

ANDALUSITE AND SILLIMANITE CRYSTALLIZATION KINETICS DURING Al_2SiO_5 -TRANSFORMATIONS

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In previous experimental works, the author with colleagues [1-3] has confirmed the formerly determined fact that general mechanism of Al_2SiO_5 -transformations is reduced to dissolution of the unstable and crystallization of stable phases in water fluid. Therefore, the dissolution and crystallization processes are the essence of the above transformations and can play the role of limiting (controlling) phase of the transformation.

Kinetic equations for rates of kyanite→andalusite, kyanite→sillimanite и andalusite→ sillimanite transformations in presence of quartz grains were obtained in paper [2]. The rates are represented as a function of temperature (the exponential one) and pressure (P) departure from the equilibrium value (P_*) (linear dependence from $(P - P_*)$). The following activation energy was determined: $E = 112 \pm 38$ kJ/mole. The equations were considered as those for the rates of crystallization, i.e. it was assumed, that andalusite or sillimanite crystallization (surface reaction of crystallization, to be more precise) controls the process. The assumption may be regarded as the proved one for the andalusite crystallization rate, because it was found that the latter does not depend upon surface area of andalusite grains. Controlling role of sillimanite crystallization is substantiated below.

Kinetic equations were derived based on a rather rough assumption as to equality of crystallization rate on the grain surface. Additional detailed investigation into the grains of polymorphs, grown during experiments of study [2], carried out by the authors using microscope, as well as thorough microscope, electron-microscope and goniometry studies [4] of the relatively large (~1 mm) synthesized andalusite crystals showed the following:

1. The thickest layer was grown on the andalusite surfaces approximating pinacoid {001} as to orientation (i.e. almost perpendicular to C axis), resulting in formation of the pinacoid itself, as well as the {101}, {011} and {111} faces. The grown layer was of columnar texture, and the surface of the most quickly growing face {001} (growth rate was ~0,01-0,02 mm/day at 820°C and $P_{H_2O} = 4,8$ kbar) was of cellular topography with small and gently sloping hills [4]. Very thin layer, bounded mainly by the {110} faces, as well as {100} and {010} ones too, was grown on the surfaces, parallel to the C axis. The most slowly growing prism faces {110} hosted the following features: flat areas ("terraces") of ~30-60 μm width, separated by ~10 μm high benches, and flat-top discs of micron dimensions. Ratio between growth rates parallel and perpendicular to the C axis ($\parallel C : \perp C$) is ~6 [4]. It should be mentioned, that in agreement with theory [5], the ratio of the kinked face growth rate ({001}) to the same of the flat one ({110}) of andalusite is to be equal to the ratio of spacing between the benches to their height. The latter is ~3-6 (~5), i.e. is close to 4-8 (~6).

2. On the sillimanite surfaces close to {001} and, obviously, {021}, sharp cones directed $\parallel C$ were grown instead of the continuous layer. Growth and formation of faces in the direction $\perp C$ (apparently the {110} and {010} faces) was very weak. The ratio between growth rates $\parallel C$ and $\perp C$ equals to or exceeds 10.

3. Based on the above face topography, one should classify the {001} face into the K-faces, growing $\parallel C$ according to the adhesive mechanism, the {110}, {100} and {010} faces belonging to the F-faces, growing $\perp C$ according to the layer-by-layer mechanism [5].

Statistical measurements of the seed polymorph grains (averaging ~30 μm) were made, showing that, provisionally, the andalusite and sillimanite grains may be regarded as the tetrahedral prisms with the following widths/lengths: 23,5 μm /40,5 μm for andalusite and 26,5 μm /44,5 μm for sillimanite, the grains being elongated parallel to the C axis.

Based on the experimental data regarding the rate of transformation [2] and taking into account: a) anisotropy of the andalusite and sillimanite growth rates, manifested as large difference between the growth rates $\parallel C$ and $\perp C$; b) starting shapes of these minerals, as well as introducing thermodynamic affinity of the surface reaction of crystallization A ($A = -\Delta G$, where ΔG – free energy of the reaction, which equals to $(P - P_*)\Delta V$, where ΔV – volume change during the Al_2SiO_5 transformation), essentially empirical kinetic equations for the transformations were derived, expressing rates of the surface

crystallization reactions for andalusite and sillimanite (represented by values of surface displacement, h), as follows:

$$(dh/d\tau)^{IC}_{Ky \rightarrow And} = 751,88 \cdot 10^{-9} RT \exp(-E/RT)(A/RT) \text{ cm/sec}, \quad (1)$$

$$(dh/d\tau)^{\perp C}_{Ky \rightarrow And} = 125,31 \cdot 10^{-9} RT \exp(-E/RT)(A/RT) \text{ cm/sec}, \quad (2)$$

$$(dh/d\tau)^{IC}_{Ky \rightarrow Sil} = 270,46 \cdot 10^{-9} RT \exp(-E/RT)(A/RT) \text{ cm/sec}, \quad (3)$$

$$(dh/d\tau)^{\perp C}_{Ky \rightarrow Sil} = 27,04 \cdot 10^{-9} RT \exp(-E/RT)(A/RT) \text{ cm/sec}, \quad (4)$$

$$(dh/d\tau)^{IC}_{And \rightarrow Sil} = 308,88 \cdot 10^{-9} RT \exp(-E/RT)(A/RT) \text{ cm/sec}, \quad (5)$$

$$(dh/d\tau)^{\perp C}_{And \rightarrow Sil} = 30,88 \cdot 10^{-9} RT \exp(-E/RT)(A/RT) \text{ cm/sec} \quad (6)$$

Crystallization of the stable Al_2SiO_5 polymorph is realized via entering of Al_2O_3 and SiO_2 in stoichiometric relation into the surface of its face. Based on the belief that formation of the new monoclinic layer on the kinked face {001} of andalusite or sillimanite is taking place by jumping of the particles into solid phase from the layer of solution located at an interatomic distance α ($\sim 10^{-8}$ cm). Number of particles in 1 cm^2 of the given layer equals to $C\alpha$, where C – concentration of molecules per 1 cm^3 of solution [6]. In the water fluid, concentration of Al_2O_3 (as two $\text{Al}(\text{OH})_3$ molecules) is 2-3 orders of magnitude lower than that of SiO_2 (as the $\text{Si}(\text{OH})_4$ molecule). Hence, the rate of crystallization is to be controlled by concentration of Al_2O_3 (or by $2\text{Al}(\text{OH})_3$) in accordance with the stoichiometry (congruence), i.e. the value of $\alpha C_{\text{Al}_2\text{O}_3}$. Account must be taken of the fact, that rate of the particles' building in the crystal lattice is proportional to probability of encountering a kink for building in by the particle [5]. Taking into consideration the above, the following equation for rate of crystallization on the kinked face {001}, that is, in the direction $\parallel C$ was derived, using theory of activated complex by Eyring at the relatively low values of A (in this case, the activated complex can be represented as conventional molecule $(\text{Al}_2\text{SiO}_5 \cdot 5\text{H}_2\text{O})^\ddagger$, located in the kink):

$$(dh/d\tau)^{IC}_{Ky \rightarrow And} = \frac{1}{9} \frac{kT}{h} \cdot e \cdot a \cdot C_{\text{Al}_2\text{O}_3}^{\text{And}} \cdot v_{\text{And}} \cdot \exp(\Delta S^\ddagger/R) \cdot \exp(-E/RT) \cdot (A/RT) \text{ cm/sec}, \quad (7)$$

where ΔS^\ddagger – entropy of activation; other parameters at 820°C and $P_{\text{H}_2\text{O}} = 5 \text{ kbar}$ are as follows: $kT/h = 2,28 \cdot 10^{-13} \text{ sec}^{-1}$; $e = 2,72$; $\alpha = 10^{-8} \text{ cm}$; $v_{\text{And}} = 85,18 \cdot 10^{-24} \text{ cm}^3$; $C_{\text{Al}_2\text{O}_3}^{\text{And}} = 10,72 \cdot 10^{16} \text{ molecule/cm}^3$.

For crystallization of sillimanite through dissolution of kyanite and andalusite, the kinetic equations and values for the parameters will be the similar ones (at the same temperature and pressure). Comparing these equations with the empirical ones (1), (3) and (5), the following values of the activation entropy for crystallization on the {001} face of sillimanite and andalusite were obtained:

$$\Delta S_{Ky \rightarrow And}^\ddagger = -38 \text{ J/degree-mole and } \Delta S_{Ky \rightarrow Sil}^\ddagger = \Delta S_{And \rightarrow Sil}^\ddagger = -44,5 \text{ J/degree-mole.}$$

Negative activation entropy indicates that the surface reactions of andalusite and sillimanite crystallization in water fall into the type of slow reactions, measurably differing from the much more speedy reactions of quartz and feldspar crystallization (by an order of magnitude and more). The obtained results can be used when studying crystallization of minerals under metamorphic conditions.

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