

## ***In situ* U-Pb dating of rutile in UHT granulites from the Gruf Complex, European Central Alps**

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*In situ* U-Pb dating of rutile directly in thin sections preserves textural information including inclusion relationships. Grains included in some minerals such as garnet may preserve older U-Pb ages than matrix grains due to sluggish Pb diffusion through the host mineral and can provide additional constraints on P-T-t evolution.

The Gruf Complex of the Central Alps consists of amphibolite migmatitic gneisses and relict ultra high temperature (UHT) charnockite and sapphirine-bearing granulites. Whether the UHT event occurred during the Permian Variscan orogeny or the Tertiary Alpine orogeny is a matter of debate [e.g. 1, 2, 3]. Amphibolite facies metamorphism and migmatization began at ~32 Ma in the Central Alps, and temperature may have remained >640°C until 22 Ma [4, 5]. The Gruf Complex lies structurally below the Bergell pluton, which crystallized between 32 and 30 Ma [6], and was intruded by the Novate granite at 24 Ma [7].

Rutile in the Gruf granulites was analyzed using laser ablation inductively coupled mass spectrometry. Inclusions in garnet, orthopyroxene, biotite, and sapphirine as well as grains in the matrix and leucosomes were dated to determine if included grains preserve older ages than matrix grains. Average <sup>206</sup>Pb/<sup>238</sup>U ages uncorrected for common Pb range from 21–25 Ma for different samples. There is no clear correlation between age and textural setting; however, the oldest concordant date of ~30 Ma is from a grain included in garnet. These ages suggest that cooling from 640°C to below the closure temperature of Pb diffusion in rutile was rapid and possibly occurred as early as 25 Ma in the Gruf Complex.

[1] Liati & Gebauer (2003) *Schweiz Miner Petrol* **83**, 159–172. [2] Schmitz *et al.* (2009) *Eur J Mineral* **21**, 927–945. [3] Galli *et al.* (2011) *Contrib Mineral Petr*, in revision. [4] Rubatto *et al.* (2009) *Contrib Mineral Petr* **158**, 703–722. [5] Berger *et al.* (2011) *Tectonics* **30**, TC1007. [6] Von Blanckenburg (1992) *Chem Geol* **100**, 19–40. [7] Liati *et al.* (2000) *Schweiz Miner Petrol* **80**, 305–316.

## **Is mineral precipitation the reverse of dissolution?**

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Mineral precipitation and dissolution are fundamental processes governing fluid-solid reactions in nature and chemical mass transfer in the crust; the accurate description of the rates of these reactions within geochemical modelling codes holds the promise to quantify in real time the fate and consequences of processes ranging from radioactive waste disposal and carbon storage to the formation of hydrothermal ore deposits. Based, on the principle of detailed balancing, it has been commonly assumed that mineral precipitation can be described as the reverse of dissolution; transition state theory rate expressions that successfully describe mineral dissolution as a function of degree of fluid saturation state have been adopted to predict corresponding precipitation rates.

Surface sensitive microscopy suggests similar mechanisms at near to equilibrium; both dissolution and precipitation adds or removes material to existing active sites resulting in a linear dependence of rates on chemical affinity. At far from equilibrium etch pits form on dissolving surfaces, and analogous nuclei form on precipitating surfaces. The differences between dissolution and precipitation, however, stem from the existence of grain edges, which are active sites for dissolution but not precipitation. Moreover, the removal of material from edge sites creates additional active sites for dissolution, but precipitation fills active sites. As a consequence, steady state precipitation is dominated by nucleation in contrast to dissolution which removes material from continuously renewed active sites. This conclusion is supported by our recent measurement of quartz and magnesite dissolution and precipitation rates [1, 2]. Precipitation on grains having pre-existing active sites is consistent with the reversibility of dissolution whereas precipitation on pristine crystals is inconsistent and following independent rate equations.

[1] Saldi *et al.* (2009) *Geochim. Cosmochim. Acta*, **73**, 5646–5657. [2] Saldi *et al.* (2010) *Geochim. Cosmochim. Acta*, **74**, 6344–6356.