

## Ostapenko G.T. Role of crystallization pressure and free surface energy in the formation of minerals during metamorphism

Institute of Magnetism, Ukrainian Academy of Science (Kiev)

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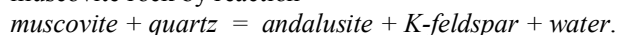
During metamorphism, minerals form in a solid media (matrix), which contains micro-pores filled with aqueous fluid. In addition, water (in dependence on the ratio of pressure on mineral grains ( $P_s$ ) and aqueous fluid ( $P_f$ )) can enter to intergranular boundaries and form intergranular films ( $\sim 10^{-5} - 10^{-7}$  in thickness), being the main catalytic agent during metamorphism [1, 9]. As petrographic observations show [3, 4], mineral crystals nucleated in micro-pores and grain boundaries [3] and, subsequently, growing in the solid matrix (surrounded by thin fluid film) are present in "straitened" conditions and have to capture a space by means of dissolution and/or pushing apart of the matrix. The major reason for this process is the crystallization pressure ( $\Delta P_s$ ). It inevitably appears in touching, through the boundary fluid film, of growing crystal with a mechanical barrier. Appearance of the crystallization pressure, reflected in displacement of the mechanical barrier (preserving the fluid film as a feeding layer) was proved by the examples of growth of water-soluble crystals at the conditions close to the room conditions [5, 6], and after that, is confirmed by the examples of crystal growth in the wide temperature ranges (from normal to 550°C) and water pressure (from several bars to 3000 bars) [7]. In the experiments, an appearance of the crystallization pressure ( $\Delta P_s$ ) at bulk crystallization (in pressurized tablets of semi-hydrated gypsum and periclase blocks) of gypsum, portlandite, and brusite [7], as well as cancrinite forming by interaction of NaOH solution with kyanite in presence of quartz, was modeled.

An appearance of the crystallization pressure during the growth of quartz monocrystals at temperature above 300°C (a wide-known method of quartz growth in the alkaline media [8] was used) was also modeled. The value of  $\Delta P_s$  was close to that of (about kg/cm<sup>2</sup>) corresponding to the value of over-saturation of a solution. It should be noted, that the results of the above experiments on bulk crystallization (where larger values of  $\Delta P_s = 10-2000$  bar were applied) can be considered, with respect of  $\Delta P_s$ , as analogous to the experiments with monocrystals. The best illustration for it is crystallization of brusite in the cylindrical blocks of periclase (by hydration). In this case, solid aggregates of thin parallel fibers of brusite, forming macroscopically even front (at the boundary with periclase) along the outer surface of the block and veinlets filling numerous cracks, could be considered as analogies of monocrystals. Such front (fibers are perpendicular to it) displaces owing to the growth of brusite fibers and pushes periclase. The experiments show a preservation of the thin fluid film or some quasi-liquid layer (the feeding layer), which governs the processes of MgO dissolution and Mg(OH)<sub>2</sub> precipitation on ends of brusite fibers at high PT-parameters. The data surely model the process of serpentinization within ultrabasic rocks. Taking to account, that the most important reactions of serpentinization at T=250-400°C and  $P_{H_2O} = 1-2$  kbar proceed with large

rate [9, 10], the values of  $\Delta P_s$  during serpentinization estimated from the periclase hydration in the "straitened" conditions [7] could be considered as substantiated.

Thus, it can be considered as proved, that the appreciable crystallization pressure can form during the growth of a crystal in matrix under metamorphic conditions. This pressure can result in mechanical spreading of grains in matrix. However, it is possible only at significant flowage of a rock, which can be produced at large  $P_f \gg P_s$ . More often, at the conditions of  $P_f \leq P_s$ , rocks preserve their solidity and mechanical firmness. In this case,  $\Delta P_s$  results in an increase of chemical potential of the matrix minerals and a release of their components into the fluid film at the contact of the crystal and the matrix, and subsequent subtraction away from this contact. Chemical potential of the growing crystal also simultaneously increases, the boundary fluid film becomes thinner. That results in a decrease of differently directed fluxes of the components from the growing crystal and the matrix. In time, a stationary state with steady  $\Delta P_s$  is established [11]. The larger the unit rate of crystallization, solubility, and molar volume of the growing crystal, the larger  $\Delta P_s$  value. The larger these features of the matrix, the less  $\Delta P_s$  value.

Consider an example of the formation of spatially confined crystals of andalusite and K-feldspar in the quartz-muscovite rock by reaction



It is shown [12] that 1) the rates of direct and reverse reactions are controlled by the rate of crystallization or dissolution of andalusite; 2) the rates of andalusite dissolution and crystallization are lower than the rates of crystallization of quartz, muscovite, and, probably, K-feldspar. Andalusite is also less soluble. It implies that the  $\Delta P_s$  value around the growing crystal should be relatively small, while the thickness of the fluid film should be large. Because of strong difference of a character and growth rates of {001} and {110} faces [13], the thickest film and the lowest  $\Delta P_s$  value should be at the {110} face. The later should assist to the formation of the {110} face as a single plane, while the rapidly growing {001} face should be uneven or does not appear at all. In contrast to andalusite, the thickness of the fluid film around K-feldspar should be relatively low, while the  $\Delta P_s$  value should be large. These parameters are equal at all the surface of K-feldspar grain because of weak anisotropy of the rate of crystallization of K-feldspar. All these factors are not in favor of the formation of euhedral K-feldspar crystals.

The important and debatable problem is an origin of different degree of idiomorphism in mineral crystals [14, 15]. The locality of idiomorphism (in the sense of a separate face) was pointed out as well [14]. On the basis of thermodynamic analysis, considering an existence of the fluid film or amorphous layer of pseudo-viscous liquid at the grain boundary, the following principles of idiomorphism were suggested [16]: an ability to idiomorphism (i.e. an ability to be flat) of some face F will be larger, if its surface energy value is larger, and, simultaneously, the value of this energy in the given crystal is lower (i.e. if the anisotropy of the surface energy is strongly expressed). If any unevenness (concave or convex) appear on such face, they will be energetically unstable and have a tendency to disappear. The above suggestion differs from that presented in [14].

The {110} face of andalusite is suitable for the above rule of idiomorphism. Therefore andalusite crystals form-

ing in the quartz-muscovite-feldspar matrix should be more idiomorphic. Slow rate of growth of andalusite crystals, especially {110} face, assists to it. In this case, unevenness disappear almost immediately, that is assisted by the relatively thick fluid film. Similar ideas could be suggested for other faces of number of metamorphic minerals ({0001} of hematite and ilmenite, {100} of kyanite, {110} and {010} of staurolite, {110} of garnet, {110} of hornblende, {001} of biotite, etc.) composing the wide-known crystalloblastic sequence.

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