ANISOTROPY ASSESSMENT FOR GROWTH RATES OF ANDALUSITE AND SILLIMANITE CRYSTALS DURING KYANITE→ANDALUSITE, KYANITE→SILLIMANITE AND ANDALUSITE→SILLIMANITE TRANSFORMATIONS

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In the paper published earlier [1], the following kinetic equations for kyanite(Ky)→andalusite(And), kyanite(Ky)→sillimanite(Sil) and andalusite(And)→ sillimanite(Sil) transformations were derived by the author:

$$(dm/d\tau)_{Ky\to And}=-5.96\cdot10^{-9}\exp(-E/RT)\ (P-P_*)\ mol/cm^2\cdot sec, \quad (1)$$

$$(dm/d\tau)_{Ky\to Sil}=-1.19\cdot10^{-9}\exp(-E/RT)\ (P-P_*)\ mol/cm^2\cdot sec, \quad (2)$$

$$(dm/d\tau)_{And\to Sil}=0.50\cdot10^{-9}\exp(-E/RT)\ (P-P_*)\ mol/cm^2\cdot sec, \quad (3)$$

where m is weight of a growing crystal (And or Sil); τ - time; E – activation energy, which equals 112±38 kJ/mol for the transformations mentioned above [1]; P and P_* - values of specific and equilibrium pressures of H_2O at the given temperature (for the Ky↔And, Ky↔Sil и And↔Sil equilibriums, respectively).

Linear dependence on $(P-P_*)$ and, respectively, on thermodynamic affinity of the reaction A ($A= -\Delta G_{reaction}= -\Delta V(P-P_*)$, where ΔV is volume changes during the reaction) is observed at the not large departures from equilibrium [2]. Equation (1)–(3) were derived basing on experimental study of the transformation degree (ξ) in mixtures, consisting of Ky + And, Ky + Sil and And + Sil grains (with addition of quartz particles). It was assumed that grains of the starting substances were of isometric (spherical) shape (of course, it was simplification due to prismatic appearance of the minerals, especially Ky and Sil) and grew in different directions with equal rates. Thorough microscopic studies of andalusite and sillimanite growth on their seed grains showed the highest build-up rates in the C direction (||C axis) and the lowest ones perpendicular to the C (⊥C axis). Faces, formed on the andalusite seed grains, resulted from a) relatively thick grown layer in the C direction (5-15 μm) most probably limited with {001} и {101} faces; b) very thin grown layer (1-3 μm) in ⊥C direction likely bounded by {110} prism face. Roughly estimated, ratio of growth rates in ||C и ⊥C directions, varies from 5 to 10. These results agree with data given [3], where it was shown that the same ratio for andalusite single crystal at the expense of kyanite grains dissolution equals ~ 4-8, that is, approximately 6, the value being very close to ones for small andalusite grains. Building up of andalusite single crystal in the direction ||C, that is growing of the {001} face, is classified as the adhesive growth mechanism on the kinked face and crystal accretion ⊥C (growing of the {110} face, which is to be classified as the flat one) is the layer-by-layer growth mechanism [3]. Sillimanite grains showed formation of sharp growth cones, contacting by the basements, in the C direction (instead of the continuous growth layer as in the case of andalusite) and extremely weak growth and formation of faces ⊥C (proved by formation of isolated growth cones). In the first approximation, ratio of growth rates in ||C и ⊥C directions, is ≥10. It seems that the kyanite crystals can be characterized by similar values of crystallization anisotropy.

Statistics resulting from measurements of grain dimensions in the starting mixtures (being ~30 μm on average [1, 2]) showed that width (m) and length (l), the latter usually being ||C, average 25.5 μm and 44.5 μm for andalusite (l:m=1.59), 26.5 μm and 44.5 μm for sillimanite (l:m=1.68) and 20.8 μm and 53.5 μm for kyanite (l:m=2.57). Assuming these starting grains to be tetrahedral prisms (m×m×l), growth pyramids can be calculated on the faces ||C and ⊥C. In this way, growth rates ||C were calculated (instead of the averaged rate values in any direction (1)–(3)):

$$(dm/d\tau)_{Ky\to And}=-10.86\cdot10^{-9}\exp(-E/RT)\ (P-P_*)\ mol/cm^2\cdot sec\ , \quad (4)$$

$$(dm/d\tau)_{Ky\to Sil}=-3.15\cdot10^{-9}\exp(-E/RT)\ (P-P_*)\ mol/cm^2\cdot sec, \quad (5)$$

$$(dm/d\tau)_{And\to Sil}=1.01\cdot10^{-9}\exp(-E/RT)\ (P-P_*)\ mol/cm^2\cdot sec. \quad (6)$$

It is useful to present the crystallization rate equations (4) – (6) as functions of thermodynamic affinity:

$$(dm/d\tau)_{Ky\to And}=14.59\cdot10^{-9}\exp(-E/RT)\cdot A\ mol/cm^2\cdot sec, \quad (7)$$

$$(dm/d\tau)_{Ky\to Sil}=5.42\cdot10^{-9}\exp(-E/RT)\cdot A,\ mol/cm^2\cdot sec, \quad (8)$$

$$(dm/d\tau)_{And\to Sil}=6.19\cdot10^{-9}\exp(-E/RT)\cdot A,\ mol/cm^2\cdot sec, \quad (9)$$

where A is in joules.

Growth rates ⊥C can be determined using (4) – (9) by dividing of numerical coefficients by 6 (for Ky→And transformation) and by 10 (for the Ky→Sil и And→Sil ones).

As follows from the equations (7)–(9), at equal values of affinities 1) andalusite grows most quickly and sillimanite – most slowly, these rate ratios ranging 2.35–2.69; and 2) Ky→Sil и And→Sil transformation rates are essentially the same, pointing that the sillimanite crystallization rate (and not the kyanite and andalusite dissolution rates) effects control during the Ky→Sil и And→Sil transformations. It can be presumed, that kyanite crystallization rate is the limiting one in the Ky→And transformation.

The obtained values of crystal growth rates for andalusite and sillimanite, as well as for the kyanite, can be used for time calculations during transformations between Al_2SiO_5-minerals (when they contact in metamorphic rocks [1]). The quantitative characteristics of dissolution and crystallization rates for the aluminosilicates dealt with in this paper and for other metamorphic minerals [4, 5] are necessary for development of a growth theory for porphyroblasts, being the volumetric bodies with different degree of idiomorphism.

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