Kinetics of Al–Si exchange in low and high quartz: calculation of Al diffusion coefficients

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Abstract: Non-uniform distribution of Al between the three symmetrically equivalent Si sites in low quartz is converted to a random distribution by dry or hydrothermal annealing above 400°C due to Al–Si exchange, as shown previously by EPR measurements. Rate equations for the Al–Si exchange are derived from the experimental results presented here. We show that the kinetics of the Al–Si exchange reaction are strongly influenced by the type of Si substitution, whether by Al+Na ([AlO4/Na]+) or Al+Li ([AlO4/Li]+). Rate constants k and activation energies E of the Al–Si exchange differ significantly under identical run conditions according to the [AlO4/Na]+ and [AlO4/Li]+ defects. Thus, it is concluded that Na and Li are involved in the rate determining step of the Al–Si exchange reaction. The role of Na and Li is discussed from the electrostatic and structural viewpoints. In the case of [AlO4/Na]+ defects, no significant effect of water pressure on the activation energy E of the Al–Si exchange is observed, while the rate constant k decreases with increasing water pressure. In the case of [AlO4/Li]+ defects, the activation energy of the Al–Si exchange in low quartz increases from 278 ± 20 KJ/mole (dry, in air) to 400 ± 25 KJ/mole at 100 MPa water pressure, while k decreases. For high quartz, no effect of water pressure is observed with respect to E and k, and the activation energy E is drastically reduced compared with low quartz. From the experimental results obtained on samples from different growth sectors of the same crystal, it is concluded that a vacancy mechanism is responsible for the Al–Si exchange. Based on the “random walk” theory, equations are derived which allow calculation of the diffusion coefficients (D⊥, and D∥) of Al from rate constants (k) of the Al–Si exchange reaction. The calculated diffusion coefficients are in the range 10⁻二十四 to 10⁻二十七 m²s⁻¹. With the method described here, diffusion coefficients can be estimated in temperature ranges where conventional methods fail (e.g. diffusion of radioactive tracers or measurements of electrical conductivity).

Key-words: quartz, electron paramagnetic resonance, Al–Si exchange, kinetics, diffusion coefficients.

Introduction

Diffusion coefficients of cations, oxygen and hydrogen are of fundamental importance in many petrological and geochronological problems (Freer, 1981), such as the reconstruction of the cooling history of minerals. From diffusion controlled segregation and order/disorder processes, the cooling paths of minerals and rocks can be quantitatively determined, if diffusion coefficients of the ions involved are known. The kinetics of intracrystalline exchange processes are also a crucial aspect of the thermal behaviour of minerals (Müller, 1970), explaining important physical properties, for example electrical conductivity. Because of their importance, such processes have been intensively studied in the last twenty years. The diffusion coefficients of many cations, as well as of O and H₂O or their dissociated products, have been determined for many crystalline silicates. These data have been summarized by Freer (1981).

Self-diffusion coefficients for O in quartz (Haul & Dümüngen, 1962; Choudhury et al., 1965;