A model for trace-element distribution in silicate structures

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SUMMARY. This paper presents an extended version of the local lattice deformation model of solid solutions (J. T. Iiyama, 1974b). It has been assumed previously that a foreign atom fixed in a crystal causes local lattice deformation, which prevents another foreign atom from occupying the deformed zone. The resulting entropy of the solid solution from this model can explain the particular behaviour of ion-exchange reactions observed with alkali and alkali-earth elements in feldspars and in muscovite. The present version assumes that the deformed zone does not prohibit foreign atoms, but that the number of foreign atoms acceptable in this region depends on the total numbers of foreign atoms already fixed in the crystal. The model is applied successfully to explain ion-exchange isotherms observed with Cs, Na, and Li in micas and permits an estimation of the apparent reaction constant of the ion exchange. This is otherwise impossible because of the lack of ideal dilute-solution behaviour in exchange isotherms even at the 10 ppm range of the foreign element fixed into the crystal. It is demonstrated that the model can explain the particular behaviour of Li in sanidine.

THE behaviour of alkali and alkali-earth trace elements in feldspars, feldspathoids, and micas has been studied experimentally by using ion-exchange reactions under hydrothermal conditions (Ghelis and Lagache, 1972; Iiyama, 1968, 1972, 1974a, 1974b; Lagache, 1968, 1969, 1971, 1974a, 1974b, Lagache and Sabatier, 1973; Roux, 1971, 1974; Roux et al., 1971; Volfinger, 1969, 1970a, 1970b, 1974, 1975a, 1975b).

The experiments showed that in many cases the solid solution of these silicates formed by the incorporation of a trace element can be considered as an ideal dilute solid solution. However, the extent of the ideality of the solid solution was often limited to very low concentrations of the trace element fixed in the mineral. The application of the widely used regular solution model requires a very large interaction energy (attaining some 10 to 100 kcal/mole) between the host and the trace components, which makes the model unrealistic (Iiyama, 1974a).

To avoid this difficulty a model is proposed here in which the crystal structure of the mineral is locally deformed around a site occupied by an atom of the trace element. The local lattice deformation results in a distribution of trace atoms in the structure different from that of an ideal solution. The entropy of the solid solution using this model was calculated and applied successfully to several ion-exchange equilibria that could not be explained by regular solution models without some unrealistic interaction parameters (Iiyama, 1974b).

In addition to the cases in which the behaviour of the trace element can be explained perfectly by regular solution models or by the local lattice-deformation model, there remains another group of ion exchange equilibria in which the solid solution ceases to

be ideal at very low concentration of the trace element but continues in the mineral far beyond the solubility limit predicted by the local lattice deformation model. It is therefore necessary to make a modification of the previous model to explain this behaviour.

This paper presents a generalized version of the local lattice deformation model and its application to observe ion-exchange reactions. To facilitate the comprehension of the theoretical derivation, the previous model will be described briefly.

Brief description of the local lattice deformation model

Imagine a silicate BR composed of N atoms of the element B and a silicate radical R. The incorporation of an element A in the silicate is assumed to occur by A–B substitution.

If the sizes of atom A and B are similar and if the structural tolerance of the crystal to accept A instead of B is great, atoms A will be distributed at random among sites occupied by B. The resulting entropy variation with the number $N(A)$ of atoms A in the structure will be equal to that ΔS^{id} of the ideal solution:

$$\Delta S^{id} = -k[N(A) \ln N(A)/N + N(B) \ln N(B)/N],$$

where k is Boltzmann's constant and $N(B)$ designates the number of B atoms in the structure $(N = N(A)+N(B))$.

If the ionic size of the element A is different from that of B and the structural tolerance of the mineral to accept A instead of B is not great enough, the fixation of the element A in the mineral will provoke a local site deformation around the substituted site. Sites occupied by B atoms in the structure will be discriminated by this A–B substitution into sites included in the locally deformed part around the site occupied by A and those in the non-deformed part. The degree of distortion of B sites and the volume of the deformed zone will depend on the size difference of A and B ions and on the elastic properties of the crystal.

In an extreme case, the site deformation can be such that the substitution of B atoms by A does not occur in the interior of the deformed zone. In this case the entropy of mixing of the solid solution is expressed by the formula:

$$\Delta S^{def} = -k[N(A) \ln \{N(A)/N\} + \{(N(B)-rN(A))/(r+1)\}\ln\{(N(B)-rN(A))/N\}],$$

where r is the number of B sites included in one deformed zone.

Assuming an athermal solution model with the entropy of mixing given by this equation, the excess molar free energy Δg^{ex} of this solid solution containing $n(A)$ moles of the constituent AR and $n(B)$ moles of BR can be expressed by:

$$\Delta g^{ex} = -RT[\{(n(B)-rn(A))/(r+1)\}\ln\{(n(B)-rn(A))/n\} - n(B)\ln\{n(B)/n\}],$$

where R is the universal gas constant and T is the absolute temperature.

Differentiating Δg^{ex} with $n(A)$ and $n(B)$, the activity coefficients $\gamma(A)$ and $\gamma(B)$ of constituents AR and BR in this solid solution are given by formulae:

$$\ln \gamma(A) = -\{r/(r+1)\}\ln\{X(B)-rX(A)\}$$

and
$$\ln \gamma(B) = \{1/(r+1)\}\ln\{X(B)-rX(A)\} - \ln X(B),$$

where $X(A)$ and $X(B)$ designate molar fractions of AR and BR respectively in the crystal.

From this relation and assuming that a hydrothermal solution containing A and B ions behaves as an ideal solution, the ion-exchange isotherms for this type of solid solution are easily calculated.

The composition of the vapour phase v_{aq} is expressed by the ratio $m(A)/m(B)$ of 'molarities' of ions A and B and x_{xal} is the composition of the solid phase expressed by the ratio $X(A)/X(B)$. The desired relation to define the isotherm of an exchange reaction $BR + A = AR + B$ is expressed by the equation:

$$\log v_{aq} = \log K_0 + \log x_{xal} - \log\{X(B) - rX(A)\} + \log X(B) \tag{1}$$

K_0 of this formula is related to the equilibrium constant k and to the standard free energy variation ΔG_0 of the reaction $BR + A \to AR + B$; $K_0 = 1/k = \exp(\Delta G_0/RT)$.

Fig. 1 represents the equilibrium relations of Li–K exchange[1] in muscovite observed at 600 °C, 1 kbar of P_{H_2O}. The curve is calculated with $K_0 = 1\cdot99$ and $r = 14\cdot8$ which gave the best fit to the observed values of v_{aq} and x_{xal}.

Inspection of equation (1) indicates that the relation between v_{aq} and x_{xal} is linear (the slope of the curve in the figure is unity) for $X(A) \ll (X(B) - rX(A))$. In this range (segment a–b of the figure) the solution has properties identical to those of an ideal dilute solution. The relation v_{aq} vs. x_{xal} deviates from linearity at a certain value of x_{xal} (point b in the figure) depending on the value of r. Finally the lattice is saturated with locally deformed zones and cannot incorporate further A atoms. This situation corresponds to the condition $X(B) - rX(A) = 0$. The isotherm in the figure becomes vertical (part c–d of the figure).

FIG. 1. Li–K exchange isotherm of muscovite at 600 °C, $P_{H_2O} = 1$ kbar. Curve was drawn with $K_0 = 1\cdot99$, $r = 14\cdot8$. Experimental points with x_{xal} 8×10^{-2} represent the equilibrium muscovite solid solution and spodumene + vapour.

Ion-exchange equilibrium relations observed with Rb and Sr in albite, Sr and Ba in sanidine and Rb in nepheline at 600 °C were also well explained by this model. Estimated values of K_0 and r for these reactions were given previously (Iiyama, 1974b).

Because of the very small amount of element A incorporated in the structure of the silicate, the corresponding increase in excess enthalpy (interaction between BR and
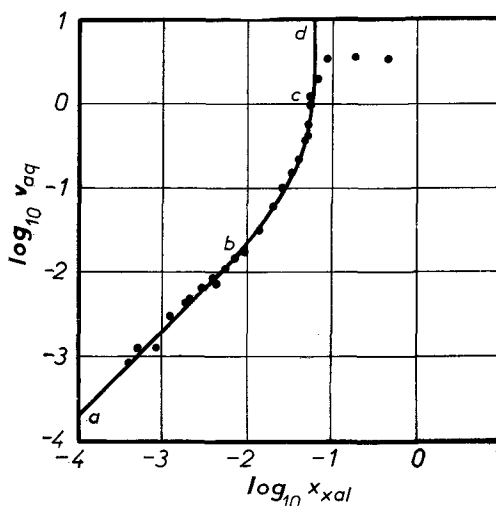
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[1] The experimental method used to obtain the isotherms of ion-exchange reactions with trace alkali and alkali-earth elements is explained in previous papers (see Iiyama, 1972, 1974a; Roux, 1974; Volfinger, 1974 for example).

AR) of the crystal as a whole is small but the entropy term of the excess free energy of the solid solution is strongly influenced by the local lattice deformation and causes the deviation from ideality of the solid solution at very low AR content in the crystal.

Local lattice deformation and substitution

To simplify the entropy calculation, it was considered that the deformed zone is unable to accept further A atoms in it. In actual cases, there is a finite probability that a substituting atom A may enter one of the deformed zones created by A atoms already fixed into the lattice. This probability will be a function of the number of deformed zones existing in the structure. To calculate the exact number of ways to place $N(A)$ atoms of the element A in the lattice using this substitution scheme is very difficult or even impossible.

It is, however, not unrealistic to explain this situation using a model in which each deformed zone has a subzone consisting of r sites forbidden for the substitution, and the size of this zone depends on the number of A atoms in the structure. The dependence of r on $N(A)$ will differ according to the nature of the crystal structure under consideration.

Therefore, let us assume that the size of r decreases in proportion to the ratio $rN(A)/(N(B)-rN(A))$, which corresponds to the ratio of the number of sites included in forbidden zones to that of free sites for the substitution:

$$r = r_0[1-FrN(A)/\{N(B)-rN(A)\}] = r_0[1-FrX(A)/\{X(B)-rX(A)\}] \qquad (2)$$

where r_0 is the size of the forbidden zone at infinite dilution ($X(A) \to 0$) of AR in the mineral BR. F is a constant of proportionality depending on the nature of the mineral. It represents a degree of the variability of the forbidden zone; a greater value of F means a more rapid decrease in the value of r with increasing $X(A)$.

Combining relations (1) and (2), the theoretical ion-exchange isotherm using this extended version of the local lattice deformation model can be calculated numerically for a given set of K_0, r_0, and F. Fig. 2A represents an example of the theoretical curve and fig. 2B shows the influence of r_0 and F on the shape of the isotherm: the curves were calculated for $K_0 = 0.1$.

As in the previous model, the parameter ν_{aq} varies linearly with x_{xal} for very small values of x_{xal} (part a–b of fig. 2A). The ordinate of the point b depends on the parameter K_0 and its abscissa on r_0. After this region of linear variation, the curve deviates from the line a–b with a slope depending on the value of F. Smaller values of F give steeper slopes. It is noted that the slope of the curve never reaches infinity except for the case with $F = 0$, which is identical with the previous model.

The slope of the curve decreases and again becomes linear (segment c–d of the curve in fig. 2A). This part alone is indistinguishable from an ideal solution isotherm but the corresponding constant K' is different from K_0. The difference between K_0 and K' is not negligible when the factor F is small.

The physical meaning of this situation is clear. The structure of the mineral BR has changed gradually with the incorporation of A atoms. At some range in $X(A)$ corresponding to the part of the curve b–c in fig. 2A, the structure approaches a state

in which it is saturated with forbidden zones. There has, however, been a gradual variation of the structure so that A atoms become progressively more acceptable in deformed zones. At point c of the figure, the structure of the crystal is completely changed from its initial state. The substituting A atom can be distributed now at random among sites occupied by B atoms.
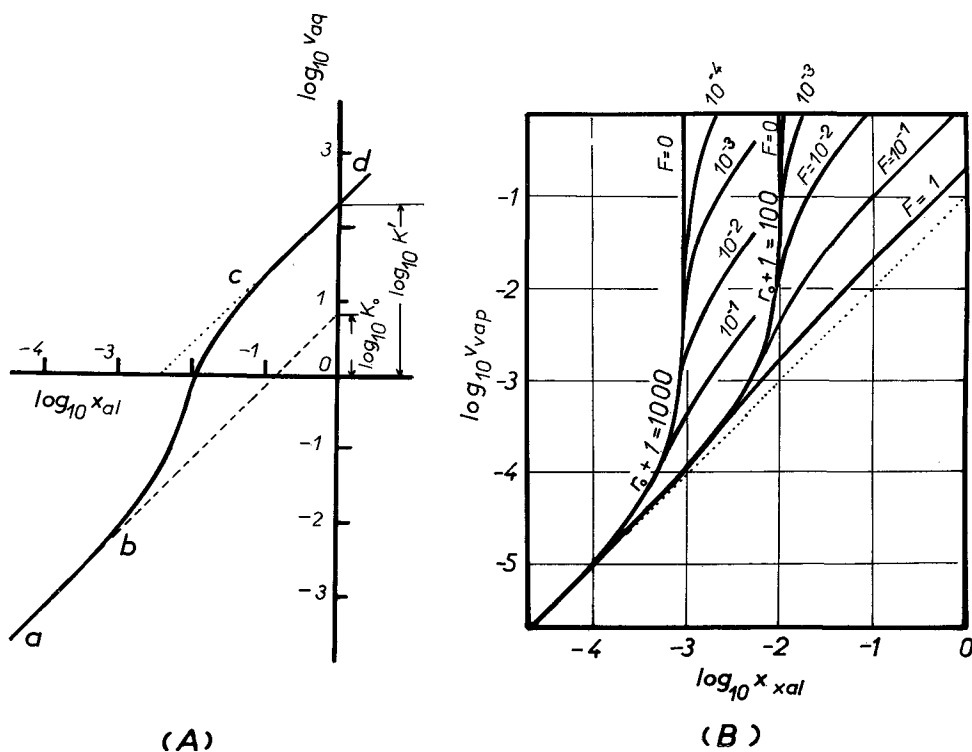

FIG. 2. (A) An example of the isotherm using the present model. (B) Theoretical curves with $K_0 = 0.1$ and different values of r_0 and F.

The apparent ideal behaviour of the ion exchange in this part is caused by this random distribution of A atoms in the lattice.

Application of the extended model

The characteristic features of the isotherms discussed above correspond well with Cs–K and Na–K *exchange* equilibria obtained with *muscovite* at 400, 500, and 600 °C at the pressure of water of 1 kbar by M. Volfinger (1969, 1970, 1975a). The first application of this model was tried using these data.

The most probable values of K_0, r_0, and F of equations (1) and (2) for each equilibrium were estimated by using the 'Direct Search' principle developed by Hooke and Jeeves (1961).

Figs. 3 and 4 compare the observed v_{aq} and x_{xal} with theoretical isotherms. The first six lines in Table I give K_0, r_0, and F values used to trace theoretical isotherms in these figures.[1]
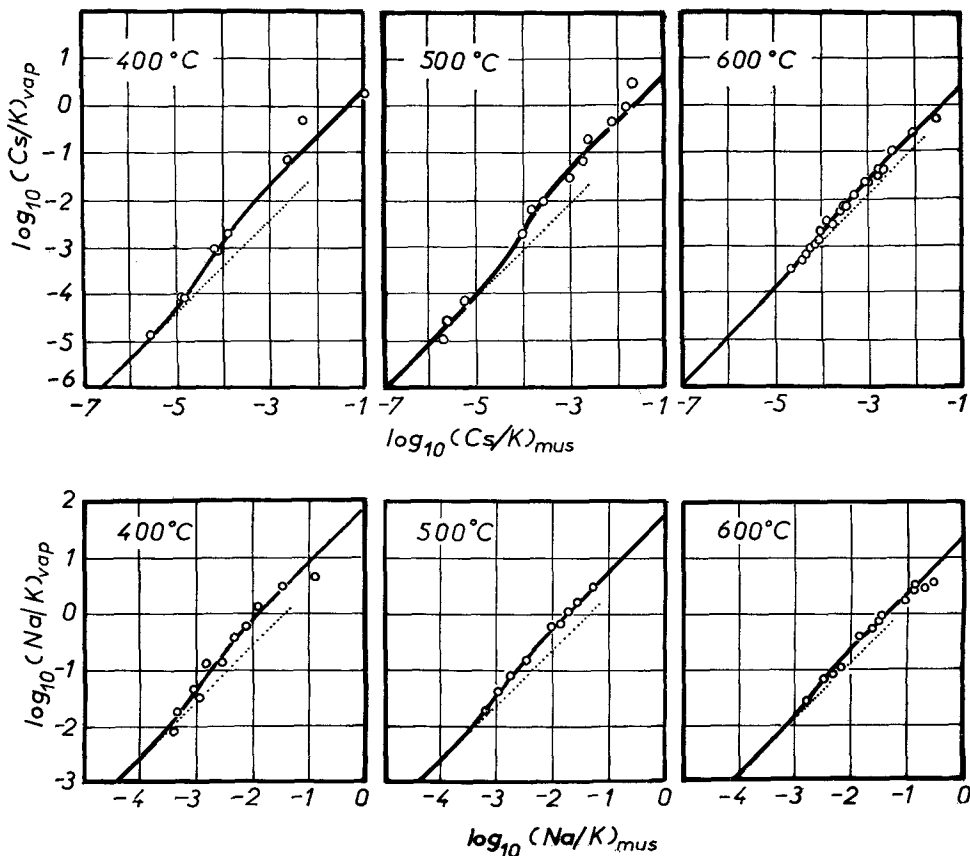
FIGS. 3 and 4: FIG. 3 (top). Cs–K exchange isotherms of muscovite at 400, 500, and 600 °C, P_{H_2O} 1 kbar. Solid curves are calculated with most probable values of K_0, r_0, and F. Dotted line indicates prolongation of ideal dilution behaviour of the solid solutions observed in the low concentration region. FIG. 4 (bottom). Na–K exchange isotherms of muscovite at 400, 500, and 600 °C, P_{H_2O} 1 kbar. Same explanations as in fig. 3 for solid and dotted lines.

As may be seen from the figures, the agreement between experimental data and theoretical curves is satisfactory. The size r_0 of the deformed zone of the lattice at infinite dilution is much greater with Cs than with Na, while the difference in ionic radii between Cs and K is of the same order of magnitude as that between Na and K. This may indicate that the local lattice deformation necessary to place a Cs ion (greater than K) extends over a greater volume than that needed to place Na in the

[1] Copies of the experimental and computer-simulated data (including K_0, r_0, and F) of isotherms in this paper are available on request addressed to the present authors.

lattice of mica. The decrease in the value of r is slightly but significantly greater with increase in $X(Na)$ than with increase in $X(Cs)$ at the same temperature, as is indicated by somewhat greater F values for the Na–K substitution than those for the Cs–K substitution. This feature may support the above interpretation on the volumes of the deformed zones. The precise relation cannot be stated, however, with small numbers of observed exchange pairs. It may be interesting to study in this connection the ion exchange of K–Na in paragonite at infinite dilution range.

TABLE I. *Parameters K_0, r_0, and F of ion-exchange equilibria estimated by the present model*

Exchange elements	Mineral	T	K_0	r_0	F	Data source
Cs–K	Muscovite	400 °C	4·5	14 855	0·22	3
		500	8·2	8415	0·20	3
		600	11·3	8385	0·69	1, 3
Na–K	Muscovite	400	24·7	583	0·39	3
		500	23·4	531	0·67	3
		600	11·3	244	1·00	2, 3
Li–K	Muscovite	600	1·99	14·8	0·000	2
	Phlogopite	600	0·39	57·6	0·007	3
	Sanidine	600	0·44	197	0·015	2

Data source: 1, Volfinger, 1969; 2, Volfinger, 1970; 3, Volfinger, 1975a, b.

All experiments at a pressure of water of 1 kb. It was noted that variations of 1 % in values of K_0, r_0, and F given above cause a significant deterioration in the best fit between experimental and calculated isotherms. It is believed that the relative precision of these values is better than 1 %

In both Cs–K and Na–K exchanges in muscovite, r_0 decreases and F increases with increase in temperature. This relation is certainly connected with the thermal vibrations of the crystalline lattice of muscovite.

The variation of K_0 with temperature for Na is in the opposite sense from that for Cs. The detailed discussion of the variation of K_0 with temperature together with all other ion-exchange isotherms obtained by Volfinger will be given in another paper (Volfinger, in press) and is not repeated here.

The Li–K *exchange reaction in muscovite* at 600 °C, 1 kbar P_{H_2O} has been given in a previous section (fig. 1). It gave $K_0 = 1·99$, $r_0 = 14·8$, and $F = 0$. The exchange reaction of Li–K in phlogopite (fig. 5) gives $K_0 = 0·39$, $r_0 = 57·6$, and $F = 0·007$.

The small values of F with Li in micas should be noted. It may indicate that the lattice shrinks appreciably around the sites in which the very small Li ion is incorporated and so has little tolerance to accept further Li ions in the deformed zones.

Among ion exchange reactions with trace alkali elements studied in this laboratory, Li–K *exchange in sanidine* at 600 °C, 1 kbar (Volfinger, 1969) can also be used as an illustration of this model. The calculation to find the three parameters gives $K_0 = 0·44$ with $r_0 = 197$ and $F = 0·015$ (fig. 6). The small value of F is also noticeable in this reaction.

Conclusion

It is often postulated that components AR and BR of the solid solution (A, B)R are distributed at random among structure sites offered for A and B ions.

Because the interaction energy between AR and BR is not negligible with respect to the configurational energy, $-T\Delta S$, the influence of A and B ion distribution in the structure on the excess free energy of the solid solution has been overlooked during studies of solid solutions containing comparable amounts of A and B ions.
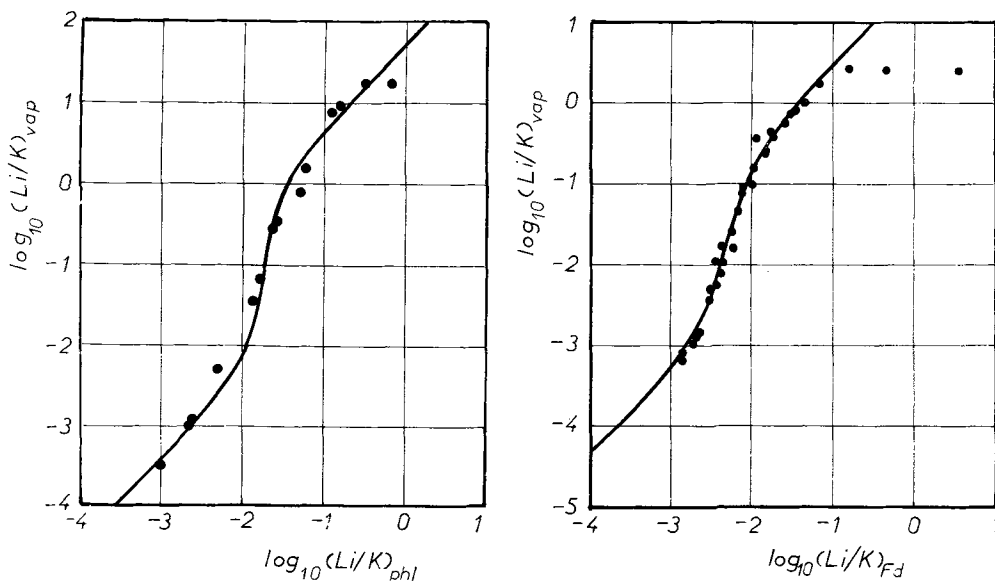
FIGS. 5 and 6: FIG. 5 (left). Li–K exchange isotherm of phlogopite observed at 600 °C, P_{H_2O} 1 kbar. Solid curve represents the theoretical calculated isotherm. FIG. 6 (right). Li–K exchange isotherm of sanidine at 600 °C, P_{H_2O} = 1 kbar. Experimental points with $x_{xal} > 10^{-1}$ represent the equilibrium of the assemblage sanidine-solid-solution+spodumene+vapour.

Thermodynamic examination of the solid solution containing very small amounts of A atoms and large amounts of B atoms provides information about the configurational energy.

Alkalis and alkali earths ion exchange data in silicates seem to show that completely random distribution of trace element ions in tecto- and phyllosilicates is relatively rare. It is limited to cases in which the substituting and substituted ions are similar in size (Rb and K, Ca and Sr for example) and those in which the crystalline structure offers very open sites for the trace element (leucite, pollucite, and analcime for example).

All other ion-exchange relations necessitate the use of the multisite model, or the local lattice deformation model, or the present model to explain the observed features of the isotherms.

It should be remarked that the present version with degeneracy of the forbidden zone is particularly suited to the micas. Other silicates often show very small or zero values of the parameter F of the equation (2). The potassium ions in the mica structure are arranged parallel to tetrahedral and octahedral sheets. The relatively weak bonding of the alkali layer sandwiched between tightly linked (Mg, Al)–O and (Si, Al)–O sheets may explain this particular situation of trace ion distribution in the mica structure.

The development of the thermodynamic model was based on the hypothesis that the fixation of the element A in the structure is realized by A–B substitution. It does not exclude, however, the case in which the element A is fixed in interstitial or vacant sites in the structure. It is impossible, with our present knowledge, to decide which is the mode of fixation actually occurring in the structure.

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