

## Phase equilibria in space and time

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Over the last decades thermodynamic data have been determined for a large number of phases of geological interest and a variety of tools have been developed for calculating equilibrium phase relations. This has contributed substantially to a better understanding of magmatic and metamorphic crystallization and to the disentangling of geological processes. Although the petrologic analysis of phase equilibria may be considered a rather mature field, there are several routes for future developments. Here we report on three case studies out of our recent work on systematic deviations from equilibrium states to illustrate a potential avenue to pursue in phase petrology.

An interesting subject concerns the incorporation of non-isostatic stress. Traditionally primarily homogeneous, hydrostatic stress has been considered in the phase petrologic analysis of rocks. As was shown in the context of coherent exsolution [1], reaction induced self stress may have a substantial effect on phase equilibria. Non-hydrostatic stress is probably the rule rather than the exception in reactive rock systems. Using the example of Na+/K+ partitioning between alkali feldspar and a NaCl-KCl salt melt [2] we investigate to what extent self stress may influence equilibrium partitioning between crystal and melt.

The notion that thermodynamic equilibrium may be established locally even if the bulk system is out of equilibrium lead to the concept of local equilibrium, which has proven particularly useful in the analysis of systems with component fluxes driven by chemical potential gradients. If chemical mass transport is rate limiting, then spatially organized structures such as reaction bands or coronas may form. If local equilibrium is assumed at the interfaces between the different mineral layers comprising a reaction band, the chemical potentials of the mobile components are fixed at the interfaces and the driving forces for chemical mass transfer may be quantified. This provides the basis for extracting component mobilities from rim growth experiments, or alternatively, for the extraction of time and rate information from reaction bands in natural systems, if component mobilities are known. A necessary consequence of the local equilibrium assumption is that element partitioning at the reaction interfaces is entirely determined by the physico-chemical conditions and, if these conditions are time invariant, must be constant during the progress of a reaction. Using experimental growth of spinel reaction rims in the MgO-Al<sub>2</sub>O<sub>3</sub> system [3] we show that major element partitioning at moving reaction fronts evolves with time showing successively decreasing deviations from local equilibrium. This reflects the transition from interface-reaction controlled to transport controlled transformation. Knowledge of the corresponding equilibrium partitioning allows for derivation of a phenomenological parameter that quantifies the mobility of the reaction interface.

Referring to exsolution in ternary feldspar, we investigate the pathways that a feldspar may take during spinodal decomposition using Cahn-Hilliard theory [4]. The approach rests on the knowledge of the free energy landscape and thus on the potential equilibrium states. Due to substantially different mobilities of the anorthite-, orthoclase- and albite components the system evolution deviates significantly from an equilibrium path. The trajectories through composition space are determined by the relative component mobilities and deviate from the conodes linking phases that constitute stable equilibria. Only after exceedingly long time, equilibrium is attained. In actual fact long lived non equilibrium states may, however, survive, which may be problematic when applying two feldspar thermometry to exsolved feldspar.

References: [1] Robin P (1974) Am Mineral, 59: 1299-1318; [2] Neusser, G. et al. (2012) Contrib. Mineral. Petrol., DOI: 10.1007/s00410-012-0741-9; [3] Keller L. et al (2010) Am. Mineral., 95: 1399-1407; [4] Cahn JW, Hilliard JE. (1958) J Chem Phys, 28:258-267.