



Coupled thermodynamic and kinetic model for plagioclase growth from a silicate melt: Implications for non-linear growth rates, chemical zoning and time scales of magma solidification

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Magmatic rocks exhibit a wide range of igneous textures, which can provide valuable information about kinetics of crystallization as well as thermal evolution and time scales of solidification in natural magmatic reservoirs. The nucleation and growth rates are often assumed to remain constant in simple models that are used to predict and compare crystal size distributions in natural samples. However, these rates are affected and enhanced by undercooling and increasing departures from equilibrium, whereas the formation of depleted boundary layers of melt and progressive changes in interstitial melt composition tend to reduce them. Hence the nucleation and growth rates are expected to vary in a complex and non-monotonous manner.

We have formulated thermodynamic and kinetic model for plagioclase growth from a silicate melt, which uses magnitude of undercooling to determine the thermodynamic driving force for crystallization and converts this variable *via* appropriate kinetic law to the crystal growth rate. The model predicts growth rates, composition and thickness of melt boundary layer while recording the chemical zoning of growing plagioclase crystal. The zoning observed in natural samples can thus be compared to model results and used to constrain how the growth rates may have varied in geological settings of interest.

Numerical simulation of crystal growth uses one-dimensional finite difference method. Partitioning of chemical components at the solid-melt interface is determined thermodynamically assuming local equilibrium, and thermodynamic affinity provides the Gibbs energy of crystallization. Kinetic relation between the thermodynamic driving force and the growth rate is based on experimental studies of plagioclase growth and has been extended to three-component haplotonalite system. Thermal and chemical gradients resulting from production of latent heat and chemical partitioning are dissipated by diffusion. Chemical diffusion is treated as multicomponent one and it incorporates dependence on local melt composition and temperature.

Calculations performed for a various initial melt compositions and undercoolings of 1 and 10 % below plagioclase liquidus at equilibrium demonstrate that (1) formation of a boundary layer in silicate melt is significant, especially at higher undercoolings. Its thickness exceeds the actual grain size; (2) the calculated zoning of plagioclase spans up to 50 mol. % anorthite component. At low undercoolings, monotonous trend towards albite enrichment is predicted whereas at high disequilibrium, transient maximum in albite concentration occurs and the crystal either maintains a constant composition or its growth reverses towards a weak anorthite enrichment outwards; (3) simulated growth rates strongly depend on the initial melt composition and tend to decrease as grain size increases. In albite-rich melts, grain sizes are always larger at greater undercoolings whereas in anorthite-rich compositions a reversal is predicted that leads to larger grains produced at lower undercoolings.

Temperature dependencies of the physical parameters that govern the model permit extrapolation of results to geologically relevant hydrous melt compositions and crystallization temperatures. We expect natural growth rates in granitic melt to be on the order of 10^{-14} to 10^{-15} m s⁻¹ at 800 °C, and they produce a 1 mm grain in 3 to 30 thousand years. Such short time spans may indicate that natural magmas solidify much faster than assumed previously and this occurs when advancing cooling front is migrating through the magma chamber. Our model highlights the importance of the counteracting effects of chemical partitioning, growth kinetics, and chemical and thermal diffusion, and reveals important non-linearities in growth rates and time scales of magmatic crystallization in natural settings.