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# Dating rock deformation with monazite: The impact of dissolution precipitation creep

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#### ABSTRACT

The U–Th–Pb system of monazite behaves differently dependent on the deformation mechanism – dissolution precipitation creep (DPC) or dislocation creep – activated in the hosting metamorphic rocks. This can be exploited to use monazite for dating deformation, as is shown in rocks subsequently deformed by dislocation creep and DPC.

In rock layers intensely deformed by DPC, mineral reactions, particularly the dissolution of feldspar and apatite increased the alkali-content and reactivity of the fluid. This in turn led to dissolution of old predeformative monazite grains. New synmetamorphic monazite grains formed as the result of inter-grain transport of material over distances within the grain-scale. This process efficiently led to complete resetting of the monazite U–Th–Pb system, even at temperatures prevailing during greenschist facies conditions. The chemical composition of the new monazite records the dissolution of the old feldspar by a less pronounced negative Eu anomaly compared to old monazite. The shape of the monazite grains that precipitated during creep indicates the sense of shear in the shear zone, thus linking the obtained ages directly to the map-scale tectonic transport.

In rock layers predominantly deformed by dislocation creep, old monazite grains survived intense mylonitization and high strain, and show a core–rim structure. The cores are patchy, reflecting intra–grain, coupled dissolution–reprecipitation replacement processes. A wide range in apparent, geologically inaccurate Th/Pb and U/Pb ages among the patchy zones is the result of incomplete removal of in-situ grown radiogenic Pb from the patchy domains, depletion of Th and U and the redistribution of Th and U among the domains. Exclusively in the rims of the old monazite, the chemical composition correlates to that of the syndeformative monazites, and the U–Th–Pb system reflects the subsequent DPC.

Accordingly, rocks pervasively deformed by DPC should be preferably used to obtain monazite most suitable for precise dating of creep episodes linked to shear deformation and for determination of deformation rates.

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#### 1. Introduction

Obtaining well-constrained ages for deformation depends on reliably dating specific deformation fabrics. Monazite, a light rare earth element (LREE) phosphate, has a high potential to set time constraints in deformed rocks with complex tectonic and metamorphic histories (Catlos and Cemen, 2005; Dumond et al., 2008, 2010; Finger and Krenn, 2007; Foster et al., 2002; Harrison et al., 2002; Pan, 1997; Parrish, 1990; Shaw et al., 2001; Williams et al., 2007). However, it commonly remains difficult to link formation/growth of the dated monazite grains or grain

domains to specific microfabrics and structural elements. Even monazite with shape preferred orientation in the matrix, which is commonly considered to date the fabric forming deformation episode, may yield older or mixed ages and not necessarily date deformation. This could lead to misinterpretation of the geodynamic history.

The scope of this study is to reveal how monazite behaves in naturally deformed rocks. In such rocks, depending on the fluid availability and strain rate, different deformation mechanisms, such as dissolution precipitation creep (DPC) and dislocation creep, may be active (Fig. 1a, b). In an earlier study, the U–Th–Pb isotopic system of monazite has been observed to respond in different ways to stress and strain, dependent on the active deformation mechanisms (Krohe and Wawrzenitz, 2000). We complement previously published ID–TIMS monazite age data from Wawrzenitz and Krohe (1998) and Wawrzenitz (1997: sample TEO 36) with new in-situ chemical and detailed microfabric data.

In this study, we discuss different responses of monazite to fluids and deformation, such as (i) fluid-infiltrating intra-grain coupled dissolution-reprecipitation; (ii) phase separation implying Th-, Y-, and Ca-rich

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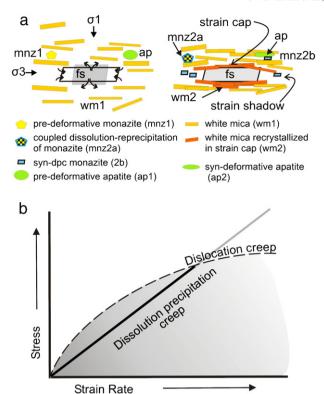
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**Fig. 1.** (a) Sketch illustrating the dissolution–transport–precipitation scenario resulting in mass transport and accommodation of deformation. Material dissolves at sites of relatively high normal stress  $(\sigma_1)$ ; leading to strain caps (e.g. fs, ap). There, (residual) phases may react with the fluid and change their composition (e.g. wm2). Dissolution results in high concentrations of dissolved elements in the fluid. Additionally, the pH value of the fluid may change, provoking/accounting for a higher reactivity with certain phases, e.g. mnz. The dissolved elements are transported toward sites with lower concentrations using fast diffusivity pathways (foliation planes etc.). Material precipitates in sites of relatively low normal stress  $(\sigma_3)$ , strain shadows, in equilibrium with the local fluid. Abbreviations according to Kretz (1983); (b) stress strain rate curves for DPC (solid line; linear – Newtonian – viscous behaviour) and dislocation creep (stippled line; exponential dependence on strain rate and stress), based on common flow laws (e.g. Carter and Tsenn, 1987; Rutter, 1983). At a given T, and lower stress magnitudes DPC accommodates higher strain rates (black line section) than dislocation creep; DPC is the dominant deformation mechanism.

inclusions; (iii) DPC and syndeformative growth at the expense of dissolved precursor phases including especially old monazite, apatite and major silicate phases. Consequently, we develop a methodological approach to dating rock deformation by DPC using U–Pb ages of monazite, combined with microfabric and mineral chemical analyses. We will demonstrate how microstructural criteria, indicative for specific deformation mechanisms activated in the rock matrix, may be used for the selection of rock samples, suitable for dating distinct deformation fabrics with monazite. This is basic to exploit the potential of monazite for dating deformation increments and deducing deformation rates.

# 2. Response of monazite and its U-Th-Pb system to fluids and deformation

### 2.1. Fluid-assisted dissolution and precipitation of monazite

Numerous studies have demonstrated that distinct monazite grains and domains in individual monazite grains may preserve different U-Th-Pb isotopic ages (Ayers et al., 1999; Catlos and Cemen, 2005; Finger and Krenn, 2007) and may even survive in a rock matrix deformed at high temperatures (Krohe and Wawrzenitz, 2000). This is a consequence of the low solid-state element diffusion rate in monazite (e.g. Zhu and O'Nions, 1999) and of the sensitive response of the U-Th-Pb system in monazite to the presence of fluids (Ayers et al.,

2006; Harlov et al., 2011; Lanzirotti and Hanson, 1996; Poitrasson et al., 1996; Seydoux-Guillaume et al., 2002; Williams et al., 2011). For example, inclusions of monazite in garnet, being protected from metamorphic fluids, preserve their old isotopic signature (e.g., Montel et al., 2000; Williams and Jercinovic, 2002), whereas monazite grains recrystallized in the matrix show isotope chemical alteration.

Fluid-assisted dissolution and precipitation of minerals represents an efficient mechanism for isotope resetting of monazite even at very low-grade conditions (Cherniak et al., 2004; Gardés et al., 2007; Putnis, 2002, 2009; Putnis and Austrheim, 2010; Rasmussen and Muhling, 2007). Fluids promote (i) recrystallization of monazite at the expense of older monazite, and (ii) formation of new monazite from other P and LREE bearing minerals by dissolution and precipitation reactions, as is shown by natural rocks and experiments. The reprecipitated monazite will change in (isotope) chemical composition, and, if Pb (dominated by situ-grown radiogenic Pb) is removed, the U–Th–Pb system of this reprecipitated monazite will be juvenated (cf. to early experiments by Harlov et al., 2011; Seydoux-Guillaume et al., 2002; Teufel and Heinrich, 1997).

Although multiple chemical "age" domains within individual monazite grains may be dated by applying in-situ analytical methods, robust criteria are missing for discriminating recrystallized grain domains with a reset U–Th–Pb system from those showing only incomplete resetting (Goncalves et al., 2005; Poitrasson et al., 2002).

Monazite commonly incorporates negligible amounts of initial Pb. However, the mechanism of intra-grain coupled dissolution-reprecipitation may result in incomplete resetting of the U-Th-Pb-system of monazite, and thus in too old ages. Seydoux-Guillaume et al. (2003) showed that during the coupled dissolution-reprecipitation process of monazite, in-situ-grown radiogenic Pb is not removed from, but concentrated as nano-scale inclusions in the reprecipitated monazite.

The redistribution of Th, U and Pb within monazite grains may result in intra-grain patchy zones, resembling overgrowth or successive monazite generations. As a consequence, such monazite may yield too high or too low U-Th-(total-)Pb ages, and even apparently older monazite rims around a younger core have been observed (Goncalves et al., 2005). Importantly, only if Pb has been completely released from the crystal structure, and Th or U have not been depleted, the U-Th-Pb isotopic system is reset and geologically meaningful ages may be obtained. Therefore, intra-grain material transport processes, resulting in such nano-scale to grain-scale heterogeneities and patchy zones, must be better understood.

Fluid composition rather than temperature is the critical parameter for the extent of the dissolution precipitation process of monazite (Harlov and Hetherington, 2010; Seydoux-Guillaume et al., 2002). An alkali-rich fluid generated from feldspars enhances the reactivity of monazite, causing the coupled dissolution–reprecipitation (Hetherington and Harlov, 2008; Hetherington et al., 2010). As a result, distinct monazite grains within a rock sample or intra-grain domains may show specific U, Pb, Th, Y and REE contents.

However, various monazite compositions may record successive monazite generations tracing the REE redistribution in the metamorphic rock cycle (e.g. Crowley and Ghent, 1999; Janots et al., 2008; Poitrasson et al., 2002). In recent studies, the bulk chemical composition of monazite has been used to reconstruct the reaction history of REE-bearing accessory phases. Relevant reactions fractionating the LREE include garnet → xenotime and monazite → allanite + epidote + apatite (e.g., Finger and Krenn, 2007; Finger et al., 1998; Pyle et al., 2001), as well as feldspar and mica (Corrie and Kohn, 2008; Kohn and Malloy, 2004). Yet, few studies exist on the interaction between rock deformation, deformation mechanisms and metamorphic reactions assisted by dissolution and precipitation (cf. Putnis and Austrheim, 2010 and references therein), esp. involving monazite, and the resetting of its Pb isotopic signature (e.g. Dumond et al., 2008; Krohe and Wawrzenitz, 2000; Terry et al., 2000; Wintsch and Yi, 2002). The preservation of old

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