

COMPARISON OF QUASICHEMICAL AND REGULAR DISORDERING MODELS FOR MINERALS WITH MELILITE-TYPE STRUCTURES *

Yu. I. Sigalovskaya, L. M. Truskinovskiy and V. S. Urusov

Vernadskiy Institute of Geochemistry and Analytical Chemistry,
USSR Academy of Sciences

A systematic comparison has been made of the results of the simulation of cation distributions in minerals having nonequivalent positions in regular and quasichemical models. For certain values of the energy parameters characterizing the short-range and long-range interactions, types of dependence of long-range order parameter on temperature can be distinguished in both models: the ordering and antiordering regions are separated in parameter space by a transitional zone showing mixed behavior. More detailed incorporation of the short-range order into the quasichemical model smooths the temperature dependence of the order parameter and eliminates the phase transitions predicted by the regular model. A description is given of the order-disorder transitions in terms of the variations in the proportions of various types of clusters, which provides a higher "resolving power" than the usual models of ideal or regular mixing. Regular and quasichemical models are devised for the disordering of Al and Si over tetrahedral positions in gehlenite. Estimates are made of the preference-energy differences of cations in the T1 and T2 positions and of the energy of interaction of the cations with their nearest neighbors. Detailed agreement between theory and experiment is obtained in both models when one incorporates the nonconfigurational contribution to the entropy, which is $S^* = (3.1 \pm 0.5)R$. The identical signs of S^* and the disordering enthalpy ΔH show that there is a balancing effect, in which $\Delta H/S^* = 2700 \pm 300$ K agrees well with the value estimated for isovalent replacement in halides: 2800 ± 500 K.

Disordering is characteristic of the crystal structure of most rock-forming minerals. The dependence of the degree of disorder on P and T enables one to use it as a major indicator for the P and T of mineral formation.

Ideal-mixing models are usually used to consider disordering in minerals. That approximation incorporates only the long-range interaction of an atom (cation) with the entire crystal, which is expressed as a positional preference. The short-range order can be incorporated in a simple fashion in a regular mixing model. Although it enables us to elucidate major qualitative features of the disordering due to short-range interactions, it remains illogical because of the assumption of the absence of correlations in the distribution of cations and their nearest neighbors [1, 2].

The quasichemical model describes the short-range order more logically; it was developed initially for alloys [3] and extended [4] to any mineral structure

*Translated from *Geokhimiya*, No. 9, pp. 1338-1351, 1990.

containing two types of nonequivalent and differently coordinated positions. This model represents the crystal as a mixture of noninteracting positional groups (clusters) with different atomic populations. In it, one incorporates the correlation in the disposition of the cations and their nearest neighbors, and the configuration entropy is therefore nonideal.

Recently, cluster methods have been used to derive phase diagrams for ordered alloys [5, 6], and Kikuchi's cluster-variation method has been used to describe disordering in carbonate phase diagrams: $\text{CaCO}_3\text{-MgCO}_3$, $\text{CdCO}_3\text{-MgCO}_3$, $\text{CaCO}_3\text{-MnCO}_3$ [7, 8] (clusters as tetrahedra) and in the hematite (Fe_2O_3)-ilmenite (FeTiO_3) system [9] (trigonal prism cluster). The application of the quasichemical model to Al-Si disordering in albite [10] (square cluster) allowed it to be described as a first-order transition and gave good agreement with experiment.

The differences in the degree of detail to which the short-range order is incorporated in the regular (R) and quasichemical (QC) models leads to qualitative discrepancies in the results of simulation of ordering. Here we perform a systematic comparison of those models for a melilite-type structure.

MIXING MODELS

Let us consider a mineral having the composition $A_{1-x}B_x[Y]$; the A and B cations participating in the disordering occupy two crystallochemically nonequivalent positions α and β that occur in the ratio $c:(1-c)$. The numbers of cation positions in the immediate environments of positions α and β are z_α and z_β , while $z_{\alpha\beta}$ is the number of positions of β type adjacent to an α position, with analogous definitions for $z_{\alpha\alpha}$, $z_{\beta\alpha}$, and $z_{\beta\beta}$.

The long-range order w is represented as the proportion of B atoms in α positions. In the completely ordered state, the maximum possible number of A atoms will occupy α positions ($w=w_0$) the completely antiorordered (inversed) state corresponds to the largest number of B atoms in α positions ($w=w_1$) and the state of complete disorder corresponds to $w=w_0 \equiv c$ [4].

The main task is to calculate the equilibrium value of $w(T)$ from the condition for a minimum in the configurational free energy $F(w, T)$. F as a function of w is determined by the model. Let us recall the basic relationships for the R and QC models (see [4, 11] for details).

Regular mixing model. This involves the assumption that all microstates having the same w are indistinguishable and have the same energy $U(w)$.

The long-range interaction of an atom with a crystal field may be characterized from the energy ϵ_k^i of an atom, e.g., of cation k ($k = A, B$) in position i ($i = \alpha, \beta$); $\epsilon_{k\ell}$ denotes the interaction energy for cations k and ℓ in adjacent positions*.

The configurational energy of the crystal is [4] dependent on ϵ_k^i and $\epsilon_{k\ell}$ only via the combinations of them $\epsilon_1 + \epsilon_3$ and ϵ_2 . Parameter $\epsilon_1 = \epsilon_A^\beta - \epsilon_A^\alpha + \epsilon_B^\alpha - \epsilon_B^\beta$ is the energy of the reaction $A(\alpha) + B(\beta) \rightarrow A(\beta) + B(\alpha)$, which characterizes the relative positional preference of the cation. The characteristic for the interaction of an atom with its cation environment is $\epsilon_2 = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}$, the energy of $2AB \rightarrow AA + BB$. Sequential incorporation of short-range cation interactions leads [4] to redefinition of the long-range interaction energy, which is made up of ϵ_1 and $\epsilon_3 = z_\alpha \epsilon_{BB} + z_\beta \epsilon_{AA} - (z_\alpha + z_\beta) \epsilon_{AB}$, the contribution due to interaction between cations and their nearest neighbors. We follow [11] in assuming

*As in [4, 11], by pair interaction energy for cations we understand the energy excess by comparison with the sum of the energies $\epsilon_k^i + \epsilon_l^j$ ($k, l = A, B$; $i, j = \alpha, \beta$), arising from lattice deformation and/or change in local valency saturation in the bridge anions when cations with other sizes and charges enter adjacent polyhedra.

that any change in ε_2 produces a proportional change in its contribution ε_3 to the long-range interaction energy, then $\varepsilon_3 = \zeta \varepsilon_2$. The coefficient of proportionality ζ characterizes the geometry of the structure; if the positions are equally coordinated ($z_\alpha = z_\beta = z$), $\zeta = z$, while if $z_\alpha \neq z_\beta$, ζ characterizes the asymmetry in the positions and interactions.

$U(w)$ can be written apart from a constant as [4, 11]

$$U(w) = Nx \left(E_1 w + \frac{1}{2} E_2 w^2 \right).$$

Here N is the total number of cations (positions), $E_1 = \varepsilon_1 + \varepsilon_2(\zeta - p)$, $E_2 = -\varepsilon_2 q$, and p and q are geometrical parameters:

$$p = z_\alpha + \frac{x}{1-c} (z_{\beta\beta} - z_{\alpha\alpha}); \quad q = \frac{x}{c(1-c)} [z_{\beta\alpha} - z_{\alpha\alpha} + c(z_\alpha - z_\beta)].$$

The configurational entropy in the R model is

$$S^{\text{id}} = Nk \{ c \ln c + (1-c) \ln(1-c) - xw \ln xw - x(1-w) \ln x(1-w) - (c-wx) \ln(c-wx) - [1-c-(1-w)x] \ln [1-c-(1-w)x] \}.$$

We minimize the free energy $F = U - TS^{\text{id}}$ with respect to w to get an equation for $w(T)$:

$$kT \ln K = E_1 + wE_2, \quad (1)$$

$$K = (1-w)(c-wx)w^{-1} [1-c-(1-w)x]^{-1}.$$

The solution to (1) is governed by the relation between ε_1 , ε_2 , and ζ ; a detailed analysis has been given [11].

General quasichemical model. Let us split the crystal into M identical groups (clusters) each containing sm α positions and $(1-s)m$ β ones. A group can be filled with A and B atoms in 2^m ways; the atomic configuration is characterized not only by w but also by the set of numbers $\{\xi_a\}$, that specify the proportions of the groups of type a , $a = 1, \dots, 2^m$.

The assumptions are: 1) the interactions between the clusters can be neglected, so the crystal energy is the sum of the cluster energies; 2) microstates characterized by identical sets of w and $\{\xi_a\}$ are indistinguishable, and the number of them $g(w, \{\xi_a\})$ is proportional to the number of permutations in the set of clusters to the power λ :

$$g(w, \{\xi_a\}, T) = g_0(w) \left[\frac{M!}{\prod_a (M\xi_a)!} \right]^\lambda.$$

Introduction of parameter λ enables us, in counting the cluster perturbations, to preserve the number of adjacent-position pairs in the sets of groups equal to the numbers in the crystal; by definition, $\lambda = (N/2rM) [c(z_\alpha - z_\beta) + z_\beta]$, where r is the number of pairs of adjacent positions in a cluster [4], while $g_0(w)$ is defined by the condition $g(T=\infty) = \exp(S^{\text{id}}/k)$.

When we shift from the crystal to the set of groups, the number of positions (atoms) should be conserved. Therefore, the ξ_α are not independent, and the corresponding constraints are

$$\sum_a \xi_a = 1, \quad \sum_a \xi_a q_i^{(a)} = b_i, \quad (2)$$

$$b_i = \begin{cases} wx/c, & i = 1, \dots, sm \\ (1-w)x/(1-c), & i = sm+1, \dots, s. \end{cases}$$

Here $q_i^{(a)}=1(=0)$ if position i in group a is occupied by an atom $B(A)$.

The condition for absence of internal conflict in the model is [4] a criterion for splitting up the crystals that restricts the choice of clusters:

$$\sum_{i=1}^{sm} \tilde{z}_i/c - \sum_{i=sm+1}^m \tilde{z}_i/(1-c) = \frac{N}{M} (z_\alpha - z_\beta)/\lambda, \quad (3)$$

in which \tilde{z}_i is the coordination number of the positions i in a group. For example, if the α and β positions have equal coordination numbers, which is typical of alloys, this amounts to equality of the mean coordination numbers for the α and β positions in a group.

Differentiation of the free energy E with respect to ξ_α and taking the (2) constraints into account allow us to express the equilibrium $\xi_\alpha(T)$ in parametric form:

$$\xi_\alpha(T) = \left[\prod_{i=1}^m \mu_i^{q_i^{(a)}} \exp(-e_a/kT) \right] / \left[\sum_a \prod_{i=1}^m \mu_i^{q_i^{(a)}} \exp(-e_a/kT) \right]. \quad (4)$$

The group energy e_α is as follows when (3) is obeyed: $e_\alpha = \lambda m_{AA}^{(a)} \epsilon_2$, in which $m_{AA}^{(a)}$ is the number of pairs of AA type in group a .

The parameters μ_i ($i=1, \dots, m$) are defined by substituting (4) into (2):

$$\frac{\sum_a \exp\left(-\frac{e_a}{kT}\right) \prod_i \mu_i^{q_i^{(a)}}}{\sum_a \exp\left(-\frac{e_a}{kT}\right) \prod_i \mu_i^{q_i^{(a)}}} = b_j. \quad (5a)$$

These equations are used with the equilibrium equation for parameter w :

$$\begin{aligned} & \left(\prod_{i=1}^{sm} \mu_i^{1/c} \right) / \left[\prod_{i=sm+1}^m \mu_i^{1/(1-c)} \right] \exp \left[\frac{\epsilon_1 + \epsilon_2 (\zeta - z_\beta)}{kT} \frac{N}{M} \right] = \\ & = \left(\frac{c - wx}{wx} \right)^{(1-\tilde{\lambda}) \frac{N}{M}} \left[\frac{(1-w)x}{1-c(1-w)x} \right]^{(1-\tilde{\lambda}') \frac{N}{M}}, \end{aligned} \quad (5b)$$

in which

$$\lambda = \lambda \frac{smM}{cN}, \quad \tilde{\lambda}' = \lambda \frac{(1-s)mM}{(1-c)N},$$

and form a closed system, whose solution in that approximation defines $w(T)$. As in the R model, the form of the solution to (5) is dependent on ϵ_1 , ϵ_2 , and ζ .

SIMULATING CATION DISORDERING IN MELILITES

In the melilite-type structure, there are two types of tetrahedral position T1 and T2 (correspondingly α and β) in a 1:2 ratio over which one can distribute the Mg^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} , B^{3+} , Si^{4+} , and so on. Direct x-ray methods [12] and structure simulation [13] have been used to study the cation distributions in the melilites. An empirical relationship of w to T has been derived for gehlenite $Ca_2Al_2SiO_7$ [13]. It has been found that order inversion occurs in the solid-solution series formed by gehlenite with borian gehlenite $Ca_2B_2SiO_7$ at the boron-

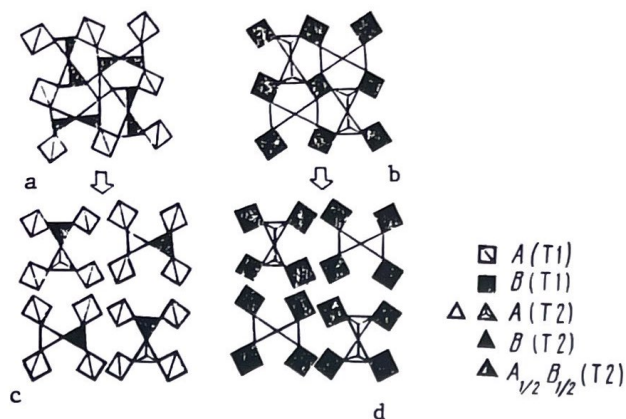


Fig. 1. Decomposition of a mixed anion melilite layer $[T1 T2]_{2\infty}$ into clusters composed of six $[T1, T2]$ tetrahedral positions: a and c) ordered state; b and d) antiordered (inversed) state.

rich end: there is a transition from an ordered structure ($0 \leq w \leq 1/3$) to an antiordered one ($1/3 < w \leq 1$).

Thermodynamic simulation of disordering in melilites in the ideal-mixing approximation [14] did not explain the inversion of order in the B-gehlenites (without change in preference energy sign).

Regular model. For melilite structures with the gehlenite composition* M_2A_2BO , $z_\alpha=4$, $z_\beta=3$, $z_{\beta\beta}=1$, $z_{\alpha\alpha}=0$, $z_{\alpha\beta}=4$, $z_{\beta\alpha}=2$, $c=1/3$, the basic equation in the R model (1) is written as

$$kT \ln K = \epsilon_1 + \epsilon_2(\zeta - 2,5) + 3,5\epsilon_2 w, \quad (6)$$

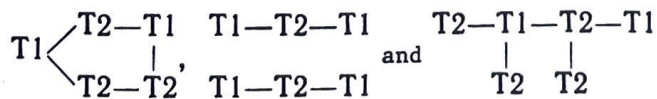
$$K = (1-w)^2 w^{-1} (1+w)^{-1}.$$

Ideal mixing corresponds to $\epsilon_2 = 0$. Order inversion in the B-gehlenites can be explained on the R model by large values of ϵ_2 .

Quasichemical model. The tetrahedral layers in a melilite structure are isolated one from another by layers of large polyhedra with eight vertices for Ca^{2+} , Sr^{2+} , Ba^{2+} , and so on, so we assume that the T cations are redistributed in each layer independently. Criterion (3) here takes the form

$$\sum_1^{sm} \tilde{z}_i - 1/2 \sum_{sm+1}^m \tilde{z}_i = r/5.$$

An examination of all decompositions of the melilite tetrahedral layer shows that for $m \leq 6$, only three of them satisfy the criterion:



It can be shown that if the equivalent α or β positions are symmetrical in a

*We consider gehlenite-type structures $M_2^{2+}A_2^{3+}B^{4+}O_7$ of main interest from the viewpoint of disordering theory; in them, of the two tetrahedral cations A^{3+} and B^{4+} , the latter has the larger preference for the T2 positions because of valency undersaturation at the unshared oxygen vertex, but the similarity in the charges and sizes of the two cations make it possible for them to be redistributed as the temperature rises. In structures of the akermanite type $M_2^{2+}A^{2+}B_2^{4+}O_7$, the difference in charge for the T cations prevents such mixing.

group, the corresponding μ_i are equal, so choosing a symmetrical cluster facilitates the solution, and on that basis, we choose the second group, which contains only two independent positions: T1 and T2. A melilite tetrahedral layer can be split up into groups of that form in a single way (Figs. 1c and d); each group nominally contains one T1 position (each T1 position belongs to four groups) and two T2 positions, so in that decomposition we have $N/M = 3$, $\lambda = 1$, $\tilde{\lambda} = 4$, $\tilde{\lambda}' = 1$.

Under those conditions (5b) becomes

$$\frac{\mu_{T1}^4}{\mu_{T2}} = \left(\frac{w}{1-w} \right)^3 \frac{u}{v^3}, \quad (7)$$

in which

$$u = \exp [-(\epsilon_1 + \zeta \epsilon_2) / kT], \quad v = \exp (-\epsilon_2 / kT)$$

and (5a) is

$$\Phi_1 = w\Phi; \quad \Phi_2 = 1/2(1-w)\Phi, \quad (8)$$

in which

$$\begin{aligned} \Phi &= v(v + \mu_{T1})^4 + \mu_{T2}^2(1 + \mu_{T1})^4 + 2\mu_{T2}(1 + \mu_{T1})^2(v + \mu_{T1})^2, \\ \Phi_1 &= \mu_{T1} [v(v + \mu_{T1})^3 + \mu_{T2}^2(1 + \mu_{T1})^3 + \mu_{T2}(1 + \mu_{T1})(v + \mu_{T1})(1 + 2\mu_{T1} + v)], \\ \Phi_2 &= \mu_{T2}^2(1 + \mu_{T1})^4 + \mu_{T2}(1 + \mu_{T1})^2(v + \mu_{T1})^2. \end{aligned}$$

To determine the equilibrium w , we thus have (7) in the quasichemical approximation (μ_{T1}, μ_{T2} are expressed in terms of w from (8)), while we have (6) in the regular mixing one. Those two equations contain the same set of energy parameters ϵ_1, ϵ_2 and ζ . Only two of these three parameters are independent, and the choice of the third is equivalent to specifying the temperature scale, so in the numerical calculations we used the dimensionless parameters $\chi = \epsilon_2/\epsilon_1$ and ζ , together with the reduced temperature $\theta = kT/\epsilon_1$.

DISCUSSION

Long-range order. Figure 2 shows the forms of solution to (6) and (7) schematically for χ and ζ .

At high temperatures, the regular model in Fig. 2a and the quasichemical one in Fig. 2b predict quantitatively similar disordering patterns; monotonal variation in w with T . For $\theta \rightarrow \infty$, we have $w \rightarrow w_\infty = 1/3$. If $\zeta > 4.25$, they both show that order inversion is lacking: w decreases as χ increases at constant θ .

In both models, there are regions in (χ, ζ) space corresponding to ordering (O) and antiordering (A) as the temperature falls, between which there is a transition zone (A/O), which corresponds to a mixed condition. The latter is characterized by the fact that $w(\theta)$ for $\theta < \theta_{cr}$ is located in the antiordering region ($\theta \rightarrow 0$ for $w \rightarrow 1$), while for $\theta > \theta_{cr}$, one has ordered values of w . The sizes and positions of the transition regions differ slightly for the two models:

$$\begin{aligned} 1/(11/3 - \zeta) > \chi_{A/O} > 1/(4.25 - \zeta) \quad R \\ 1/(11/3 - \zeta) > \chi_{A/O} > 1/(4 - \zeta) \quad QC \end{aligned}$$

Qualitative differences appear when we examine in detail the behavior of $w(\theta)$ in each of the (χ, ζ) regions. In R, the model predicts additional equilibrium states for certain values of the parameters, and thus transitions between

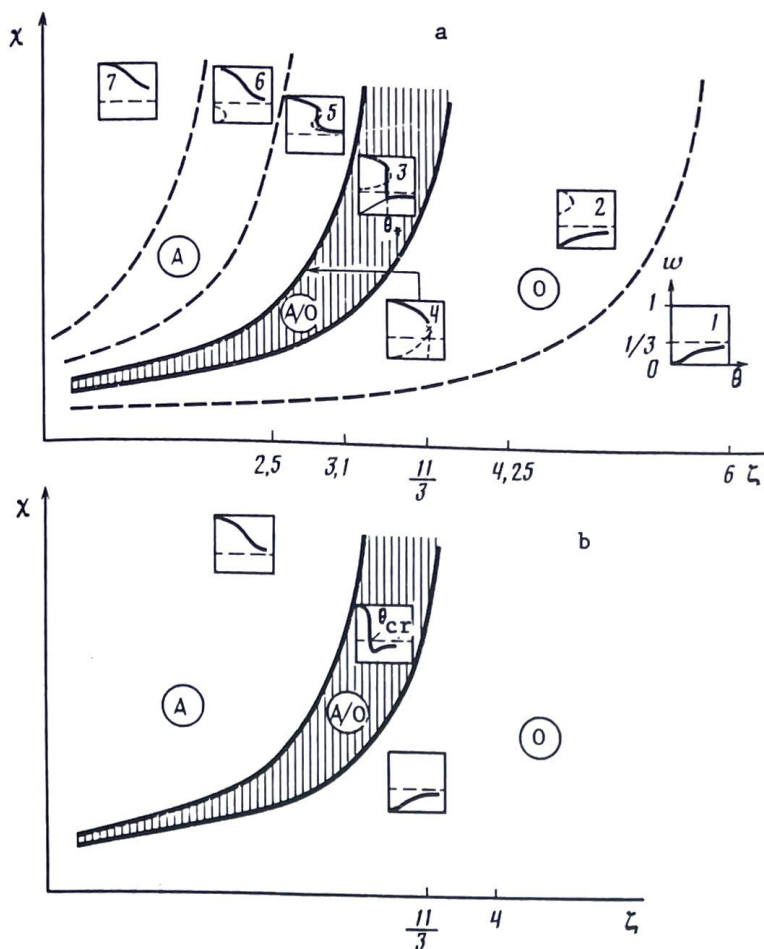


Fig. 2. Regions in χ and ζ space differing in disordering for the regular model (a) and quasichemical one (b) [10]. O ordering region; A antiordering, A/O transitional zone. The insets show the corresponding $w(\theta)$ schematically.

them (insets 3-5 in Fig. 2a). In QC, there is only one solution to the equilibrium equation in the range $(0, 1)$, and $w(0)$ is continuous at all temperatures. In the A/O zone in R, one can determine θ_* , the temperature of the first-order phase transition of disorder \rightarrow order type. In QC, the analog of θ_* is θ_{cr} , the point where $w(0)$ meets the straight line $w = 1/3$. θ_{cr} may vary throughout the temperature range as (χ, ζ) vary, whereas the θ_* range is finite from 0 to θ_*^1 , the temperature of the antiorder \rightarrow disorder transition that is absent for the QC model. The first-order transition predicted by R of antiorder \rightarrow antiorder type in region $1/(3.1 - \zeta) > \chi > 1/(11/3 - \zeta)$ (curve 5 in Fig. 2a) is also absent from QC; there is merely some increase in the slope of $w(0)$ near the boundary between the A and A/O regions.

More detailed incorporation of the correlation in the disposition of the cations and the nearest neighbors in QC thus smooths the $w(0)$ curves derived from R and causes the additional roots in the equilibrium equation to vanish. In QC, there is a smaller variety of forms for $w(\theta)$, and the additional division into subregions in A and O is eliminated. In spite of these qualitative (topological) differences in the $w(0)$ curves for the two models, there is general qualitative agreement between them for given values of ϵ_1 , ϵ_2 and ζ (Fig. 3).

Configurational entropy. In these approximations, the expressions for the configurational entropy in the two models differ:

$$\begin{aligned}
 & 1/(11/3 - \zeta) > \chi_{A/O} > 1/(4.25 - \zeta) \quad R \\
 & 1/(11/3 - \zeta) > \chi_{A/O} > 1/(4 - \zeta) \quad QC \\
 S_P = R [2 \ln 2 - w \ln w - 2(1 - w) \ln(1 - w) - (1 + w) \ln(1 + w)], & \quad (9)
 \end{aligned}$$

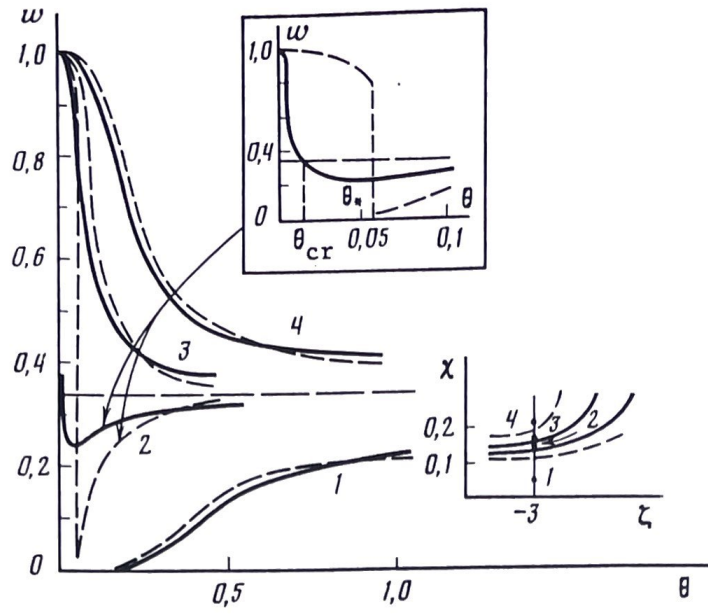


Fig. 3. Melilite $w(0)$ from regular (dashed line) and quasichemical (solid line) models; 1-4) points in χ and ζ space and corresponding $w(0)$ curves. The inset shows the $w(0)$ curves for the A/O region.

$$\begin{aligned}
 S_{KX} = & -3R [w \ln w + (1-w) \ln (1-w)] - \\
 & -R [-\ln \Phi + 4w \ln \mu_{T1} + (1-w) \ln \mu_{T2}] + \\
 & + R \frac{\varepsilon_2}{kT} \frac{v(v + \mu_{T1})}{\Phi} [(v + \mu_{T1})^3 + 4v(v + \mu_{T1})^2 + 4\mu_{T2}(1 + \mu_{T1})^2].
 \end{aligned} \tag{10}$$

The equilibrium $S(T)$ from these are shown in Fig. 4a. At high temperatures, the two models indicate a monotonal increase in S with asymptotic approach to $S_\delta = R(3 \ln 3 - 2 \ln 2) = 3.742$ eu for $\theta \rightarrow \infty$. At low T , there is a qualitative difference, which reflects features in the behavior of $w(\theta)$. In R , there are entropy steps at the phase transitions (Fig. 4b), while in QC, $S(\theta)$ varies monotonally as θ falls from S_δ to $S_0 = 2R \ln 2 = 2.775$ eu in O and from S_δ to zero in A and A/O regions (Fig. 4a).

Number of neighbor pairs. The short-range order parameter can be taken as the number of pairs of adjacent atoms:

$$\sigma = \frac{N_{AB} - N_{AB,\infty}}{N_{AB,0} - N_{AB,\infty}},$$

in which N_{AB} , $N_{AB,0}$, and $N_{AB,\infty}$ are the numbers of AB pairs correspondingly for the given temperature, zero temperature, and infinitely high temperatures. It has been assumed that the atoms are randomly disposed in the sublattices in the R model, so the number of pairs of adjacent atoms is determined by the product of the probabilities of encountering the atoms in the corresponding positions [4, 11]:

$$N_{AB,R} = N_A^\alpha \left(z_{\alpha\alpha} \frac{N_B^\alpha}{N^\alpha} + z_{\alpha\beta} \frac{N_B^\beta}{N^\beta} \right) + N_A^\beta \left(z_{\beta\alpha} \frac{N_B^\alpha}{N^\alpha} + z_{\beta\beta} \frac{N_B^\beta}{N^\beta} \right),$$

in which z_{ij} is the number of j positions in the immediate environment of an i position ($i, j = \alpha, \beta$).

For melilites we have (per position)

$$N_{AB,R} = (7w^2 - 4w + 5)/6.$$

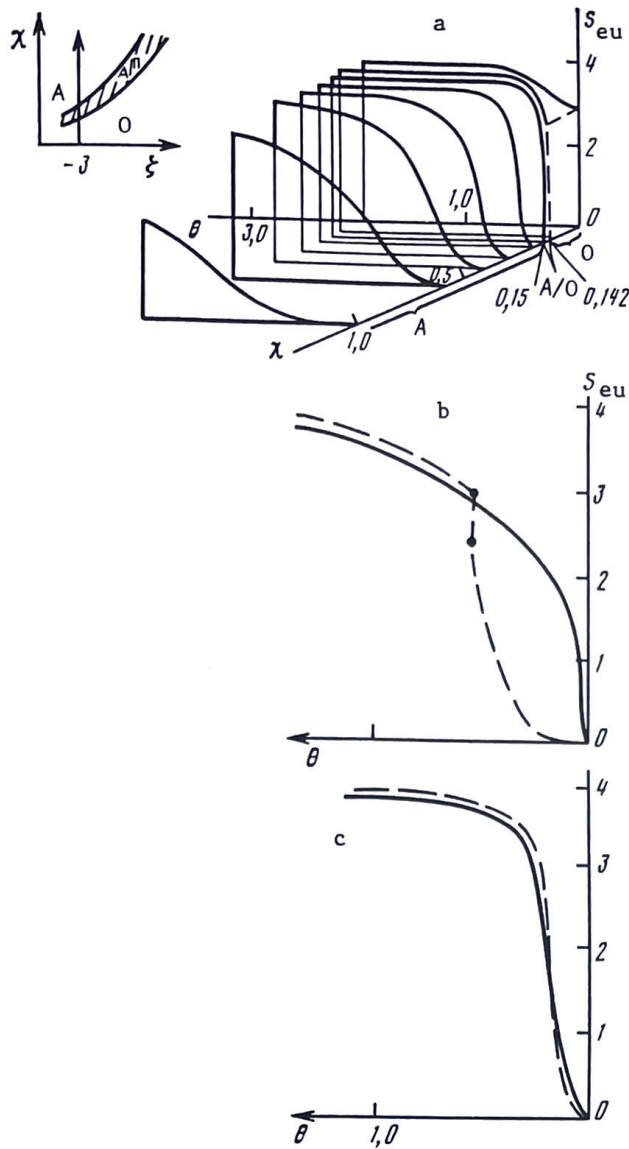


Fig. 4. Configurational entropy of melilite as a function of $\theta = kT/\epsilon_1$: a) based on the QC model with various $\chi = \epsilon_2/\epsilon_1$; b and c) based on the QC (solid line) and R (dashed line) models for $\chi = 0.144$ (b) and $\chi = 0.2$ (c).

In a state of complete order at zero temperature, $N_{AB,R}(\theta = 0, w = 0)$ is $5/6$ for an antioderred structure and $N_{AB,R}(\theta = 0, w = 1)$ is $4/3$; for $0 \rightarrow \infty$ and $w \rightarrow w_0 = 1/3$ we get $N_{AB,R}(\theta \rightarrow \infty) = 20/27$. Figure 5 (dashed lines) shows the equilibrium dependence $\sigma_R(\theta)$.

In QC, $N_{AB,QC}$ is given by $N_{AB,QC} = \sum_a \xi_a m_{AB}^{(a)}$, where $m_{AB}^{(a)}$ is the number of AB pairs in a cluster of type a . In the O region for (χ, ζ) , with $\theta \rightarrow 0$, the crystal consists only of ordered clusters (Fig. 1c) and $N_{AB,QC}(\theta = 0, w = 0)$ per position is $1/2$; in the A and A/O regions, for $\theta = 0$ the structure consists only of antioderred clusters (Fig. 1d) and $N_{AB,QC}(\theta = 0, w = 1)$ is $2/3$. For $\theta \rightarrow \infty$, we get

$$N_{AB,QC}(\theta \rightarrow \infty) = \sum_a \xi_a(\theta \rightarrow \infty) \cdot m_{AB}^{(a)} \cong 0,3704.$$

At high θ , $\sigma(\theta)$ in either approximation behaves in much the same way; for

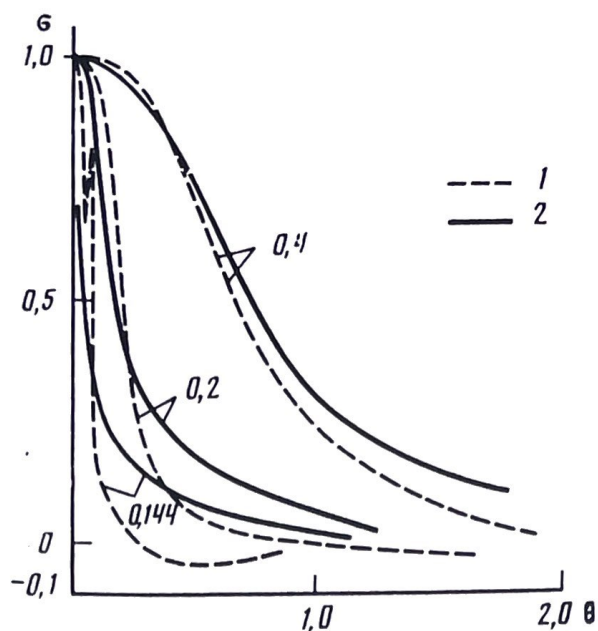


Fig. 5. Temperature dependence of the normalized number of unlike pairs of nearest neighbors in the regular (1) and quasichemical (2) approximations. $\zeta = -3$, numbers of the curves χ .

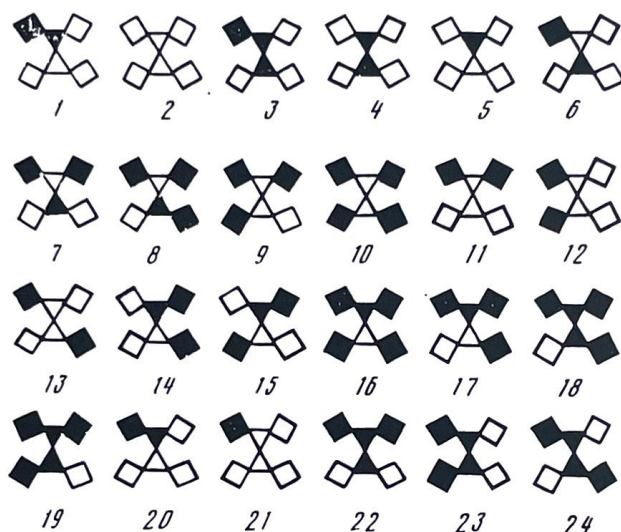


Fig. 6. Independent methods of filling a $T1-T2-T1$ cluster with A and B atoms.

$\theta \rightarrow \infty$, $\sigma \rightarrow 0$ in both cases (Fig. 5). At low θ , the equilibrium $\sigma(\theta)$ curves have qualitative differences, which reflect the features in the behavior of $w(\theta)$. The transitional zone in the R model is characterized by stepped nonmonotonal behavior in $\sigma(\theta)$, while in the model QC, the corresponding curves are monotonal and continuous. QC is distinguished by the absence of a minimum on $\sigma(\theta)$ which is predicted by R for the 0 region in χ and ζ .

Disordering mechanism. Let us now consider the temperature dependence of the cluster proportions with particular atomic arrays in the QC model.

For a melilite, the chosen decomposition into clusters means that there are 64 ways of filling the clusters with A and B atoms, of which only 24 are independent because of the symmetry of the cluster (Fig. 6). The state of complete order (Fig. 1a and c) corresponds to a cluster array in which one T2

position is occupied by a B atom*, while the other positions contain A atoms; we call that array completely ordered (group No. 5, Fig. 6). Similarly, a completely antiordered structure can be split up into groups that contain B atoms in the T1 positions and A in T2; corresponding groups will be called completely antiordered (Fig. 1d, group No. 10 in Fig. 6).

The symmetrically equivalent positions in a cluster have identical μ_i [7], so only two of the μ_i out of the six are independent for our cluster: one for the T1 positions equivalent one with the other, μ_{T1} , and the other for the T2 positions, μ_{T2} . To determine those two quantities, we have two equations in (5a), which can be solved for them:

$$\begin{aligned} \mu_{T1} &= \left[-1 - v \frac{1-3w}{1-w} + \sqrt{\left(1 + v \frac{1-3w}{1-w}\right)^2 + \frac{16vw}{1-w}} \right] / 4, \\ \mu_{T2} &= \left(\frac{v + \mu_{T1}}{1 + \mu_{T1}} \right)^2 \left[\frac{w}{v(1-w)} + \sqrt{\frac{w^2}{v^2(1-w)^2} + \frac{1+w}{v(1-v)}} \right]^{-1}, \\ v &= \exp(-\chi/\theta). \end{aligned} \quad (11)$$

We substitute (11) into (7) to get the equilibrium $w = \bar{w}(\theta, \chi, \zeta)$ and determine $\mu_{T1} = \bar{\mu}_{T1}(\theta, \chi, \zeta)$, $\mu_{T2} = \bar{\mu}_{T2}(\theta, \chi, \zeta)$, and then $\xi_a = \bar{\xi}_a(\theta, \chi, \zeta)$.

For $\theta \rightarrow \infty$, ξ_a is not dependent on how the cations are distributed over the positions and is determined only by the cluster composition; (4) with $\mu_{T1, T2}(\theta = \infty) = 1/2$ gives

$$\xi_a(\theta = \infty) = 2^{\sigma - \sum_{i=1}^6 q_i^{(a)} / 3^6} = 0,0137 \cdot 2^{n_A^{(a)}},$$

in which $n_A^{(a)}$ is the number of A atoms in an a group. For $\theta = \infty$, the mixture of groups includes seven types as regards the number of B atoms in each ($n_B^{(a)} = 0, \dots, 6$); the proportions of the groups of the given types in the mixture are equal.

We have $v \rightarrow 0$ for $\theta \rightarrow 0$, so up to terms of higher order in the small parameter v

$$\mu_{T1} = v \frac{2w}{1-w}; \quad \mu_{T2} = v^3 \frac{(1+w)^2}{2w(1-w)}. \quad (12)$$

Substitution of the asymptotic (12) expressions into (4) gives a result dependent on w for $\theta = 0$. For $w(\theta = 0) = 0$, the numbers of all clusters apart from the ordered one (No. 5) are zero; for $w(\theta = 0) = 1$, a nonzero value occurs only for the number of antiordered clusters (No. 10). Thus ordering (antiordering) is attained in a single fashion: at $\theta = 0$, all configurations vanish apart from the completely ordered (antiordered) ones.

Simulation shows that there are three types of cluster as regards $\xi_a(\theta)$. The first type contains groups Nos. 1-6 (Fig. 6), whose numbers in the O model initially increase as θ falls but then decrease. In the A region, clusters of that type show a monotonal decrease in ξ_a as θ falls, with $\xi_a < \bar{\xi}_a(\theta \rightarrow \infty)$.

The second type consists of Nos. 7-18 (Fig. 6), where A shows nonmonotonal behavior but O shows monotonal character.

*It is assumed that an ordered crystal contains equal numbers of groups in which the B atoms are in each of the two T2 positions, so we do not consider possible ordering over the equivalent positions.

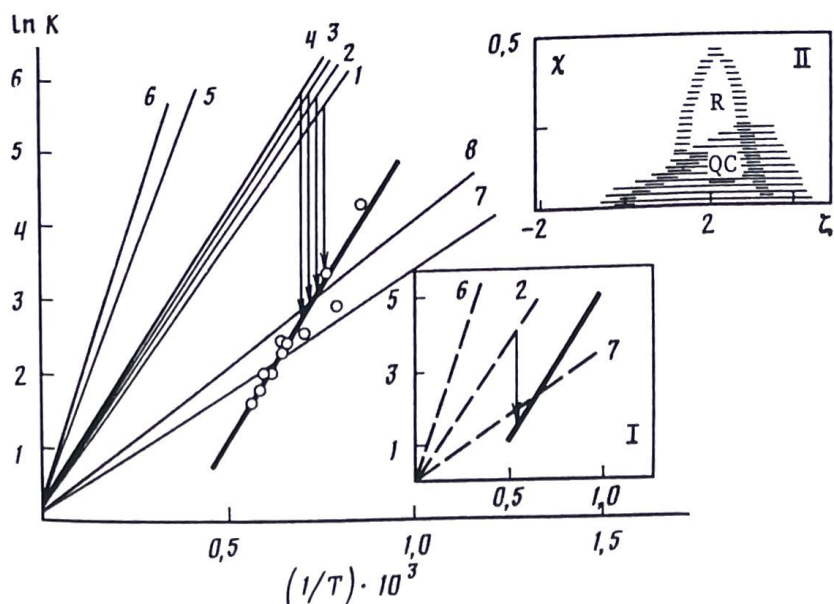


Fig. 7. Al-Si disordering in gehlenite. Experimental data from structural simulation [13]. Calculations in the QC approximation: 1) $\epsilon_1/k=8000$ K, $\zeta=1$, $\epsilon_2/k=300$; 2) $\epsilon_1/k=8000$ K, $\zeta=2$, $\epsilon_2/k=300$; 3) $\epsilon_1/k=800$ K, $\zeta=3$, $\epsilon_2/k=200$ K; 4) $\epsilon_1/k=8000$ K, $\zeta=4$, $\epsilon_2/k=200$ K; 5) $\epsilon_1/k=16000$ K, $\zeta=1$, $\epsilon_2/k=1000$ K; 6) $\epsilon_1/k=16000$ K, $\zeta=1$, $\epsilon_2/k=1000$; 7) $\epsilon_1/k=4000$ K, $\zeta=1$, $\epsilon_2/k=300$ K; 8) $\epsilon_1/k=4000$ K, $\zeta=3$, $\epsilon_2/k=300$ K; inset I is from the regular model, while inset II shows the ranges in χ and ζ in which theory and experiment agree (within the experimental error for R and QC models, the latter hatched).

The third type has numbers that decrease monotonally as θ falls for any χ and ζ (Nos. 19-24, Fig. 6).

The assignment of a cluster to a type is correlated with the number of positions whose filling is different from that for the completely ordered or anti-ordered clusters. If for example the numbers of such discrepancies (numbers of incorrect atoms) are more than two, the corresponding clusters are disfavored by energy, so their numbers decrease as θ falls. On the other hand, some increase in ξ_a as θ falls occurs in configurations having one or two incorrect atoms, but further θ reduction leads to differentiation for that type of cluster in accordance with the number of incorrect atoms: at first, the numbers of groups containing two such atoms decrease (No. 3) and then these with only one (Nos. 1, 2, 4 and 6), and finally only the ordered configuration remains (No. 5).

Al-Si disordering in gehlenite. The R model cannot describe the θ dependence of w for gehlenite found by experiment in any detail [11], as there are discrepancies in curvature between the empirical and theoretical $w(T)$, which is particularly evident in a plot of $\ln K$ against $1/T$ (Fig. 7, inset 1). Varying ϵ_1 , ϵ_2 , and ζ cannot bring these curves into coincidence. The curves in the R model can be brought into coincidence by adding an additional term TS^* to the first part of (6). S^* ; which is $\sim 2.9 \pm 0.3 R$, has the dimensions of entropy and is independent of w and T . When S^* is incorporated, a fit is obtained between theory and experiment with $\epsilon_2/k \leq 2000$ K, $0 \leq \zeta \leq 4$, and $\epsilon_1/k \approx 8000$ K.

Here ϵ_1/k is comparable as regards order of magnitude with the positional preference energies in other aluminosilicates. In magnesian tschermakite [15], the energy from Al-Si exchange in the tetrahedral positions is equivalent to 4915 K. For completely ordered albite at room temperature, the ϵ_1/k derived from the Madelung position potentials [16] is ~ 4000 K with effective charges for the aluminum of +1.0 and for the silicon of +1.1-1.15.

The Madelung potentials and lattice energies may be calculated with the [12] cell parameters and atomic coordinates to estimate ϵ_1/k for gehlenite. The

formal-charge model corresponds to a preference energy of 87 700 K, which is clearly an overestimate. Calculation for charges of Al from +1.0 to +1.3 and of Si from +1.1 to +1.4 gives $\epsilon_1/k \approx 2600-12\ 000$ K, while ϵ_1/k of 8000 K is obtained with $\text{Al}^{+1.15}$ and $\text{Si}^{+1.4}$, which are close to the empirical values [17].

In the R model, if $\epsilon_1/k = 8000$ K, the fit between theory and experiment for $\ln K$ as a function of $1/T$ persists within the experimental error in the ranges in χ and θ shown on inset 2 to Fig. 4*. The largest χ giving agreement with experiment is ~ 0.25 for $\zeta \approx 2$, and an estimate exists for an analogous quantity for clinopyroxenes [15]: ϵ_2/k for Ca-tschermakite is 4380 K for $\chi \approx 0.89$.

It is found [6] that $\zeta = \epsilon_3/\epsilon_2 \equiv (4\epsilon_b/\epsilon_a + 3)/(\epsilon_b/\epsilon_a + 1)$ in which $\epsilon_a = \epsilon_{\text{AlAl}} - \epsilon_{\text{AlSi}}$, $\epsilon_b = \epsilon_{\text{SiSi}} - \epsilon_{\text{AlSi}}$. Taking into consideration that the melilite layer geometry provides deviations in the sum of the bond strengths to the bridge anions from the former oxygen charges that are identical in magnitude during the formation of the Si-Si and Al-Al pairs (with allowance for the Ca^{2+}), while the entry of Al and Si into adjacent tetrahedra leads to complete saturation of the bridge O^{2-} [13], we put $\epsilon_a/\epsilon_b \approx 1$, which implies that $\zeta \approx 3.5$, so the regular model gives somewhat underestimated ζ for gehlenite.

Figure 7 shows the results of calculations in the QC approximation. Varying χ and ζ indicates that the empirical $\omega(T)$ curve cannot be reproduced in that model. Agreement can be obtained again by multiplying the right-hand side of (7) by $\exp(S^*)$, in which S^* is close to the analogous quantity estimated in the R model. The slopes of the theoretical and empirical curves in $\ln K$ plotted against $1/T$ agree for $\epsilon_1/k \approx 8000$ K, and the fit persists within the experimental error for a region in χ and ζ displaced from the corresponding region in the R model towards larger ζ (inset 2 in Fig. 7, hatched). This implies the constraint $\chi \leq 0.2$; the maximum χ occurs for $\zeta \approx 3-3.5$.

The range in ϵ_1/k derived from the Madelung potentials gives an upper bound to the short-range interaction energy for gehlenite and an estimate of the contribution from it to the long-range interaction energy:

$$\text{R: } 1040 \leq \epsilon_2/k \leq 4800 \text{ K, } 2600 \text{ K} < \epsilon_3/k \leq 12\ 000 \text{ K.}$$

$$\text{QC: } 500 \leq \epsilon_2/k \leq 2400 \text{ K, } 1500 \text{ K} \leq \epsilon_3/k \leq 7200 \text{ K.}$$

In either model, S^* , the excess entropy, is much the same. The QC model makes a more detailed correction for the short-range order but has little effect on S^* , so we conclude that the excess entropy is not of configurational origin. S^* indicates a compensating effect [18]: a linear correlation between the mixing enthalpy ΔH and the nonconfigurational entropy S^* . The above estimates of the energy parameters give $\Delta H/S^* \approx \epsilon_1/S^* = 2700 \pm 300$ K, which agrees well with the value [18] $\Delta H/S^* = 2800 \pm 500$ K for isovalent replacement in halides.

It has recently been shown [19] that one cannot match the gehlenite thermodynamic functions to experimental data based on phase equilibria involving that mineral in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$ system. The nonconfigurational entropy of gehlenite provides for making appropriate corrections to calculations of phase equilibria.

We are indebted to L. S. Dubrovinskiy for calculating the Madelung potentials for the gehlenite positions.

REFERENCES

1. Urusov, V. S., 1977. Teoriya izomorfnoy smeshimosti [Theory of Isomorphous Miscibility], Nauka, Moscow.
2. Kurepin, V. A., 1981. Termodinamika mineralov peremennogo sostava i geologicheskaya termobarometriya [Thermodynamics of Variable-Composition Minerals and Geological Thermobarometry], Nauka, Dumka, Kiev.

*There is a maximum in χ because ω is insensitive to χ for ζ close to ζ_{cr} .

3. Li, Y. Y., 1949. *Phys. Rev.*, v. 76, 942.
4. Truskinovskiy, L. M., Yu. I. Sigalovskaya, E. E. Senderov and V. S. Urusov, 1987. *Geokhimiya*, No. 11, 1511.
5. Mohri, T., J. M. Sanchez and D. De Fontaine, 1985. *Acta Metall.*, v. 33, No. 7, 1171.
6. Mohri, T., J. M. Sanchez and D. De Fontaine, 1985. *Acta Metall.*, v. 33, No. 8, 1463.
7. Burton, B. P. and R. Kukuchi, 1985. *Amer. Miner.*, v. 69, No. 1-2, 165.
8. Burton, B. P., 1987. *Amer. Miner.*, v. 72, No. 3-4, 329.
9. Burton, B. P., 1985. *Phys. Chem. Miner.*, v. 11, No. 1, 132.
10. Senderov, E. E. and A. Korovin, 1987. *Geokhimiya*, No. 6, 766.
11. Sigalovskaya, Yu. I., L. M. Truskinovskiy and V. S. Urusov, 1988. *Geokhimiya*, No. 7, 931.
12. Kimata, M. and N. Ii, 1982. *Neues Jahrb. Mineral. Abh.*, v. 144, No. 3, 254.
13. Sigalovskaya, Yu. I., P. A. Sandomirskiy and V. S. Urusov, 1984. *Mineral. Zhurnal*, v. 6, No. 2, 3.
14. Waldbaum, D. R., 1973. *Contribs. Mineral. and Petrol.*, v. 39, No. 1, 33.
15. Cohen, R. E. and C. W. Burnham, 1985. *Amer. Miner.*, v. 70, No. 5-6, 559.
16. Senderov, E. E. and V. V. Surikov, 1981. *Geokhimiya*, No. 8, 1165.
17. Urusov, V. S., 1975. *Energeticheskaya kristalloghimiya [Energy Crystallochemistry]*, Nauka, Moscow.
18. Urusov, V. S. and I. F. Kravchuk, 1983. *Crystal Res. Technol.*, v. 18, No. 5, 629.
19. Moecher, D. P., 1988. Ph. D. Thesis, Michigan Univ., Ann Arbor.

UDC 549.641.23

THE NATURE OF ORIENTED ILMENITE SEGREGATIONS IN ILMENORUTILE AND CORUNDUM*

N. R. Khisina, V. G. Senin, L. V. Petushkova and V. O. Polyakov

Vernadskiy Institute of Geochemistry and Analytical Chemistry,
USSR Academy of Sciences

The conditions governing the formation of platy ilmenite segregations in ilmenorutile, magnetite and corundum have been considered in order to discuss the origin of the mineral in reactions in the $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$, $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2\text{-Nb}_2\text{O}_5$, and $\text{Al}_2\text{O}_3\text{-FeO-Fe}_2\text{O}_3\text{-TiO}_2$ systems. The decomposition in corundum is of the oxidative type, which characterizes the high-temperature pegmatite stage. Platy ilmenite in ilmenorutile arises from reductive decomposition of the latter, which occurs in the late low-temperature stages. Oriented ilmenite segregations in oxide minerals can be used to indicate the redox conditions in the different temperature stages of mineral formation.

Oriented mineral intergrowths are quite common and can form at various stages in the formation of rocks and minerals: during crystallization (eutectoid structures, epitaxial intergrowths, twine); during subsolidus cooling (solid-solution decomposition structures, polysynthetic twinning); and as a result of metasomatism (topotaxis intergrowths). These intergrowths may be macroscopic or may consist of submicron inclusions of one mineral in another. The general crystallographic and thermodynamic regularities in these intergrowths

*Translated from *Geokhimiya*, No. 9, pp. 1352-1359, 1990.