	0·313	0·458	0·330	0·245	0·304	0·182
$R^{2+} R^{3+}_2$	0·025	0·000*	0·000*	0·107	0·001*	0·004*	0·037	0·000*	0·000*
R^{3+}_3	0·001	0·000*	0·000*	0·011	0·001*	0·001*	0·002	0·000*	0·000*
$R^{2+}_2 \square$	0·094	0·094	0·003*	0·135	0·110	0·009*	0·111	0·121	0·003*
$R^{2+} R^{3+} \square$	0·018	0·024	0·090	0·097	0·154	0·217	0·034	0·049	0·127
$R^{3+}_2 \square$	0·001	0·001	0·022	0·016	0·042	0·063	0·003	0·008	0·023
$R^{2+} \square_2$	0·004	0·000*	0·001*	0·020	0·000	0·002	0·007	0·000*	0·002*
$R^{3+} \square_2$	0·001	0·000*	0·000*	0·007	0·000*	0·000*	0·000	0·000*	0·000*
$\square_3$	0·000	0·000*	0·000*	0·000	0·000*	0·000*	0·000	0·000*	0·000*

* Indicates combination forbidden by V restriction.

Geometrical considerations suggested that restrictions on permitted cation combinations might impose a degree of order on the cation arrangement and the program was modified to print out the actual network of symbols after restrictions were imposed. Fig. 2 shows the effect of increasing restriction on a random distribution of cations. In the random distribution (fig. 2A) anomalous groups may appear, for instance, the block of nine trivalent cations in neighbouring sites; vacancies associate with only one or two trivalent cations and may occur in a block of divalent cations. The restriction $4 \leqslant V \leqslant 8$ (fig. 2B) eliminates $R^{3+}R^{3+}R^{3+}$ and the combinations containing two or more vacancies, and its introduction into the program separates the trivalent cations into pairs, but vacancies still occur randomly. The contrast between the restrictions $4 \leqslant V \leqslant 7$ and $5 \leqslant V \leqslant 8$, which cover the same range of V, is interesting. The former restriction, which additionally prohibits $R^{2+}R^{3+}R^{3+}$, isolates the trivalent cations from each other by intervening divalent cations or vacancies so that vacancies rarely combine with more than one trivalent cation (fig. 2C). The latter restriction, which allows $R^{2+}R^{3+}R^{3+}$ but prohibits $R^{2+}R^{2+}\square$, favours the grouping of three or more trivalent cations around vacancies and the beginning of alternate trivalent-cation-vacancy ordering is found (fig. 2D). The strict Pauling rule condition, $5 \leqslant V \leqslant 7$, orders trivalent cations and vacancies more regularly (fig. 2E) either into isolated trigonal groups
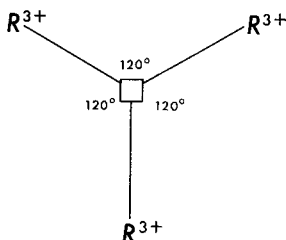
that may coalesce into chains, or into chains of the type
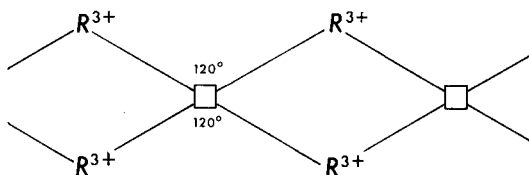
The first type of chain will be called 'Y' chains and the second 'X' chains.

For a mica that contains more trivalent cations and vacancies than biotite 3a, these arrangements may extend through the whole network; fig. 3 shows the patterns that form in biotite 1, all the vacancies grouping into a double Y-chain on the left of the diagram and a X-chain on the right. It is noteworthy that single Y-chains contain no $R^{3+}R^{3+}\square$ combinations, only combinations of the types $R^{2+}R^{3+}\square$ and $R^{2+}R^{2+}R^{3+}$, and that X-chains must end in a prohibited combination, either $R^{2+}R^{2+}\square$ or $R^{2+}R^{3+}R^{3+}$.
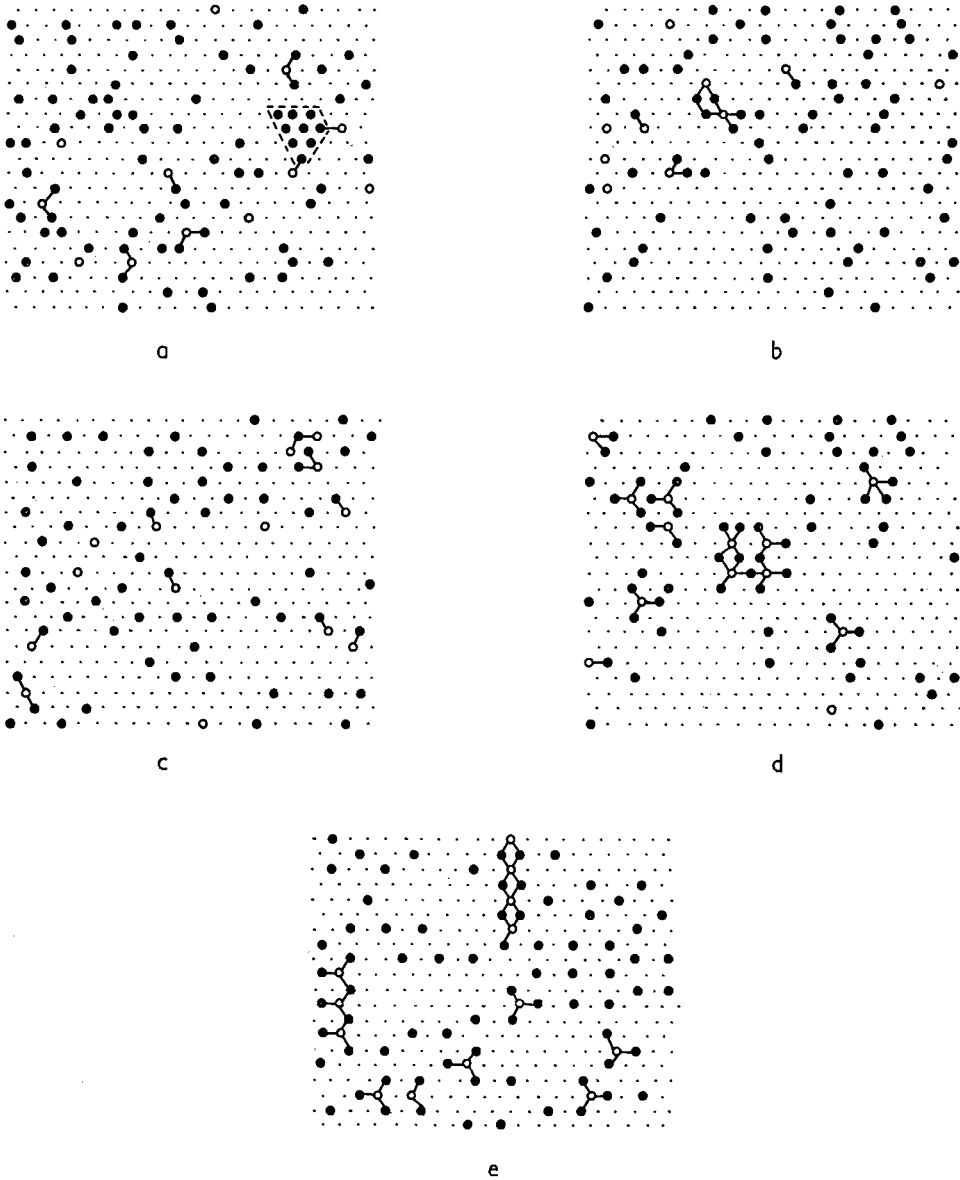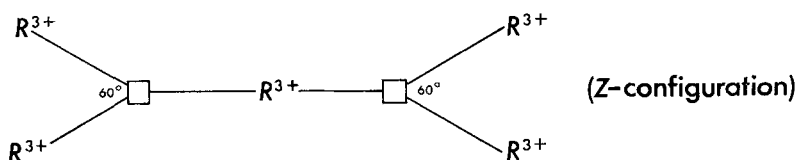
FIG. 2. Computer synthesis of cation distributions in biotite B3a with different V restrictions: (a) unrestricted; (b) $4 \leqslant V \leqslant 8$; (c) $4 \leqslant V \leqslant 7$; (d) $5 \leqslant V \leqslant 8$; (e) $5 \leqslant V \leqslant 7$. $\cdot = R^{2+}$; $\bullet = R^{3+}$; $\circ = $ vacancies.

One other type of configuration is allowed within the restrictions $5 \leqslant V \leqslant 7$:

(Z-configuration)

It is not often generated when R^{3+} occupies only a small proportion of the octahedral sites, but it rapidly becomes more frequent as the proportions of R^{3+} and $\square$ increase. However, long chains with this configuration do not develop, probably because the ratio $R^{3+}:\square$ in such chains approaches $1:1$ rather than the ratio $2:1$ required for charge balance.

If a vacancy in one part of an X- or Y-chain occurs at a site with hydroxyl anions at opposite vertices (trans–OH sites), all the vacancies in the chain are at trans–OH sites. X- and Y-chains are therefore compatible with a dioctahedral structure and a completely dioctahedral arrangement can be built up by laying these chains side by side. Likewise, an X- or Y-chain could be positioned with all vacancies at sites with hydroxyls at adjacent vertices (cis–OH sites), for the computer program does not distinguish between the two types of site, so that it is usual to find chains based on both cis- and trans-OH sites in a synthesis. If the proportions of R^{3+} and $\square$ are sufficiently large, the chains develop into larger ordered regions that meet. Should the meeting regions be bas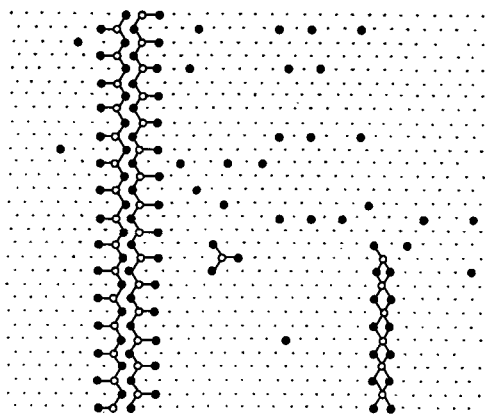ed on equivalent vacant sites, the two regions are compatible but if they are not equivalent, a Z-configuration or an impermissible combination is formed at the join. This is illustrated by the arrangement of atoms obtained for the hypothetical composition $R^{2+} = \frac{1}{3}$, $R^{3+} = \frac{4}{9}$, $\square = \frac{2}{9}$, using the restrictions $5 \leqslant V \leqslant 8$ and $5 \leqslant V \leqslant 7$ (fig. 4). By contrast, a synthesis using the ideal muscovite composition, $R^{2+} = 0$, $R^{3+} = \frac{2}{3}$, $\square = \frac{1}{3}$, generated a structure that was completely ordered with either V restriction, except for the slight imperfection that results when the actual proportion of $R^{3+}:\square$ departs from the ideal ratio of $2:1$.

FIG. 3. Computer synthesis of cation distribution in biotite B1 for $5 \leqslant V \leqslant 7$; $\cdot = R^{2+}$; $\bullet = R^{3+}$; $\bigcirc = $ vacancies.

The ability of the program to synthesize a fully ordered dioctahedral layer from a random distribution of trivalent cations and vacancies is convincing confirmation that the principles used in the synthesis are essentially sound. Furthermore, these last two examples suggest another use of the computer synthesis, namely to study the

restrictions that Pauling's electrovalence rule may impose on the chemical composition of micas and this possibility is at present being investigated.

Conclusions. The program rearranges a random distribution of cations in a trigonal network so that the electrostatically improbable combinations are eliminated. During this process, trivalent cations and vacancies are brought to adjacent sites, the regularity
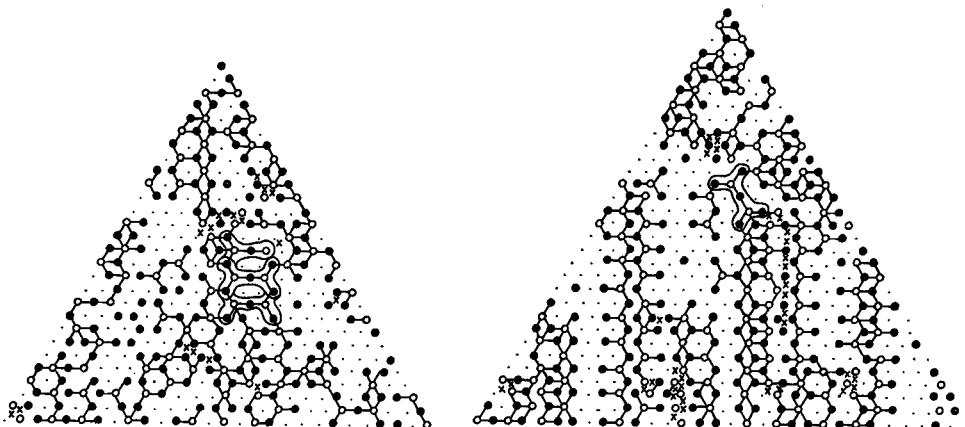

FIG. 4. Computer synthesis for the hypothetical composition $R^{2+}_{2 \cdot 0} R^{3+}_{2 \cdot 67} \square_{1 \cdot 33}$: $\bullet = R^{2+}$; $\bullet = R^{3+}$; $\bigcirc$ = vacant sites; $\times$ = impermissible combination; Z-configurations are outlined. (a), left, $5 \leqslant V \leqslant 8$; (b), right, $5 \leqslant V \leqslant 7$.

of the ordering depending on the stringency of the restrictions. If Pauling's electrostatic valence rule is applied strictly, the conditions imposed order the trivalent cations and vacancies into chains of 3 different configurations. X and Y configurations are compatible with vacancies at trans–OH sites only, whereas Z configurations and impermissible combinations imply that some vacancies must occur at cis–OH sites. If these theoretically predicted patterns of cation ordering actually exist in micas, there should be observable consequences in their properties, especially in their resonance spectra, and this aspect will be discussed in a later paper.

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