



The rutile-titanite reaction: (II) Material transport along mineral interfaces and dissolution patterns on rutile

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Three interfaces are discerned in our experiments on titanite growth around rutile in the Al-free system $\text{TiO}_2\text{-SiO}_2\text{-CaO-NaCl-H}_2\text{O}$ with complete titanite overgrowth: (1) between the Ti source and the titanite, i.e. rutile - titanite, (2) grain boundaries between titanite - titanite in the overgrowth, (3) between titanite and the Ca and Si source, i.e. titanite - fluid. Dissolution of rutile, shown by 3D-patterns after removal of the overgrowth, is controlled by the overgrowth patterns of titanite, especially the titanite - titanite interface. Deep titanite filled 'valleys' in the rutile form beneath the titanite-titanite grain boundaries whereas away from the titanite-titanite boundaries the dissolution of rutile diminishes. Material transport through the titanite rim is clearly focused at the titanite-titanite grain boundaries, independent of run time. Mobile elements Ca and Si are brought to the titanite-rutile interface, but also the less mobile Ti is transported to the titanite-fluid interface. Direct evidence of Ti transport is found in the growth of titanite crystals on titanite, never forming a complete second layer of titanite crystals, but present in all experiment of variable duration. We also observe titanite growth into the fluid and thickening of the overgrowth with increasing duration. Further, the volume of titanite is ~ 3 times larger than that of rutile. This implies, provided all dissolved Ti remains at the titanite - rutile interface and forms titanite that the increasing volume has to be accommodated by deformation mainly in the overlying titanite. In TEM images of various experiments no substantial deformation is seen in the titanite or rutile and we conclude that Ti must have been removed from the site of dissolution.

Porosity is restricted to the rutile-titanite and titanite-titanite interfaces and does not occur within crystals. SEM images of polished sections and TEM images of FIB-cut foils show some porosity on titanite-titanite or less common on rutile-titanite interfaces at the μm to 100 nm scale. Most grain boundaries on TEM images of titanite-titanite and titanite-rutile interfaces are tight. The overall impression especially from the SEM images is that porosity is always present but not abundant. The uniform 3D-dissolution patterns on the rutiles' surface require, however, an average similar dissolution rate, i.e. a time-averaged uniform transport of material along the titanite-titanite interface. Porosity along the titanite-titanite grain boundaries could be a transient feature that moves quickly (provided that the information from 2D images is sufficient to trace a connected porosity).

Work in progress aims to quantify dissolution in relation to its variable spatial distribution on the rutile using well-defined synthetic rutile in time series experiments with the same setup used in experiments with natural rutile.