Application of Zirconium-in-rutile and Titanium-in-zircon Geothermometry to UHT Metamorphic Rocks from the Epembe Unit (Epupa Complex, NW Namibia)

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Summary

This study deals with the application of zirconium-in-rutile and titanium-in-zircon geothermometry to UHT metamorphic rocks. Besides a systematic comparison of the different calibrations for each thermometer a comparison of both thermometers is presented.

Besides other trace-elements, the crucial elements for the applied thermometers were measured and temperatures were calculated. A broad range of temperature values was obtained covering a range of several 100°C from below minimum values of the calibration to ~1200°C for the Zr-in-rutile and ~750°C to ~1250°C for the Ti-in-zircon thermometer.

This somewhat unexpected result (all samples experienced the same ultrahigh-temperature metamorphic conditions) is interpreted to be related to proceeding trace-element exchange by fluid-mediated recrystallization during the retrograde metamorphic evolution. Discrepancies between both thermometers may be attributed to the different diffusion rates and closure temperatures of the respective minerals. Moreover the different behavior of zircon and rutile during recrystallization and dissolution under retrograde conditions is probably also a decisive factor.

In general, zircon seems to be more robust during retrogression from UHT conditions, compared to rutile, since Ti-in-zircon thermometry yields on average higher temperatures and a higher percentage of peak-metamorphic UHT conditions.

Introduction

Due to methodical advancements new (trace element-dependant) geothermometers involving accessory minerals such as titanite, rutile and zircon were introduced over the last couple of years. These geothermometers are a considerable improvement compared to 'conventional' geothermometers, since their application only requires analysis of certain trace elements in single accessory minerals. Furthermore, their 'closure' temperature is often much higher than that of conventional geothermometers. This study deals with the zirconium-in-rutile and titanium-in-zircon geothermometers and provides a systematic comparison of the different calibrations. Additionally, the applicability of these thermometers to rocks which have experienced an ultrahigh-temperature metamorphic event and a strong retrograde overprint was investigated.

Regional setting

The samples investigated in this study stem from the Epembe Unit of the Epupa Complex, a high-grade metamorphic gneiss terrane which is exposed in north-western Namibia. The volcano-sedimentary protoliths of the Epembe Unit were accumulated in the early Palaeoproterozoic in a back-arc basin along the south-western margin of the Congo Craton (Brandt et al., 2003, 2007). During the Eburnian Orogeny (ca. 2.25 to 1.6 Ga) the volcano-sedimentary rocks were buried into mid-crustal levels, accompanied by the emplacement of granite intrusions during the post-collisional stage (Brandt et al., 2003). In the Mesoproterozoic (ca. 1.5 Ga, Seth et al., 2003) the ortho-and paragneisses of the Epembe Unit were affected by ultrahigh-temperature granulite-facies metamorphism with PT conditions of 9.5 kbar and 970 – 1000°C (Brandt et al., 2003; 2007). The emplacement of the huge massif-type anorthositic Kunene Intrusive Complex is suggested to be responsible for the UHT metamorphism of the Epembe Unit.

Theory and/or Method

Besides other trace elements, zirconium was determined by LA-ICP-MS in 99 rutile grains (a total of 130 spots) and zirconium was measured in 49 zircon grains (a total of 57 spots). In order to check trace-element zoning within single rutile grains, additional electron microprobe analyses (BSE images, mapping) were conducted for selected grains (with more than one LA-spot, bigger grain-size, Zr-concentration >1 wt.%).

Eleven different samples which represent six different rock types were selected for analyses (i.e. mafic Grt-Cpx granulite, metagreywacke-type Grt gneiss, metapelitic Grt-Sil gneiss (Qtz-bearing and Qtz-free), metagreywacke-type Mg-rich Grt-Opx gneiss, Qtz-rich Grt-Opx rock and saphhirine-bearing Opx-Sil gneiss).

For temperature calculation the calibrations of Zack et al. (2004), Watson et al. (2006), Tomkins et al. (2007) and Ferry & Watson (2007) were applied for Zr-in-rutile geothermometry and a comparison of the calibrations of Watson et al. (2006) and Ferry & Watson (2007) was conducted for Ti-in-zircon geothermometry.

Results

Apart from the calibration of Zack et al. (2004), all other Zr-in-rutile geothermometers give a similar temperature range from below minimum values of the calibrations to ~1200°C, while the two Ti-in-zircon thermometers yield a temperature range between ~750°C and ~1250°C.

Some grains – in particular rutile which has on average a larger grain-size than zircon – exhibit chemical inter-grain variation. However, no uniform trend was observed since both peak and retrograde metamorphic trends occur on thin section scale.

Some rutile grains contain tiny exsolutions of a Zr-silica-phase, which is visible in BSE images and occurs in local domains or throughout the respective grains (Fig. 1 and 2). Consequently LA-ICP-MS measurements in an area with such Zr-rich exsolutions yield higher Zr concentrations than in a part of the mineral without inclusions. However, these exsolutions only occur in a few grains and therefore this local feature does not substantiate the wide range of Zr concentrations in the analyzed rutile grains. ^{29}Si was checked as an indicator for submicroscopic Zr-silica-rich exsolutions in rutile grains.

A further important result of the study is that systematic chemical differences, which could be related to the textural position of the respective grain are not observed. Rutile and zircon grains, of the matrix (open system) or enclosed and shielded by other minerals (with a tendency to closed system) record a similar wide range of for peak-metamorphic conditions.

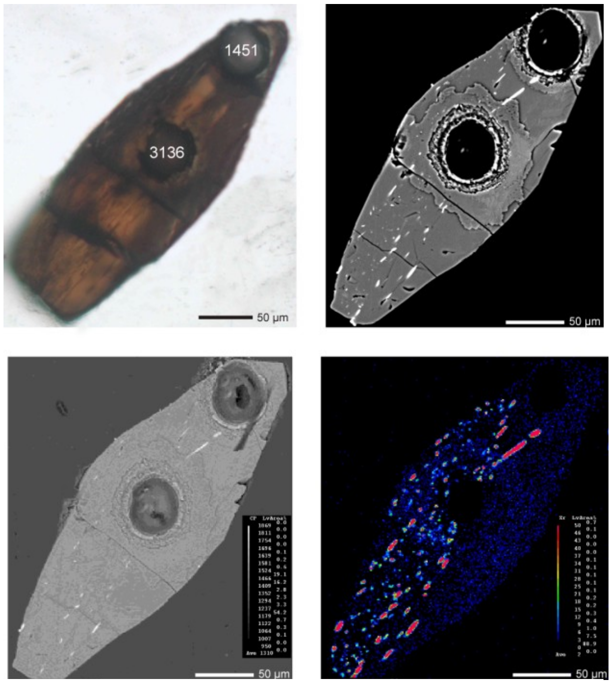

Fig. 1: Tiny Zr-rich exsolutions in only part of a rutile mineral grain cause heterogenous Zr-element distribution (sample 693-1).

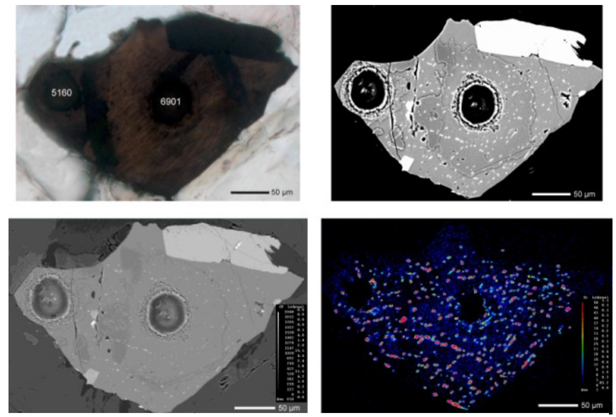

Fig. 2: Tiny Zr-rich inclusions homogenously distributed in a rutile grain (sample 693-4).

Conclusions

The wide range of temperatures was somewhat unexpected since all samples experienced the same ultrahigh-temperature metamorphic conditions and thus should have preserved trace-element concentrations in agreement with this high-grade metamorphic event. The estimated wide temperature range is interpreted to be related to proceeding trace element exchange by extensive fluid-mediated recrystallization during the retrograde metamorphic evolution. This interpretation is supported by the presence of abundant retrograde reaction textures preserved in all samples. Several retrograde metamorphic stages have been reconstructed from these reaction textures and mineral assemblages. While the early retrograde evolution is characterized by the development of decompressional corona and symplectite textures around peak-metamorphic phases, subsequent cooling led to the re-growth of biotite and garnet (Brandt et al., 2007).

There is a significant discrepancy between the temperature range obtained by the Ti-in-zircon and the Zr-in-rutile thermometry. The wider temperature distribution displayed by the Zr-in-rutile thermometer may be attributed to the different diffusion rates and closure temperatures for trace elements in zircon and rutile (e.g. Cherniak and Watson, 2007; Cherniak et al., 2007). Moreover the different behavior of zircon and rutile during recrystallization and dissolution under retrograde conditions is probably also a decisive factor. The closure temperature of rutile is suggested to be much lower than that of zircon and diffusion-rates for Zr in rutile are higher than Ti in zircon, which is decisive for diffusion-related processes under high temperature conditions. Thus, it is likely that rutile preserves UHT conditions less frequently than zircon.

This assumption is supported by the present study, since only 15% (20 of 130) of the rutile trace element measurements yield sufficient Zr consistent with UHT conditions whereas about 33% (19 of 57) of the zircon analyses display sufficient Ti. Moreover, the partly very low temperatures (700°C and below) recorded by the Zr-in-rutile thermomometer are consistent with a less robust behaviour of rutile, compared to zircon, during retrogression from UHT conditions. These observations indicate that the recognition of peak-metamorphic UHT conditions is more likely with the application of the Ti-in-zircon geothermometer.

However, about 67% of the analyzed zircon grains do not preserve enough Ti to be in agreement with UHT conditions. Some of these grains contain microfabrics indicating melt-relicts which are an important feature in order to explain retrograde conversion and zoning of single minerals. Evidence of a melt as given by these microfabrics or a migmatitic texture is important since it allows for much faster diffusion rates in the otherwise dry metamorphic system causing additional retrograde re-equilibration.

A further surprising result of this study is that the trace element composition of rutile and zircon does not depend on the textural appearance of these minerals.

Acknowledgements

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