American Mineralogist, Volume 97, pages 828–839, 2012

The morphology of the reaction front of the dissolution-precipitation reaction rutile + wollastonite = titanite in time series experiments at 600 °C/400 MPa

FRIEDRICH LUCASSEN,[1,2,*] GERHARD FRANZ,[1,†] RICHARD WIRTH,[2] MATTHIAS WEISE,[3] AND ANDREAS HERTWIG[3]

[1]Technische Universität Berlin, Fachgebiet Petrologie—ACK 9, Ackerstrasse 71-76, 13355 Berlin, Germany
[2]Deutsches GeoForschungsZentrum, Telegrafenberg, 14473 Potsdam, Germany
[3]Federal Institute for Materials Research and Testing, Unter den Eichen 44-46, 12203 Berlin, Germany

ABSTRACT

Fluid-assisted mass transport reactions by dissolution-precipitation, where a precursor mineral reacts with a fluid, play an important role in metamorphism and metasomatism. We investigated titanite growth on rutile in time series experiments between one and 107 days at constant P-T conditions of 600 °C and 400 MPa in the system TiO_2-CaO-SiO_2-Na_2O-HCl-H_2O. A two-capsule assemblage allows for transport of Ca and Si from dissolving wollastonite to dissolving rutile, the Ti-source, in a NaCl-bearing aqueous fluid, according to the general reaction $CaSiO_3 + TiO_2 = CaTiSiO_5$. Complete overgrowth of rutile by titanite occurred after just one day of experiment. Fine-grained lozenge-shaped titanite crystals of short-time runs (up to 14 days) reorganize to larger predominantly prismatic crystals after >14 days.

After investigation by scanning electron microscopy, the titanite overgrowth was removed from the rutile by hydrofluoric acid, to provide a three-dimensional view of the dissolution-reaction front on the rutile surface. The morphology of the rutile surface is dominated by humps or ridges beneath the central region of a titanite crystal and valleys at the grain boundaries between adjacent titanite crystals. The dissolution pattern on the rutile surface mimics the titanite overgrowth and changes with changing grain size and shape of the titanite with longer run times. The preferred dissolution of rutile in the valleys is clearly linked to the position of the titanite grain boundaries, which served as pathways for fluid-assisted element transport. Rutile-titanite and titanite-titanite boundaries show a significant porosity in transmission electron microscopy images of foils prepared by focused ion beam milling. The large-scale dissolution pattern on the rutile surface is independent of the crystallographic orientation of the rutile and entirely dominated by the arrangement of titanite crystals in the overgrowth. Dissolution features on a scale smaller than ~1 μm are dominated by stepwise dissolution and etch-pits following the crystallographic orientation of the rutile. Similar observations were made in experiments with an additional Al-source, although these experiments result in a different overgrowth pattern; i.e., an exposed rutile surface is always present and solitary titanite crystals are accompanied by partial overgrowths. Quantitative characterization of the surface morphology by white-light interference microscopy demonstrates that, with increasing grain size of titanite, dissolution of rutile is strongly enhanced at the titanite grain boundaries.

Natural examples of titanite overgrowths on rutile show the same relations between element pathways, arrangement of titanite crystals and 3D dissolution pattern on rutile as in the experimental systems. We conclude that the transport of Ti away from the rutile and of Ca + Si into the reaction rim occurred in a grain boundary fluid, the composition of which must have been strongly different from the composition of the bulk fluid in the experiment, as well as in the natural system. The reaction progress depends on the availability of a fluid, and relicts of rutile in titanite indicate restricted availability of fluid in the natural system (e.g., a fluid pulse that was consumed by the reactions). The reaction examined here can serve as a proxy for other reactions of the conversion of oxide minerals (e.g., spinel or corundum) into silicates.

Keywords: Experimental mineralogy, rutile, titanite, dissolution-precipitation, reaction morphology