

## U-Pb discordance in titanite and the interpretation of the thermal history of metamorphic rocks

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Titanite is a common accessory mineral suitable for precise U-Pb dating of metamorphic and fluid events. In polymetamorphic terrains titanite may record multiple geological events either as new crystallization, recrystallization, or Pb-loss. Discordance, both normal and reverse, is commonly observed and may be caused by a variety of processes including: mixing, recrystallization, Pb-loss, inaccurate common Pb composition, as well as analytically-induced U-Pb fractionation. Understanding the cause of discordance is essential for accurate geological interpretations. Because titanite incorporates significant Pb, reverse discordance can result from incorporation of radiogenic Pb during the recrystallization or breakdown of pre-cursor, high- $\mu$  minerals in metamorphic rocks. However, in many cases the Pb composition required is not geologically reasonable. U-Pb fractionation may result during mineral preparation and dissolution. Approximately 7% of ~350 titanite analyses (> 1000 Ma) carried out at the GSC over a four year period in the 1990's are greater than 1.0% negatively discordant, with a small number up to -25% discordant. Dissolution was carried out in HF-HNO<sub>3</sub> in high-pressure Teflon vessels similar to those used for zircon. Experiments have been carried out to test for differential leaching of Pb and U in titanite during mineral preparation prior to analysis. Titanite was leached in cold and warm, 1 to 3N HNO<sub>3</sub> and 1 N HBr solutions over periods of 5 to 60 minutes. Up to 6% of total radiogenic Pb\*, along with common Pbc were leached during the washing process. Maximum Pb\* leaching occurred in warm HNO<sub>3</sub> after 5 minutes with little additional extraction at 15 and 60 minute intervals. HBr solutions had the least affect. Leaching is enhanced with temperature. In contrast, leached U accounted for less than 1% of the total U in the sample. Preferential leaching of Pb\* is consistent with it being located in radiation-damaged sites and acid washing is most likely to produce normal discordance in the residue. This produces scatter about Concordia that can mistakenly be interpreted as real age variation. However, leaching is it not a viable explanation for reverse discordance. Alternative explanations including incomplete dissolution or the effects of insoluble fluorides need to be further evaluated.

## (U-Th)/He dating of epidote and andradite garnet

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In order to expand the range of dateable minerals and temperature range of thermal histories accessible by the (U-Th)/He system, we have explored the potential of He dating of andradite garnet and epidote from several locations, including skarn deposits and hydrothermal Alpine veins, using laser-heating in Nb-foil for He extraction/measurement, followed by total dissolution and isotope dilution for U-Th measurements.

Multiple replicates of core chips of large (~1 cm) andradite garnet crystals from the 76 Ma Ocna de Fier (OF) skarn deposit in SW Romania yield strongly contrasting U contents (<1 to >40 ppm), but reproducible He ages of  $73.8 \pm 2.6$  Ma ( $2\sigma$ ). The similarity of these cooling ages to the zircon U/Pb and FT ages (76 and 73 Ma, respectively) from this deposit indicate rapid cooling, however, preventing estimation of a garnet (U-Th)/He closure temperature, except to say that it must be significantly higher than that of apatite fission-track (~110 °C), which yields an age of 68 Ma.

Epidote analyses from subaerial rocks with well-constrained thermal histories (OF skarns and Wallowa Mtns., Oregon) yielded U concentrations in the range of < 0.2 -3.0 ppm, and He ages systematically younger than apatite He ages on the same rocks, but poor reproducibility. Multiple replicates of OF skarn epidotes, for example, gave He ages of 16-29 Ma, compared with apatite and zircon He ages of 36 and 76 Ma, respectively, and Wallowa Mtns. epidote gave He ages of 2-11 Ma, compared with apatite and zircon He ages of 15-16 and 95-100 Ma, respectively. If the effective epidote He closure temperature is actually lower than that of apatite, small thermal perturbations like wildfires and diurnal heating may partially reset epidote He ages in subaerial samples. We tested this by dating epidote crystal core chips from the Knappenwand Alpine vein (Tauern Window, Austria), which was not exposed to surficial temperature fluctuations until recent mining. Similar to other samples, multiple replicates of these relatively U enriched (1 – 5 ppm) epidotes yielded He ages (4.5-6.0 Ma) younger than the apatite FT ages (~8 Ma), but in contrast to the subaerially exposed samples, the Knappenwand epidote ages showed much better reproducibility.

We suggest that epidote has an unexpectedly high He diffusivity, given its ionic porosity, and a (U-Th)/He closure temperature lower than that of apatite, making it sensitive to thermal perturbations less than 50-60 °C. Ongoing He diffusion experiments will further constrain He diffusivity characteristics in epidote. While high He diffusivity may make dating of subaerially exposed samples difficult, it may also provide a powerful tool for thermochronometry of submarine or subterranean samples, or other applications.