

Deformation induced dissolution-precipitation of zircon in greenschist facies metasediments

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Dissolution-precipitation coupled to mass transfer via an intergranular fluid is an essential mechanism to allow growth of metamorphic minerals and continuous equilibration during prograde metamorphism at greenschist facies conditions where the temperature is too low for allowing significant solid-state diffusion. As the prevailing stress field may control sites of preferred dissolution and precipitation, and mass transfer in the fluid may be highly anisotropic depending on the orientation and abundance of grain boundaries, all processes involved are inevitably linked with deformation. Although dissolution-precipitation and fluid-mediated mass transfer is well established for major components and growth metamorphic index minerals, little is known about the effects of these processes on accessory minerals that are considered nonreactive during metamorphism, consisting of elements that are considered as chemically immobile (e.g. Zr, Ti, Th). In this contribution, we present two case studies from the Staufen-Höllengebirge Nappe (Austroalpine Unit, Eastern Alps) which allow us to investigate the behaviour of Zr during greenschist facies prograde metamorphism in metasediments. At each locality we characterized detrital and metamorphic zircon populations with high-resolution SEM imaging and use a novel laser-ablation based strategy termed ‘bulk inclusion dating’ (Hollinetz et al. 2022) as a proxy for quantifying the extent of metamorphic zircon formation.

The first case study focuses on a chloritoid-bearing schist sampled at the base of the Staufen-Höllengebirge Nappe. Thermodynamic modelling predicts chloritoid growth in a P-T field between 450–490 °C and 0.5–0.7 GPa, indicating upper greenschist facies conditions. A conspicuous feature of this rock are numerous minute (0.1–3 µm), euhedral zircon crystals found both in chloritoid porphyroblasts and as matrix phases. From the zircon morphology, crystal size distribution, orientation and spatial distribution of different micro-zircon populations in the chloritoid core, its rim and the matrix, we interpret syntectonic zircon precipitation and progressive coarsening from a Zr-bearing fluid migrating along grain boundaries. Since no detrital zircon grains are observed in this sample, the Zr source is most likely a detrital Ti-phase that broke down during prograde metamorphism (e.g., titanite). Bulk inclusion dating of the chloritoid rim and its zircon inclusions yields a U-Pb age of 116.7 ± 9.1 Ma (MSWD: 1.5, n: 79), consistent with the Early Cretaceous timing of nappe stacking (Ortner et al. 2008). Systematic imaging of the targeted chloritoid domain combined with trace element data clarifies the abundance and size of different U-Pb bearing inclusions and unambiguously link the U-Pb age to micro-zircon inclusions. Our data therefore implies total mobilization of Zr during late prograde metamorphism.

The second case study focuses on metaconglomerates and -sandstones sampled in the Permian cover of the Staufen-Höllengebirge Nappe. In these lower greenschist facies samples, sedimentary features are preserved, but overgrown by a metamorphic mineral assemblage

consisting of chloritoid + pyrophyllite + muscovite + hematite + rutile + quartz that is consistent with P-T conditions of c. 350 °C and 0.2-0.6 GPa. Although all samples contain the same metamorphic mineral assemblage, they preserve significant differences regarding their primary sedimentological features (i.e., size of detrital clasts, layering) as well as secondary structural features (i.e. pressure solution cleavages). We investigated low-strain samples that exhibit a weakly developed fabric and high-strain samples with a pronounced spaced cleavage. Large, rounded detrital zircon grains that are occasionally fractured and/or porous are abundant in all samples. However, only in high-strain samples we find tiny zircon outgrowths on detrital grains and sparse submicron zircon (0.1–1 µm) in chloritoid. U-Pb ages of detrital zircon dominantly are between 700–400 Ma with the youngest concordant ages at c. 290 Ma. Bulk inclusion micro-zircon data in low-strain samples yield pre-Cretaceous dates younger than the detrital population, which indicates limited metamorphic zircon growth. In the “high-strain” samples, the bulk inclusion dates suggest significant micro-zircon crystallization in the Early Cretaceous. Combining microstructural observations and bulk-inclusion zircon data strongly suggests that Zr mobility and metamorphic zircon growth may be linked to intensity of deformation assisted by dissolution-precipitation.

We document deformation assisted Zr mobility in greenschist-facies metasediments and show that dissolution-precipitation coupled to mass transfer via an intergranular fluid is a process that is also relevant for elements reputed as immobile. As ongoing technological advances continuously shrink the limits imposed by instrumentation, the bulk-inclusion strategy can fill the gap in our understanding of the geological process leading to the precipitation of micro-zircon. This approach allows integration between metamorphic conditions, deformation and age constraints and opens up new applications in the investigation of low-grade metamorphic rocks, potentially including dating of deformation.

Hollinetz MS, Schneider DA, McFarlane CRM, Huet B, Rantitsch G, Grasemann B (2022): Bulk inclusion micro-zircon U–Pb geochronology: A new tool to date low-grade metamorphism. - *J Metamorphic Geol* 40, 207-227

Ortner H, Ustaszewski M, Rittner M (2008): Late Jurassic tectonics and sedimentation: breccias in the Unken syncline, central Northern Calcareous Alps. - *Swiss J Geosci* 101, 55-71