



The rutile-titanite reaction: (I) 3D-View of a reaction front for a dissolution-precipitation reaction

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Titanite growth on rutile was studied experimentally in the systems $\text{TiO}_2\text{-SiO}_2\text{-CaO-NaCl-H}_2\text{O}$ and $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-NaCl-H}_2\text{O}$ ($\pm\text{CaF}_2$) at 600°C and 0.4 GPa and variable run duration (1, 3, 7, 14, 30, 60, and 107 days). Natural rutile crystals in a perforated Pt-tube were placed into an Au-capsule containing natural wollastonite crystals, gamma-Al₂O₃, optional powdered CaF₂, and a mixture of NaCl and H₂O 1:1 by weight. Elements between the Ca, Si (and Al) sources and the Ti source are transported by the NaCl-brine. The titanite exclusively forms on the Ti-source, i.e. the rutile. Ti is immobile compared with Ca, Si, and Al (for details: Lucassen et al. 2010). After the run, titanite was removed by dissolution in warm HF, which does not attack the essentially insoluble rutile. The titanite overgrowth leaves an impressive imprint on the rutile surface, allowing to view the reaction front between the two minerals.

In the Al-free system, the rutile is completely overgrown already after 1 day with small lozenge shaped titanite crystals that are commonly arranged in floral textures. With longer run times the size of the crystals increases and the arrangement of the crystals is dominated by prismatic habits with euhedral crystal faces at the fluid-titanite interface. The trace of the titanite overgrowth on the rutile surface is independent of the tetragonal symmetry of rutile, i.e. does not differ among the crystal faces parallel to c (110; 100) and the less common faces (101; 011). The dissolution pattern at a scale $>1\mu\text{m}$ is entirely dominated by the changing arrangement of the titanite crystals: dissolution of the rutile is large in the vicinity of titanite-titanite grain boundaries and diminishes towards the centre of the titanite crystals. This results in a 'hump-and-valley' morphology on the rutile. In long-time runs, flat-bottomed holes with stepped walls occur in the rutile surface. The holes possibly mark locations with stable grain boundaries in the titanite overgrowth. Sub- μm large etch-pits restrict to flat bottoms and terraces in the walls of such holes. The shape of the etch-pits, however, reflects the tetragonal symmetry of the rutile.

In the Al-system, solitary euhedral titanite crystals grow and the interface rutile-fluid (with a free rutile surface) persists in all runs. The prismatic crystals have a length up to $100\mu\text{m}$ already after 1 day. With longer run-times the size of titanite increases and groups of coarse grained titanite crystals form. The rutile crystal becomes partially overgrown by titanite. Growth of large euhedral titanite into the fluid is common. On the rutile surface, three areas are distinguished, the free rutile surface, rutile beneath solitary titanite crystals and beneath polycrystalline titanite overgrowths. Dissolution at the free rutile surface is uniform and pronounces features like c-axis parallel striation and steps that are already present in the unreacted rutile. Solitary titanite crystals rest on humps and overgrow the slope that evolves successively with the lowering of the free rutile surface by dissolution. Rutile surfaces beneath connected titanite overgrowth show a very pronounced 'hump-and-valley' morphology following the outline of the grain boundaries between the titanite crystals.

Similar dissolution patterns on rutile outlining the titanite-overgrowth were observed in natural systems that represent a much larger time scale than our experiments. We conclude that the reaction rate is mainly controlled by dissolution of TiO₂ and its transport through the growing rim.

References

Lucassen F, Franz G, Rhede D, Wirth R (2010) Ti-Al zoning of experimentally grown titanite in the system CaO-Al₂O₃-TiO₂-SiO₂-NaCl-H₂O-(F) - evidence for small scale fluid heterogeneity. *American Mineralogist* 95, 1365–1378