HIGHLIGHTS AND BREAKTHROUGHS

Small grains and big implications: accessory Ti- and Zr-minerals as petrogenetic indicators in HP and UHP marbles

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Abstract:

The paper by Proyer et al. (2014) demonstrates that Ti- and Zr-bearing accessory minerals (rutile, titanite, zircon) record through their reaction textures part of the metamorphic history of a UHP marble. Calculation of relevant petrogenetic grids has the power to constrain the retrograde *P-T* path based on phase stability fields and the geothermobarometric evaluation of H_2O-independent mineral reactions involving these Ti- and Zr-bearing minerals. They calculated simple petrogenetic grids in the system TiO_2-ZrO_2-CaO-MgO-Al_2O_2-SiO_2-CO_2-H_2O (TZCMASCH) for calcite-dolomite marbles with forsterite/antigorite in excess and including those Ti- and Zr-bearing minerals for which thermodynamic data are known (rutile, titanite, geikielite, zircon, baddeleyite) and delineated their stability fields as well as the succession of their stability regions. This approach allowed the authors to infer the shape of the retrograde *P-T* path. Thus the combination of very careful petrography, calculated simple petrogenetic grids and the application of geothermometry involving these Ti- and Zr-bearing accessory minerals becomes an indispensible tool when reconstructing a metamorphic rock's evolution.

Keywords: rutile, titanite, zircon, UHP, petrogenetic grid, Rhodope Mountains

Though accessory minerals by definition make up less than 5% of the minerals in metamorphic rocks they provide significant information about a rock during its geological evolution. This information is based on both geochronology (e.g. crystallisation age and/or the age of various metamorphic events) and petrology/geochemistry (*P*-*T*-*X* constraints). High-pressure (HP) to ultrahigh-pressure (UHP) metamorphic rocks in continental collision zones record orogenic processes from subduction to exhumation, and thus provide insights into geodynamics of plate convergence along continental margins. Therefore constructing a reliable *P*-*T*-*t* path is a key to understand the tectonic evolution of subduction-zone rocks. This requires accurate determination of not only the timing of HP and UHP metamorphic events but also extracting *P* and *T* conditions of different stages of continental collision. Zircon, titanite and rutile have attracted much attention not only because of the power for precise U-Pb dating (e.g. Gao et al. 2011) but also due to the relatively well established Ti-in-zircon- (e.g. Watson et al. 2006; Ferry and Watson 2007), Zr-in-rutile- (e.g. Zack et al. 2004; Tomkins et al. 2007) and Zr-in-titanite geothermometers (Hayden et al. 2008). Therefore application of these Zr- or Ti-bearing geothermometers in combination with the use of relevant net-transfer reactions involving rutile and titanite (e.g. Tropper and Manning 2008) and linking the obtained *P*-*T* conditions by using these accessory minerals to geochronology (*P*-*T*-*t* path), has the power to provide new insights into continental crustal reworking, and especially subduction-zone metamorphic processes.

Despite their geothermometric importance, relatively little is known about the stability relations and crystallization sequences of Ti- and Zr-minerals in subduction-related rocks and almost no petrogenetic grids outlining their stability fields exist. One recent exception is the thermodynamic (pseudosection) approach to a Ti- and Zr-bearing chemical system by Kelsey and Powell (2011) which involves rutile and zircon and allows quantitative modelling of Zr between coexisting phases and melt in high-grade metamorphic rocks. On the other hand the occurrence of Zr- and Ti-bearing accessory phases like baddeleyite and zirconolite has long been recognized to be related to contact metamorphism of carbonates (e.g. Gieré et al. 1998). Phase diagrams and Schreinemakers analysis of relevant mineral reactions allows constraints on *T*, *a*(SiO_2) and *f*CO_2 (e.g. Gieré et al. 1998; Tropper et al. 2007). Ferry (1996) was also able to identify zircon- and baddeleyite-bearing isograds in contact metamorphic siliceous dolomites. Titanite-rutile-involving phase equilibria have shown to provide additional information about *P*-*T*-*f*O_2-*a*(H_2O) conditions of regionally metamorphic rocks (e.g. Frost et al. 2000) and have been applied to UHP rocks but the results also revealed large *P*-*T* shifts due to uncertainties in the exact nature of titanite activity models (Tropper and Manning 2008).

In their article Proyer et al. (2014) describe with great detail rutile, titanite and zircon in several samples of high-*P* calcite marbles with an early UHP history. During subsequent stages of retrograde metamorphism a complex set of secondary Ti-minerals formed. Even though no memory of the UHP path is preserved in the accessory minerals anymore, their successions and inferred reaction relationships in general turned out to be 1.) extremely useful for constraining the shape of the retrograde *P*-*T* path and 2.) potentially very useful for geothermobarometry since a number of H_2O-independent equilibria where Ti- and Zr-phases participate could be formulated. With respect to 1.) calculation of simple petrogenetic grids in the system TiO_2-ZrO_2-CaO-MgO-Al_2O_2-SiO_2-CO_2-H_2O (TZCMASCH) for calcite-dolomite marbles with forsterite/antigorite in excess and including Ti- and Zr-minerals (rutile, titanite, geikielite, zircon and baddeleyite) were used to delineate the stability fields of these accessory minerals and allowed to extract different segments of the retrograde *P*-*T* path based on their textural successions. Their results for the Ti-bearing phases showed that geikielite is stable at highest pressures, followed by rutile and titanite which requires a retrograde *P*-*T* path involving decompression with significant *T* increase. The sequence of the Zr-bearing minerals indicates that baddeleyite is stable at higher *P* and *T* compared to zircon. With respect to 2.)

due to the simple chemical formulae of most of these Ti- and Zr-minerals, some of the univariant reactions such as the simple reaction geikielite + diopside = titanite + forsterite are H_2O-independent and could thus be highly suitable for geothermobarometric purposes. Several of these univariant equilibria are also pressure-sensitive and if X_{Al} in titanite is <0.1 (Tropper et al. 2002) these curves could provide highly valuable geobarometric information which is usually very hard to obtain from the main mineral assemblage. If X_{Al} is higher then the influence of the type of activity model for titanite on the shift of the curves has to be evaluated (Tropper and Manning 2008).

The study of Proyer et al. (2014) impressively demonstrates that the succession of Ti- and Zr-bearing accessory minerals records in their observed reaction textures a large part of the metamorphic history of a rock. Calculation of simple petrogenetic grids not only allows to put constraints on the shape of the retrograde *P*-*T* path but also allows geothermobarometric evaluation of simple net-transfer reactions involving Ti- and Zr-bearing accessory phases such as rutile, titanite and zircon. If suitable equilibria can be calculated much better refined information about the metamorphic path and hence better insights on the nature of *P*-*T* paths from subduction-related rocks will be obtained. This study also shows that careful petrography is still the key for further thermodynamic modelling of metamorphic rocks.

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