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# Integrating geochronological and mineral-scale trace element data to understand metamorphic histories: examples from the Limpopo Belt, South Africa.

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## Introduction

Constraining the timing of high-grade metamorphism is commonly difficult because age determinations that involve U-Pb geochronology of accessory phases need to be linked to pressure-temperature-time (P-T-t) paths recorded by the growth/resorption of P-T sensitive silicate minerals. Making this link is non-trivial because accessory phases may potentially: 1) pre-date metamorphism (eg detrital zircon); 2) grow during along prograde, peak or retrograde segments of the P-T-t path; or 3) form due to solid-state recrystallization of pre-existing grains at any time during metamorphism. In addition, metamorphic terranes may have been metamorphosed to high grade more than once. Determining whether rocks have mono- or polycyclic high-grade histories is itself commonly difficult because major element compositional discontinuities that might indicate, for example, multiple garnet growth events are commonly erased by volume diffusion at temperatures above $\sim$700-750 ˚C. In contrast, diffusion rates for trace elements, including the REE are commonly much slower than for major elements such as Fe and Mg in garnet, making it possible to use these tracers to determine growth histories in otherwise compositionally homogeneous grains. Integration of high-spatial resolution geochronology with the intra-grain scale trace element chemistry of dated accessory phases and major rock-forming minerals provides a mechanism for better constraining the timing of high-grade (poly)metamorphism.

The Central Zone of the Limpopo Belt of southern Africa is a terrain where the timing and distribution of polyphase granulite-facies metamorphism is uncertain. The Central Zone contains metasediments whose precursors were deposited at $\sim$3.3 Ga and at $\sim$2.7-2.2 Ga. It underwent high-grade metamorphic events at $\sim$2.7-2.5 Ga and $\sim$2.03 Ga. The importance of, and P-T-t path associated with these events remains controversial, as does which parts of the CZ experienced only the last ($\sim$2.03 Ga) granulite-grade event. In this contribution we integrate U-Pb geochronology of accessory phases and La-ICPMS trace element geochemistry of these accessory phases and coexisting silicate minerals to address several aspects of the temporal evolution of the Limpopo Belt.

**A U-Pb and trace element study of the petrogenesis of unusual feldspar-free metapelites**

Aluminous garnet-, cordierite-, biotite- and gedrite-bearing, feldspar-free gneisses from the western Central Zone reached granulite-facies conditions ($T>800$ ˚C at 8-10 kbar) followed by decompression. Garnet from one such sample shows significant zonation in trace elements but little in major elements. Zoning patterns imply that multiple accessory phases contributed to the garnet trace element budget, and suggest that the rock experienced a single high-grade metamorphic event. Inclusions of staurolite in garnet indicate that the rock followed a prograde path from the amphibolite to the granulite facies. Monazite from the sample yielded a SHRIMP weighted mean $^{207}$Pb-$^{206}$Pb age of 2028 $\pm$ 3 Ma, indistinguishable from a SHRIMP zircon age of 2022 $\pm$ 11 Ma measured on metamorphic overgrowths on $\sim$2.69 Ga detrital zircon cores of igneous provenance. New zircon and monazite formed before, or at the metamorphic peak, and occur as abundant inclusions in peak-metamorphic garnet. Monazite appears to have formed through the breakdown of early allanite$\pm$apatite. Both monazite and low $\sim$2.02 Ga Th/U zircon overgrowths appear to be in approximate trace element equilibrium with garnet, suggesting that the rock underwent a single cycle of high-grade metamorphism at $\sim$ 2.03 Ga.

The plagioclase and K-feldspar-free bulk composition of the garnet-cordierite-gedrite metasedimentary gneisses requires open system processes such as intense hydrothermal alteration of protoliths or advanced chemical weathering. In the studied sample, the $\sim$2.69 Ga igneous zircons show prominent negative Eu anomalies, suggesting equilibrium with plagioclase. In contrast, the other minerals either show very small negative ($\sim$2.03 Ga monazite), no ($\sim$2.02 Ga zircon and garnet) or positive Eu anomalies (gedrite). This suggests that the usual bulk compositions of the garnet-, cordierite- and orthoamphibole-bearing rocks were set in after $\sim$2.69 Ga but before the peak of the 2.03 Ga event, while the protoliths resided at shallow or surficial crustal levels.

**A U-Pb and trace element study of alteration of high-grade metabasites**

High-grade metabasites (amphibolites: quartz-hornblende-clinopyroxene-plagioclase) from the easternmost Central Zone are locally cut by discordant, patch-like epidote-bearing pegmatites. The pegmatites are spatially associated with discordant quartz vein stockworks in the amphibolites; these are surrounded by alteration halos rich in either diopside or tremolite that replace the host amphibolite. Textural evidence suggests that the tremolite alteration zone itself replaces the diopside zone. Alteration of the metabasites was related to sub-solidus processes, most likely due to exsolution of fluid from crystallisation of the pegmatites during cooling. MC-ICPMS dating of titanite from the alteration zones yields a weighted mean $^{207}$Pb/$^{206}$Pb age of 2029$\pm$1 Ma. The significance of this age is unclear. It is the same as recorded in peak granulite-facies assemblages elsewhere in the Central Zone. However, local anatectic patches in these migmatitic rocks locally contain zircons as young as $\sim$2.05 Ga, suggesting that they did not cool below the solidus until this time. This suggests either that the titanite in the metabasite alteration zones is inherited from the unaltered amphibolite, or that it formed in the alteration zones; the latter requires that the easternmost Central Zone was at amphibolite-facies (sub-solidus) temperatures at the same time that the western and central parts of the Central Zone were at granulite-facies conditions.

Several lines of evidence suggests that titanite formed as part of the alteration halo associated with crystallisation of the pegmatites: 1) it contains inclusions of Mg-rich diopside ($X_{Mg}$ = 0.97-0.98) that is identical in major element composition to that in the diopside alteration zones, but distinct in composition from that in the host amphibolite ($X_{Mg}$ =0.79); 2) it is abundant in the alteration zones but very rare to absent in the host amphibolites; 3) based on empirical titanite-clinopyroxene-hornblende REE partitioning at similar grades, titanite in the alteration zones is too REE-rich to have been in equilibrium with clinopyroxene or hornblende in the unaltered amphibolite host rock. In contrast, it is in approximate REE equilibrium with REE-poor diopside in the diopside-rich ($>$98% diopside) alteration zones. It has identical REE patterns in the diopside and tremolite alteration zones; however it is not in REE equilibrium with tremolite in the tremolite-rich alteration zone. The massive diopside alteration zones developed at $\sim$2.029 Ga, at the same time that granulites in the west and central parts of the Central Zone reached peak granulite-facies conditions. This suggests that either cooling across the Central Zone was diachronous, or that parts of the Central Zone never reached granulite-facies conditions.

In both case studies correct interpretation of the geochronological data requires its integration with textural information and high-spatial resolution trace element data.