Microscopic model for nucleation pathways of polymorphic minerals from solutions

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Rock-forming processes in the Earth (e.g., reaction, mass transport, deformation) are usually too slow for us, and thus it is difficult to obtain the direct time-series data of the system. Therefore, it is important to develop the methodology how we extract the information on dynamics of rock-formation from "frozen pictures" (textures). In this study, as an example, we focus on the nucleation of metastable phases from solutions, because the formation of metastable minerals is essential on the progress of some rock-forming reactions (hydrothermal and metamorphic reactions), and often provides unique textures.

A phenomena, that a metastable mineral firstly crystallizes from liquid and translates into more stable phases, has been known as the Ostwald rule, and such phenomena has been reported in crystallization of various materials, including proteins, clay minerals, iron oxides, carbonate (Pouget et al., 2009) and silica (Morse and Casey, 1988). Okamoto et al. (2010) found characteristic textures of silica that cristobalite is formed as a cover of spherical amorphous silica particles, and that quartz is formed within a deposit of cristobalite. The phenomena following the Ostwald rule would result from competitive processes of bulk chemical potential and interface energies for solid-solid and solid-liquid; however, the detailed dynamics is not clear.

Inspired by the occurrences of silica polymorphs, we present a microscopic model (two-dimensional Potts lattice gas model; c.f., Sanders, 2007) for understanding nucleation mechanism of polymorphic phases from solutions. We construct a system which is composed of a solvent (s4) and three polymorphic solid phases (s1, s2, s3). The configuration energy is expressed as combination of interaction term and bulk chemical potential. One of the most characteristic features of this model is that both state and position of the solid phases are updated by Metropolis dynamics. We evaluated the equilibrium conditions by exchange Monte Carlo method (Hukushima and Nemot, 1996), as well as temporal evolution of the system. At temperature higher than critical temperature ($kbT/J = 1.1$), nucleation of the solid phase does not occur. At lower temperature, a large nucleus of the least stable phase is initially formed and then it translates into more stable phases following the Ostwald rule. The resulting textures are similar to those observed in natural system (i.e. silica precipitates from aqueous solutions), indicating that our simplified model captures an essential process of the Ostwald rule. The free energy surface of the system, which has several local minimums, changes depending on temperature and cluster size, which controls the nucleation pathways. In usual, the interfacial energies among the minerals are much more difficult to be estimated than bulk chemical potential (i.e., solubility); therefore, the characteristic textures among the polymorphic minerals could be useful for evaluating the magnitudes of the interfacial energies relative to the chemical potential values, by comparing the snapshots of the configuration in the microscopic model.

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