Hem-switching, chemically induced grain boundary migration, and rocks

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Based on observations of the microstructure of Bavarian granites, Voll (1960) described a process that he called *Wechselsäume*¸ i.e., hem-switching, in which mixing and unmixing could occur via intergrowth of two mineral phases. The geometry, microstructure and chemistry that he described are equivalent to those formed during chemically induced grain boundary migration, a process recognized nearly 20 years later during laboratory experiments in metals with (Yoon and Huppman 1979) and without partial melts (Hillert and Purdy, 1978) and, later still, in ceramics and minerals. In the laboratory, the process is favored under conditions where the distance of boundary migration is greater than that associated with lattice diffusion of the reactants. During solid-solution reactions, the kinetic driving force appears to be constrained by elastic coherency forces along the migrating interface. As boundaries migrate though the solvent phase, the solute concentrations incorporated in the zone are smaller than that of a homogeneous solid-solution.

In order to understand the kinetics and driving forces for this process we have been studying the solid solution of divalent cations into calcium carbonates. In bicrystals, the coherency strain hypothesis explains many, but not all, of the aspects of mixing (Hay and Evans, 1992). More recently, we conducted experiments in which calcite and dolomite at 800°C react to form high magnesian calcite. After an early induction period, grains of both high Mg-calcites and Ca-rich dolomites are nucleated and grow slowly. This growth is then followed by rapid replacement of the early nucleation products by more stoichiometric dolomites. Thus, the overall dolomitization reaction occurs by at least three elementary reactions: nucleation of reactive intermediates, growth of the metastable phases, and replacement by dolomites with thermodynamically optimized stoichiometry. Thus far, CIGM has been produced in the laboratory only in the carbonate system, but it seems likely that such a process is possible during the formation of solid solutions in any mineral phase, and that CIGM be a wide-spread natural process.

References

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A new thin film approach to study grain boundary transport in an incompatible matrix

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Recently, Dohmen and Chakraborty [1] have developed a general kinetic model for an exchange reaction between two solids mediated by an “intergranular fluid phase”. One application of the model is that it allows to evaluate the integrated transport properties of an interganular fluid phase by modeling of the compositional profiles in the solid reactants. As a test of the model and as an alternative way to study grain boundary transport in e.g, metals, oxides or silicates, a new experimental setup was developed. The general idea is that single crystals (e.g. olivine) are deposited with inert polycrystalline thin films (e.g. ZrO_2) of defined geometry and chemistry, such that any exchange with the covered surface of the single crystal has to pass this inert layer.

Single crystals of San Carlos olivine (Fo_{90}) were deposited with 100 to 500 nm thick layers of ZrO_2 by Pulsed Laser deposition [2]. Two sets of diffusion experiments were performed with these samples: (1) Diffusion anneals in the temperature range 900 – 1100°C in which the samples have an additional olivine thin film with Fo_{30} composition on top of the ZrO_2 layer. (2) Diffusion anneals at 1200°C, where olivine samples were packed into olivine powder with Fo_{30} composition. The analyses of the final chemical zoning with either Rutherford Backscattering or Electron Microprobe show that in the lower temperature range (<1100°C) the ZrO_2-film is not any kinetic barrier for the exchange between the olivines. However, in the experiments at 1200°C (experimental set 2) we observe non-equilibrium phenomena partly related to the ZrO_2 film and partly related to the insufficient contact with the surrounding powder. According to [1] this reaction system is controlled by solid state + fluid diffusion. Further experiments (e.g. a time series) at these conditions are going to be performed and the analytical observations as well as a quantitative modeling of the chemical zonings will be presented at the meeting.

References

[1] Dohmen, R, and Chakraborty, S. (2003) Am. Min., 88, 1251-1270.
[2] Dohmen, R., Becker, H.-W., Meißner E., Etzel T. and Chakraborty S. (2002), Eur. J. Mineral., 14, 1155-1168.