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New rutile and titanite phase stability constraints at subsolidus conditions in a mafic system

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Rutile, titanite and ilmenite are the most common Ti-bearing minerals found in metamorphic rocks of variable grades. Rutile and titanite, in particular, are extremely useful minerals as they can be dated using U-Pb, and Zr concentrations are calibrated as geothermometers for both minerals, making them valuable petrochronometers. Previous experimental studies on MORB composition [1] established that titanite is more stable at LT-LP, rutile at HP (> 12 kbar), while ilmenite at HT-LP metamorphic conditions. Despite these phase stabilities, the natural occurrence of rutile at LP (< 12 kbar) and titanite at HP (> 20 kbar) and ilmenite at both HP and LP indicates strong uncertainties on our current understanding about their stabilities. [2] demonstrated a non-trivial compositional effect mainly driven by CaO content, on the titanite-out reaction for granitoid compositions (2-4 kbar). For MORB compositions, experimental constraints are currently lacking in the 400-600 °C temperature range.

Here we present the results of a set of experiments run in a piston-cylinder apparatus using a gold capsule with a NNO oxygen fugacity buffer. We tested multiple starting materials, with different Ti/Ca values, including: 1) a pulverised eclogite (MORB composition) powder with titanite and rutile as well as a few initial eclogitic silicate mineral seeds, promoting nuclei for mineral overgrowth, 2) the same eclogite, glassed and pulverised in the lab, with fewer product seeds, and some of these with added Ti powder; 3) a different MORB powder with crushed titanite and kaersutite seeds. More than 30 experiments were conducted, with pressure ranging between 12 and 23 kbar, and temperature between 400 and 750 °C in water-saturated conditions and using a cold pressure-seal capsule technique. Due to the challenging LT experiments, equilibrium is not attained, but dissolution and precipitation features are often observable. Epidote is one of the first minerals to nucleate and grow when the initial water content is > 10 wt%, and crystallisation is followed by amphibole. We show that when Ti/Ca is high, rutile is stable even at lower pressures, and when Ti/Ca is low, titanite seeds appear metastable even at higher pressures (19 kbar) and low temperatures. This is in agreement with petrological observations (i.e. peak titanite reported in blueschist rocks). At lower water saturation conditions (10 wt%), reactions are more sluggish, but successful experimental assemblies show that at 600 °C and 14 kbar titanite seeds become unstable and start reacting with the basalt bulk rock powder to form ilmenite. We found that H₂O content, as well as Ti/Ca ratios appear to influence the stability of these Ti-phases in a mafic system. These results can be used to constrain the stabilities of rutile, titanite and ilmenite, which

in turn elucidate the P-T-X conditions that these accessory minerals are able to record.

[1] Liou, et al. (1998). *Schweiz. Mineral. Petrog. Mitt.*, 78, 317-335. [2] Angiboust, S., & Harlov, D. (2017). *Am. Min.*, 102, 1696-1708.