High-precision U-Pb dating of actinide-rich accessory minerals - Using high-precision petrochronology to unravel the timing of complex magmatic and metamorphic processes

Schaltegger, U.[1,*]

[1] University of Geneva, Department of Earth Sciences, rue des Maraîchers 13, CH-1205 Geneva
** E-Mail: urs.schaltegger@unige.ch*

Accessory minerals are important containers of information about time and intrinsic parameters during the crystallisation of the mineral constituents of a rock. In addition, they may reveal the sources of melts or fluids and are also capable of recording multiple geological cycles of formation and destruction of geological materials.

Actinide-rich accessories, mainly zircon ($ZrSiO_4$) and baddeleyite (ZrO_2), but also the phosphates monazite ($CePO_4$) and xenotime (YPO_4), and titanite ($CaTiSiO_5$), play an exceptional role in reconstructing the timing of geological processes, because they are amenable to isotopic age determination. Linking time with the chemical and physical state of the system in which these minerals crystallize is called "petrochronology". The aim of petrochronology is to relate an age determination as closely as possible with elemental and isotopic composition of the dated mineral (trace element concentrations and Hf, Nd, Pb or Sr isotopes; see Fig. 1 for an example of a workflow). In an optimal case, the mineral grain has already been characterized for its textural and petrological environment (using, e.g., QEMScan on polished thin sections), and has been imaged using CL and or BSE prior to chemical and isotopic analysis. In-situ analysis using laser ablation or ion beam sputtering can yield information on chemical (trace elements, REE) and isotopic (O, Hf) composition, and is followed by high-precision, chemical abrasion, isotope-dilution TIMS U-Pb geochronology (Schaltegger et al. 2015) of carefully selected grains, possibly even followed by TIMS-TEA trace element and Hf isotopic analysis (Schoene et al. 2010). Magmatic processes last for 10^4 to 10^5 years and are therefore too rapid to reasonably apply low-precision LA-ICP-MS or SIMS U-Pb dating techniques for rocks that are older than 10 Ma.

Petrochronology of zircon in intermediate to felsic magmatic rocks will allow reconstruction of the temperature variations in the magma, causing successive periods of growth and resorption. It allows us to reconstruct the evolution of a magmatic plumbing system at intermediate to upper crustal levels, to model crystal fractionation paths and crystal content (see recent review by Schaltegger and Davies 2017).

The discrepancy between thermal models predicting 10^3-10^4 years' durations of crystallization at emplacement level, and the 10^5–10^6 years apparent duration of zircon crystallization implies that zircon is mostly crystallized at larger depth than the final intrusion level, is stored at temperatures close to the solidus in mushes and gets rejuvenated during phases of recharge by hot magma, which remobilizes crystal mushes and injects them to upper crustal levels. The resulting probability density distribution curves of zircon dates allows estimation and quantitative modeling of crystal contents of magmas, and of magma volumes and fluxes (Caricchi et al. 2014). The final solidification at upper crustal level may be approximated by ID-TIMS dating using titanite. However, due to the presence of initial Pb, titanite often cannot provide significant age information when compared to high-precision zircon dates.

High precision U-Pb geochronology in mafic rocks is limited by the abundance of zircon. Application of chemical abrasion techniques to zircon ensures that the effects of

Pb loss are removed, resulting in reliable and accurate ages. Another datable mineral in mafic systems is baddeleyite, for which there are no currently accepted techniques to remove the effect of Pb loss; therefore, baddeleyite dates are often scattered and biased to various degrees by post-crystallization Pb loss. Theoretically, in a cooling mafic melt with high Zr concentrations, baddeleyite saturation may be reached before silica saturation and zircon crystallization. Both zircon and baddeleyite will be saturated only at a late stage of evolution in a felsic residual melt, after abundant fractional crystallization of olivine, pyroxene, amphibole and plagioclase, and thus date the final eutectic solidification.

Monazite and xenotime are used for age determination in metamorphic rocks and in crustally-derived granites, where ID-TIMS zircon U-Pb dates are biased by inherited radiogenic Pb from the previous evolutionary history. Monazite shows similarly refractory behaviour even under conditions of partial melting, as long as it is not involved in chemical reactions. Complex U-Pb systematics (multiple growth periods, dissolution/reprecipitation, recrystallization) of monazite in amphibolite facies metamorphic rocks are leading to age scatter and require careful application of petrological tools prior to dating.

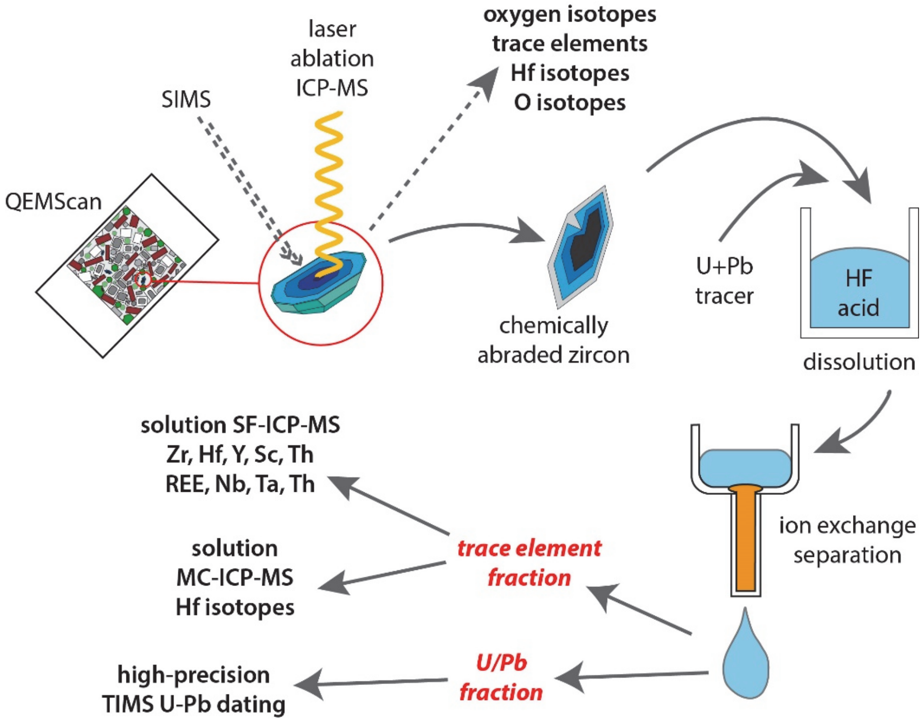

Fig. 1. *Petrochronology workflow*

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