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Titanium in Quartz: Time series experiments reveal a possible non-classical crystallization pathway

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Application of titanium-in-quartz thermobarometry (TitaniQ) to volcanic and plutonic rocks has generated sustained debate. Temperatures derived from TitaniQ are commonly 100-150 °C lower than those obtained by other thermobarometers applied to the same rocks, which affects the interpretation of how magma is stored, rejuvenated, and erupted. Because TitaniQ is based on principles of equilibrium partitioning among quartz, rutile, and fluid, its accuracy depends on the attainment of chemical equilibrium during crystal growth, both in nature and in the lab. While equilibrium may be attainable for slowly grown quartz in natural settings, it is less likely for rapidly grown crystals in laboratory experiments.

Since deviations from equilibrium are manifested in time-dependent behavior, we seek to characterize the time evolution of SiO_2 and TiO_2 in piston-cylinder experiments. The TitaniQ calibration is based on experiments lasting multiple days carried out across a range of temperatures and pressures. Our experiments differ only in that we focus on a single set of conditions (800°C and 1 GPa) but variable durations from 5 minutes to several days. An unanticipated result, revealed by FIB-SEM imaging, is the existence of an amorphous surface zone on the crystals that thickens systematically with run duration, from ~150 µm after 1 day to ~250 µm after 4 days. Quartz grown in anatase-free control experiments do not develop this amorphous zone. These observations indicate that experimental quartz grown with abundant TiO_2 can proceed via a nonclassical crystallization pathway involving an amorphous precursor. A migrating amorphous crystallization front could accommodate elevated Ti concentrations that are later incorporated into crystalline quartz during structural reorganization. We will discuss the implications of our findings in regard to applications of TitaniQ as a geothermobarometer.