

Heterogeneous nucleation, Ostwald step rule and Potts model: Implications for precipitation of silica polymorphs

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The rock-forming minerals include several polymorphic minerals such as aluminosilicates, serpentine, carbonates, carbon, and silica. These minerals have been used as indicators of P-T condition and/or fluid compositions, when they formed. It is also well known that metastable phases commonly appear especially during fluid-rock interaction, including aragonite in carbonate sinters, and opals in silica sinters. Okamoto et al. (2010) found that the dominant silica minerals precipitated from aqueous solutions in order of amorphous silica, cristobalite to quartz, and that quartz is dominant in the solutions including minor Al and Na. The formation of less stable phase prior to the most stable phase is called as the Ostwald step rule. The phenomena following the Ostwald step rule is explained by relative differences in growth rate among the polymorphic minerals in the presence of seeds of all phases, but nucleation of these seeds should be considered. In this study, heterogeneous nucleation and the effects of impurity are investigated by a simple microscopic model, Potts model, in Monte Carlo simulation.

In the Potts model, each spin (molecule) in a lattice has one of q states (phases). Each lattice site i has a spin s_i taking values in the range of 1 to q , and the energy of a configuration s is given by the Hamiltonian, $H = - [J]_{s_i, s_j} - [h_a M_a]_a$ (eq. 1), where M_a is the number of spins of the spin type a . The first term is the sum of nearest-neighbor pairs of spins with the symmetric interaction energy (surface energy), and the second term describes the effect of external fields h_a acting on spin type a (bulk free energy). To evolve the system, we employed discrete-time Metropolis dynamics. Here, we consider spins of four states (1-4) in a 30×30 square lattice in two dimensions and periodic boundary conditions. We set $T = 0.80$, and impose the external fields as $h_a = 0.1 \times (a - 1)$, indicating that state 4 is the most stable. When we set the diagonal elements of the interaction matrix to unity and the other elements to zero, any metastable phase does not appear. The sequential nucleation of metastable phases following the Ostwald step rule is realized when we introduce a non-diagonal interaction, $J_{a, a+/-1} = F1 > 0$ (attractive), between neighboring phases, and all other non-diagonal interactions have $J_{a, b} = F2 < 0$ (repulsive) (Sanders et al. 2007). The successive nucleation of metastable phases in order of 1, 2, 3 and 4 appears with $F1 = 0.1$ and $F2 = -1.0$. We also find that phase i nucleated in phase $i-1$. This result is qualitatively same to the occurrences of the silica minerals in the pure Si solution of Okamoto et al. (2010): homogeneous nucleation of opal-A from the solution, heterogeneous nucleation of opal-C upon opal-A and that of quartz on opal-C. A new phase preferentially nucleates on the next-less-stable phases, as they are probably more structurally similar to new phase than are other phases.

The effect of impurities was introduced as $-[J_{pa}]$, that is the interaction between the impurity, p , and spin a into equation 1 following Sear (2005). To consider the case of silica, we propose that an interaction between phase 4 and an impurity equals 1, and that interactions between other states and an impurity are zero. The simulation results reveal that the evolution of the system varies with increasing number of impurities. When the number of impurities is small, nucleation of the most stable phases occurs via the formation of metastable phases. In contrast, with a larger amount of impurity, phase 4 is able to nucleate directly. The direct nucleation of quartz in the solution with small amounts of impurities (Okamoto et al. 2010) indicates the strong interaction between quartz and these cations.

References:

- Okamoto A. et al. (2010) *Geochim Cosmochim Acta*, 74, 3692-3706.
- Sanders DP. (2007) *Phys Rev B*, 75, 132101.
- Sear PS (2005) *J. Phys. Condens. Matter* 17, 3997-4004.

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