[1]Azimov P.Ya., [2]Shtukenberg A.G. Numerical modeling of the growth zoning in metamorphic garnets

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Chemical zoning in metamorphic garnets was discovered due to microprobe analysis in the beginning of 60th years. Since, numerous studies appeared, which considered mechanisms and conditions of the formation of the zoning. The formation of the zoning is considered to be related to the fractionation during garnet crystallization in the closed system (1), variation of temperature and pressure during the "equilibrium crystallization" (2) and the diffusion redistribution of components between minerals (3). The theory of the diffusion zoning is worked out in detail (4-6), in contrast to the growth zoning. Although the zoning is non-equilibrium phenomenon appearing during the non-stationary crystallization, its formation was regarded by the equilibrium thermodynamics (7, 8). Such approach does not allow to account for an influence of kinetics and recognize the significance of individual mechanisms (9). A composition and a dynamics of a fluid, which is a medium for the mineral formation and mass transfer during metamorphism, is not regarded as well.

In order to analyze the kinetics of the growth of zoned crystals and mechanisms of the zoning formation, we created mathematical models of the growth of mixed crystals from the aqueous solution (fluid). The models are based on the systems of differential equations, which describe an evolution of the fluid composition during crystallization. They describe the growth of the crystals of solid solutions during isothermal decrease of an oversaturation and the non-isothermal crystallization in the closed system, during the non-isothermal crystallization from the fluid of constant composition and during the isothermal crystallization in the open system penetrated by the fluid flux. Parameters of the models are thermodynamic and kinetic conditions (temperature and pressure, composition, oversaturation, and fluid flux velocity, crystallization rates, and temperature growth rates).

An absence of experimental data on the Mg-Fe distribution coefficient between garnet and fluid compelled us to work out a thermodynamic model of the component redistribution between solid solution and aqueous fluid (11) and calculate the distribution coefficients (9). An analysis of the obtained data (Fig. 1) shows that during fractionation a center of garnet growing from the neutral and acid fluid is enriched in Fe, while a rim and fluid are enriched in Mg (direct zoning). In the alkalic fluid, the inversion in the component distribution occurs. The core becomes enriched in Mg, while the rim is enriched in Fe (reverse zoning).

Profiles of zoning were computed from the kinetic models. Their shape and contrast depend on the conditions and the mechanisms of crystallization. During the isothermal crystallization in the closed system, then the fractionation is the basic mechanism, simple dome-like profiles form (Fig. 2). These profiles resemble the profiles of natural garnets with the direct zoning. X_{Mg} increases, while X_{Fe} decreases toward the rim of grain. The zoning of garnets growing in the closed system during heating is similar to the above profiles. During crystallization from the fluid of constant composition, the zoning is weak, even at rapid heating (200-1000°C/Ma). That means that the fractionation is a leading mechanism of the zoning formation in the closed system. In fact, the calculations show that duration of crystallization is from first years to tens of thousands years. Temperature varies insignificantly during this period, and the crystallization, properly, is isothermal. The contrast of the zoning depends on the non-stationary manner of crystallization and the fluid oversaturation. The larger these parameters the more the contrast of the zoning. In the open system, the profile shape depends on both the fluid oversaturation and its dynamics (fluid flux velocity). High flux velocity results in the flattening of the zoning. At low flux velocity, the profiles are close to those of garnets growing in the closed system. Average values result in the non-monotonous profiles (Fig. 3). Such profiles appear even at the stationary fluid flux. The zoning in the open system forms due to the fractionation.

Inversion of the fractionation tendency occurs during crystallization from the alkalic fluid. That results in growth of garnets with the reverse zoning. Such inversion can proceed at alkali concentration of $\sim n \cdot 10^{-3}$ mole/kg H_2O, which is characteristic for the fluid from the zones of migmatization (12). The complicated shape of profiles, which is usual for garnets with the reverse zoning, can be explained by the fluid flux in the metamorphic system.
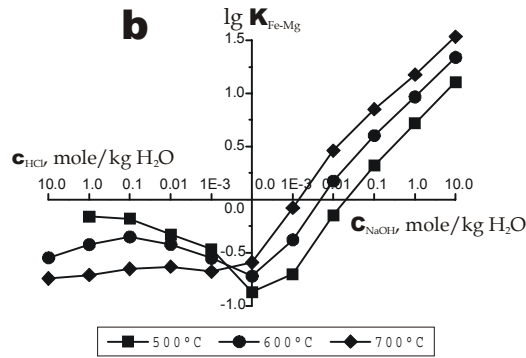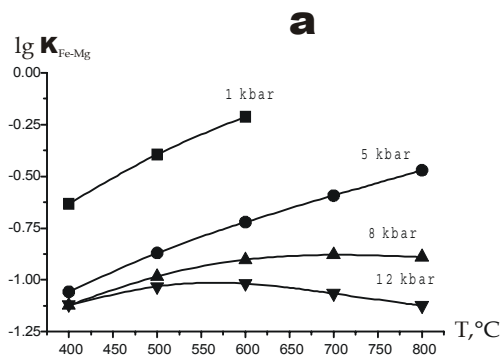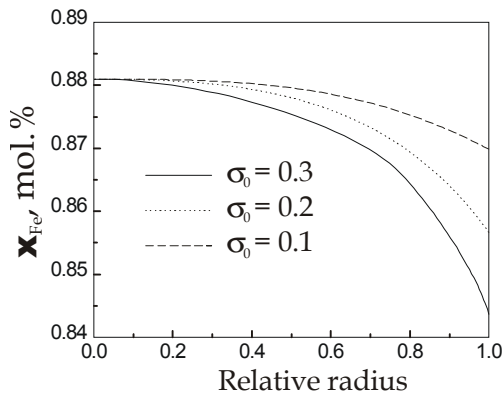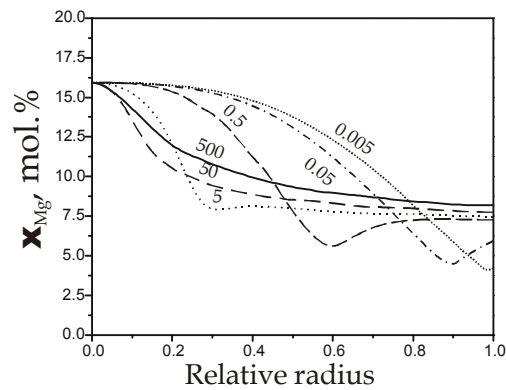
Fig. 1. The dependence of the distribution coefficient K_{Mg-Fe} between pyrope-almandine garnet and aqueous fluid on temperature and pressure (*a*), on the content of HCl and NaOH in the solution (*b*). P_{tot} = 5 kbar.

Fig. 2. Zoning in Fe-Mg garnet crystallized during the isothermal decrease of oversaturation in the closed system (500°C, 5 kbar). Legend shows the values of the initial oversaturation.

Fig. 3. Zoning in Fe-Mg garnet crystallized from the alkalic fluid in the open system (600°C, 5 kbar, σ_0 = 0.3). The values of the fluid flux velocities are shown at the curves.

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