HIGHLIGHTS AND BREAKTHROUGHS

Zircon dissolution and growth during metamorphism

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The mineral zircon ($ZrSiO_4$), found in igneous, sedimentary and metamorphic rocks, is ubiquitous within the rock cycle. Because zircon contains relatively high concentrations of many trace elements (e.g., uranium, heavy rare earth elements), the growth and dissolution of zircon plays a major role in distribution of trace elements during many geologic processes. Variations in zircon textures (Corfu, 2003) and compositions (Hanchar, 2007) preserve a wealth of information commonly used to reconstruct geologic histories. Zircon solubility in crustal melts as a function of temperature and composition has long been known (Harrison and Watson, 1983; Watson and Harrison, 1983), and recently confirmed for pressures <25 kbar (Boehnke et al., 2013). However, with few exceptions (Dempster and Chung, 2013; Dempster et al., 2004; Kelsey and Powell, 2011) zircon petrogenesis under metamorphic conditions has not received as much attention. In this issue Kohn et al. contribute to our understanding of zircon dissolution and growth in hydrous MORB and metapelite bulk compositions under metamorphic conditions (Kohn et al., 2015). They evaluate the propensity for zircon saturation, in rocks containing common metamorphic minerals in equilibrium with zircon, to assess what minerals (besides zircon) affect whole rock Zr mass balance. Their results indicate that mineral reactions over a range of metamorphic grades could play an important role in the dissolution and growth of metamorphic zircon, with Zr preferentially incorporated into melt, rutile, garnet and hornblende with increasing temperatures and decreasing pressures.

Models of Zr mass balance for hydrous MORB and metapelitic bulk compositions were used to assess conditions of zircon dissolution and growth for P-T paths typical of 1) UHP evolution (e.g., Alps), 2) HT-HP evolution (e.g., Western Gneiss region of Norway) and 3) continent – continent collision (e.g., Himalaya). These bulk composition specific pseudosections were found to be sufficiently accurate in terms of Zr mass balance so that the first order effects of zircon abundances could be assessed. For the hydrous MORB composition, it was found that the pressure range over which zircon is expected to grow is significantly reduced in rocks following isothermal decompression paths, and heating during decompression, such that there is a limited pressure range over which zircon is expected to grow. In contrast, UHP paths (e.g., Alps) predict zircon growth over a larger range in pressure. For metapelite bulk compositions Kohn et al.'s (2015) models confirm those of (Kelsey et al., 2008) and (Kelsey and Powell, 2011) that partial melting reactions dominate zircon dissolution and growth.

A major implication of Kohn et al.'s (2015) zircon dissolution and growth models relates to the interpretation of isotopic ages of metamorphic zircons (e.g., U-Pb zircon chronology used to determine the timing, and duration of metamorphism). If zircon grows during much of the retrograde part of the P-T path, what do U-Pb ages for metamorphic zircons actually record? Because zircon dissolution and growth varies as a function of bulk composition and occurs over a wide range of P-T conditions during metamorphism and exhumation to the surface, interpreting U-Pb zircon data for rocks that have undergone complex metamorphic paragenesis is problematic. This is especially true for ultrahigh pressure (UHP) rocks in which mineral assemblages are partially to completely recrystallized, and mineral abundances change, but nevertheless preserve a record of transport into the mantle, metamorphism at UHP conditions, and return to the surface.

What are the implications of Kohn et al.'s (2015) zircon dissolution/growth models? The first is that U-Pb ages on zircons separated from UHP rocks cannot *a priori* be assumed to date the timing of UHP metamorphism. Their models predict a restricted P-T range for growth of zircon at UHP conditions and indicate that most zircon grows at much lower pressures (i.e., primarily during subsequent exhumation and cooling). Their models also indicate that zircons from felsic rocks in UHP terranes most likely date melt crystallization at relatively low pressures.

A re-evaluation of zircon U-Pb age probability density distributions from two UHP terranes (i.e., the Western Gneiss region of Norway and eastern Papua New Guinea) support Kohn et al.'s (2015) model predictions. In the case of the Western Gneiss terrane a comparison of titanite (crystallized at < 15 kbar) U-Pb ages and zircon U-Pb ages indicates that 75% of these U-Pb ages are concordant. Kohn et al. (2015) suggest that in this case zircon growth primarily occurs at the same P and T conditions as titanite. In other words zircon growth does not occur at UHP conditions, but rather is triggered by rutile to titanite reactions that occur during subsequent exhumation, and crystallization of *in situ* melts at relatively low pressures. They argue that titanite U-Pb ages provide minimum ages for the timing of UHP metamorphism in the Western Gneiss region and that zircon formed during uplift and cooling at P< 15kbar and therefore zircon ages do not directly date UHP metamorphism.

In the case of the Papua New Guinea UHP terrane, a re-evaluation of zircon U-Pb age probability density distributions also indicates that nearly 70% of dated zircons could be interpreted as having formed following UHP metamorphism. U-Pb ID-TIMS zircon geochronology (DesOrmeau et al., 2014; Gordon et al., 2012) has been interpreted to date the timing of UHP metamorphism from 5.6- 4.6 Ma. However, so far, coesite has been confirmed in only one mafic eclogite (Baldwin et al., 2008). For the coesite eclogite sample, in situ U-Pb zircon ion probe analyses, primarily of zircon inclusions in garnet, yielded a $^{206}Pb/^{238}U$ age of 7.9 ± 1.9 Ma (2σ) (Monteleone et al., 2007). This $^{206}Pb/^{238}U$ age for zircon is concordant with both a garnet Lu–Hf isochron age of 7.1 ± 0.7 Ma (2σ) (Zirakparvar et al., 2011) and a $^{40}Ar/^{39}Ar$ phengite weighted mean age of 7.93 $\underline{+}$ 0.20 Myr (2σ) (Baldwin and Das, 2013), and in review), all obtained on the coesite eclogite. These concordant ages, obtained on three minerals from the coesite eclogite using three different radiometric techniques (i.e., U-Pb SIMS zircon, Lu-Hf garnet, and $^{40}Ar/^{39}Ar$ phengite), as well as consideration of textural relationships and P-T constraints, are interpreted as the timing of UHP metamorphism. In contrast, zircons separated from the quartzo-feldspathic gneiss that encapsulates the coesite eclogite yielded U-Pb depth profiles that indicate intragrain geochemical heterogeneities (variations in Hf, Ti, and Y) suggesting chemical disequilibrium over the interval of zircon growth at 3.66 ± 0.13 Ma (2σ), significantly post-dating the timing of UHP metamorphism (Zirakparvar et al., 2014).

From other samples at the Papua New Guinea UHP locality, in-situ LA-ICP-MS $^{206}Pb/^{238}U$ ages on separated zircons range from 9.1 ± 0.6 to 3.8 ± 1.0 Ma (2σ) in retrogressed eclogite, and from 7.4 ± 1.1 to 4.1 ± 1.3 Ma (2σ) in “fresh” eclogite (Gordon et al., 2012). Chemical abrasion (CA)-TIMS $^{206}Pb/^{238}U$ ages range from 5.82 ± 0.2 to 4.78 ± 0.17 Ma (2σ) for zircons separated from another mafic eclogite at the UHP locality (Gordon et al., 2012).

Taken together these studies indicate that zircon crystallization at the Papua New Guinea UHP locality occurred over a range of P-T conditions from 9.1 to 3.7 Ma, as the Kohn et al. (2015) models predict. Currently, the best estimate for the timing of UHP metamorphism is 7-8 Ma based on concordant ages for zircon (U-Pb), garnet (Lu-Hf), and phengite ($^{40}Ar/^{39}Ar$) from coesite eclogite as discussed above. In contrast, zircons from felsic gneiss that hosts the coesite eclogite, crystallized ~4 million years later (Zirakparvar et al., 2014), at relatively low P as predicted by Kohn et al. (2015) models.

There are many other implications of Kohn et al's (2015) models. For example, zircon dissolution during prograde metamorphism rarely, if ever, approaches 100%. This means that subsequent zircon growth (rims) will likely occur on relict cores. In the Alps, >25% of zircon grown during the Variscan orogeny was dissolved during Alpine metamorphism (Malusà et al., 2013). According to Kohn et al's (2015) models, in this case dissolution most likely occurred during prograde Alpine metamorphism, with U-rich and strongly metamict zircon grains preferentially dissolved. Because considerable amounts of Zr become available during metamorphism, zircon can and often does recrystallize extensively on the retrograde path, dependent upon the bulk composition, and P-T-t path. U-Pb single grain zircon ID-TIMS ages are reported with < 0.1% precision (Schoene et al., 2010), but can such precise ages be accurately interpreted with respect to the time it takes for metamorphic zircons to grow? Under some circumstances a reassessment of the interpretation of zircon U-Pb ages may be warranted in light of these models.

To summarize, from a theoretical framework, Kohn et al. (2015) further paves the way to understanding zircon dissolution and growth during metamorphism. Under most metamorphic conditions, zircon growth occurs well below the closure temperature for loss of Pb (Cherniak and Watson, 2001). Temperatures of zircon crystallization can also be determined using Ti thermometry (Ferry and Watson, 2007). U-Pb ages on metamorphic zircons can be used successfully to interpret timescales, rates and the P-T evolution of UHP rocks (McClelland and Lapen, 2013; Rubatto and Hermann, 2007) provided that methods capable of detailing spatial, temporal, and geochemical variations within metamorphic zones are employed (e.g., SIMS depth profiling) (Breeding et al., 2004; Trail et al., 2007; Zirakparvar et al., 2014). Analytical methods exist to document isotopic, thermal, and geochemical heterogeneities within single zircon crystals, with results that can be related to transport through the rock cycle, if the P-T conditions of growth can be integrated with careful spatial analysis that provides temporal and thermal conditions of zircon crystallization.

The future is bright for studies that utilize chemical and isotopic variations within zircon to reveal temperature-time histories, and together with pressure estimates from thermodynamic models, allow for the interpretation of data with respect to the P-T-t paths of metamorphic rocks. Understanding the timescales and rates of zircon growth during metamorphism will be realized when geochronologists interpret zircon U-Pb data with respect to zircon dissolution and growth, as shown by Kohn et al.'s (2015) models. Only then can U-Pb zircon geochronology be used in general to constrain geodynamic models, and in particular to assess mechanisms of UHP exhumation.

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