Sequential kinetics of a muscovite-out reaction: A natural example

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ABSTRACT

A natural example of sequential kinetics for the muscovite dehydration reaction in highly deformed mylonitic gneisses is analyzed. Studied textures consist of deformed pegmatitic muscovite crystals surrounded by fibrolitic sillimanite tightly intergrown with biotite and with potassium feldspar in the pressure shadows. Potassium feldspar, andalusite, biotite, and quartz appearing in the crystal core constitute the products of muscovite breakdown produced by topotactic replacement of muscovite within a single crystal. Non-isochemical decomposition of muscovite is proposed in which diffusion of K⁺ outward from the crystal took place along the muscovite interlayer and shear planes parallel to (001). The chemical potential gradient calculated for K capable of producing the texture observed within the pegmatitic crystals, results not only from the overstepping of the muscovite-out reaction but also from the difference in free energy between andalusite and sillimanite under P-T conditions where andalusite is stable. The overall reaction within the andalusite stability field consists of the transformation 1 Ms + 1 Qtz → 1 And + 1 Kfs + 1 H₂O and of the indirect replacement 0.25 Sil → 0.25 And. Andalusite nucleation and growth took place completely inside muscovite, whereas most of the potassium feldspar was produced outside, preferentially at pressure shadows, after outward intracrystalline diffusion of K⁺ and fibrolitic sillimanite dissolution in the matrix. The rate-limiting step of this reaction process was initially the migration rate of the muscovite-andalusite and muscovite-potassium feldspar interfaces. However, it was followed by a diffusion-controlled step. The change in the relative rates of the reaction mechanisms was due to the coarsening of the reaction products, the low amount of energy and time required for non-reconstructive transformations (periodic bond chains of the tetrahedral sheet of muscovite are inherited by potassium feldspar and those of the octahedral sheet by andalusite), the magnitude of the heat flow associated with a possible contact metamorphic episode, and the slow diffusion of K⁺ within the crystal. Intracrystalline diffusion took place through a double monolayer of absorbed molecules of water (~10 Å) localized at microcleavages produced by basal slip in the interlayer level, instead of a proper lattice diffusion process. The derived rate law at constant P and T (considering the cases of 2 kbar and 605 °C and 3 kbar and 639 °C) for the diffusion-controlled process gives a time span of about 10,000 years for the growth of these metamorphic textures, which seems to be a reasonable estimate for a contact metamorphic event.

INTRODUCTION

The rate of a mineral reaction is determined by the rate of the slowest one of the following processes: (1) dissolution of reactant phases; (2) diffusion of chemical components from dissolved areas to those where the new minerals precipitate; (3) nucleation and growth of products; and (4) changes in temperature and pressure that produce the free-energy driving force. However, the first three rate-controlling steps are generally considered the only kinetic processes responsible for the preservation of minerals outside their stability fields when rocks passed along the P-T-t path of regional metamorphism. This is due to the generalized assumption that the rates of change for temperature and pressure associated with this kind of metamorphism are so slow that the reactions remain close to equilibrium (Thompson and England 1984). Extensive disequilibrium can occur for reactions with very small entropy changes, such as the andalusite to sillimanite transformation. The effect of the large enthalpy (entropy) changes of the devolatilization reactions on the overstepping required to allow nucleation and growth of the reaction products, and on the rock temperatures has been evaluated by Ridley and Thompson (1986) and Ridley (1985). Walther and Wood (1984) have demonstrated that for dehydration reactions, with entropy changes of 20 cal/mol/°C at 500 °C and only 1 °C of overstep, the reaction proceeds to completion quite rapidly (<1000 y) when the dissolution rate of the reactants is the rate-controlling step. Schramke et al. (1987) experimentally obtained complete transformation of muscovite plus quartz to andalusite and potassium feldspar, under low-pressure prograde metamorphism, close to the equilibrium boundary, with the rate-controlling surface area being that of the growing andalusite.