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Textural, geochronological and chemical constraints from polygenetic titanite and monogenetic apatite from a mid-crustal shear zone: An integrated EPMA, SIMS, and TIMS study

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Abstract

Titanites extracted from a 520±9 Ma syn-orogenic syenite at Otjimbingwe (Damara orogen, Namibia) show shape, colour and U–Pb systematics that vary with position in the syenite relative to a major shear zone. Most titanite fractions from syenite cropping out outside the shear zone are characterized by a medium brown anhedral core overgrown by a pale brown subhedral rim. EMPA and SIMS analyses show that the cores are enriched in Al, Fe and sometimes Na, Mg and Mn but also in REE, Nb and Zr relative to the rim. TIMS U–Pb ages from these titanites gave relatively imprecise $^{207}Pb/^{206}Pb$ ages between 680±21 Ma and 695±20 Ma as well as 570±8 Ma to 604±9 Ma mainly due to their low $^{206}Pb/^{204}Pb$ ratios. Combined Th–U–Pb relationships suggest that these titanites contain a component similar to ca. 715–750 Ma-old titanite populations observed so far only in Neoproterozoic syenites from the northern part of the orogen. Titanites from syenites within the shear zone are dark brown, mostly euhedral to subhedral and display only occasionally a pale brown rim. These titanites show decreasing concentrations of Na, Mg, Al and Fe and increasing concentrations of Mn from core to rim, interpreted to reflect growth zonation. Abundances of MREE, HREE, Y, Nb and Zr are higher in the rim than in the core. $^{207}Pb/^{206}Pb$ ages obtained on these titanites range from 470±2 Ma to 538±3 Ma for most samples. Only the samples with the highest $^{206}Pb/^{204}Pb$ ratios (between 350 and 230) have U–Pb ages similar to the previously published U–Pb zircon age of 520±9 Ma from the same complex. Other titanite fractions with lower $^{206}Pb/^{204}Pb$ ratios have slightly older ages than ca. 520 Ma, indicating some inheritance. Inherited titanite survived multiple metamorphic episodes in the Damara orogen between ca. 750 Ma and 470 Ma and the igneous event that lead to the intrusion of the Otjimbingwe syenite at 520 Ma; these data imply a high closure temperature of U–Pb in titanite of 650–>700 °C consistent with previous studies. Coeval apatite has no apparent inheritance, low $^{206}Pb/^{204}Pb$ ratios between 55 and 170 and U–Pb ages similar to, or only slightly younger than the U–Pb zircon or titanite age obtained on the titanite fractions with the highest $^{206}Pb/^{204}Pb$ ratios. Assuming a closure temperature for U–Pb of ≥900 °C for zircon, ~700 °C for titanite and ~450 °C for apatite, initial fast cooling of the complex can be inferred. Our data demonstrate that titanite can contain multiple age domains, preserving a chronological and chemical record of previous igneous events.

Keywords: U–Pb geochronology; Trace elements; Titanite; Apatite; Syenite; Damara orogen

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1. Introduction

Detailed studies of U–Pb chronology of accessory minerals (zircon, monazite, titanite, allanite, apatite, xenotime) together with high-spatial resolution analyses of major and trace elements of these accessory mineral phases are an essential prerequisite to understanding tectonometamorphic and/or igneous processes. Titanite is an accessory mineral that can contain U abundances at a sufficiently high level to make it a valuable chronometer. In contrast to zircon, titanite has chemical constituents that are major rock-forming elements and the mineral reactions that define the stability of titanite and the variable effects of pressure and temperature on solid solution compositions are reasonably well understood (for an excellent review see Frost et al., 2000). However, because numerous mineral phases in a titanite-bearing rock also contain Ca and Ti, titanite is much more reactive in high-temperature metamorphic and igneous environments than other accessory minerals which may result in complexly zoned titanite populations or multiple titanite populations, often displaying distinct ages.

The geological significance of U–Pb titanite ages is still a matter of debate (e.g. Frost et al., 2000) although titanite is a widely used geochronometer in metamorphic terranes (Mezger et al., 1991, 1993; Scott and St-Onge, 1995; Verts et al., 1996; Romer and Rötzler, 2003) and magmatic environments (Corfu, 1996; Zhang and Schärer, 1996; Pidgeon et al., 1996; Corfu and Stone, 1998). Titanites tend to yield concordant to moderately discordant U–Pb TIMS ages, which are close to or younger than the primary magmatic or metamorphic age as defined by coexisting zircon. However, there is often no clear distinction whether the U–Pb titanite ages reflect (i) the time of mineral formation, (ii) later closure during cooling, or (iii) subsolidus recrystallization and/or (iv) new growth during later events. U–Pb TIMS titanite ages that are younger than the age displayed by co-existing zircon are conventionally interpreted as a function of closure temperature which itself is dependent on diffusivity, the effective diffusion radius and cooling rate. Early empirical estimates for the closure temperature of U–Pb in titanite were ca. 500 °C based on studies that determined a temperature at which U–Pb ages of titanite were reset as a function of regional metamorphism (i.e., Tucker et al., 1986). Similarly, Mezger et al. (1991) have shown that titanite from slowly cooled (<1.5 °C/Ma) terranes may have a closure temperature of 500–550 °C although these authors also document similar U–Pb titanite, garnet and monazite ages from the same terrane, indicating that in this case, the analysed (large, 2 cm) titanite has a higher closure temperature of ca. 680–700 °C. More recent studies indicated similar high closure temperatures of 660 °C–>700 °C for various grain sizes and cooling rates (Scott and St-Onge, 1995; Verts et al., 1996). These higher estimates for U–Pb closure temperature in titanite are also compatible with experimental results provided by Cherniak (1993) who indicated closure temperatures between 660 and 700 °C for a grain size of 0.1 mm and cooling rates between 10–100 °C/Ma. In summary, an inferred maximum closure temperature for the U–Pb system in titanite of ca. 700 °C is lower than the inferred U–Pb closure temperature of zircon (>900 °C; Cherniak and Watson, 2001) but higher than the closure temperature of U–Pb in apatite (~450 °C; Chamberlain and Bowring, 2000). Thus, the age of titanite extracted from an igneous rock may be close to the age of the initial crystallization event.

Some studies have shown that diffusive Pb loss alone cannot explain complex U–Pb TIMS titanite data and inheritance of older components can severely complicate U–Pb systematics of titanite. Such distinct titanite populations are usually distinguished on the basis of grain size, colour and U–Pb ages (Corfu, 1996; Pidgeon et al., 1996; Verts et al., 1996; Zhang and Schärer, 1996; Aleinikoff et al., 2002; Romer and Rötzler, 2003). Igneous titanite may have fairly high U abundances (20–1000 ppm; Frost et al., 2000) but relatively minor amounts of common (i.e. non-radiogenic) Pb (0.2–10 ppm; Frost et al., 2000) whereas metamorphic titanite tend to have lower abundances of U and higher concentrations of common Pb. Therefore, an appropriate choice of the initial Pb isotope composition for correction of common Pb is required which should be obtained by analysing co-existing mineral phases with a low to very low U/Pb ratio, such as K-feldspar.

In contrast to titanite, the U–Pb systematics of igneous apatite are probably solely controlled by simple volume diffusion, whereas evidence of secondary growth or recrystallization is not available (see Chamberlain and Bowring, 2000 for an excellent review). Apatite, like titanite generally has low to moderate abundances of U ranging from 5 to 150 ppm and also low to moderate abundances of Pb (3–135 ppm; Chamberlain and Bowring, 2000). These characteristics usually result in low to moderate ratios of radiogenic Pb to common Pb. It is conventionally argued that U and Pb are lattice-bound and therefore the U–Pb systematics are not controlled by microinclusions. The closure temperature for the U–Pb system in apatite is estimated to range from ca. 400 °C to 530 °C at diffusion radii of 10–50 μm and cooling rates of 2–100 °C/Ma (Cherniak et al., 1991,