A new method for cassiterite ID-TIMS U-Pb geochronology and limitations on the accuracy of common Pb-bearing hydrothermal mineral ages

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Cassiterite (SnO_2) is the most common ore phase of Sn. Typically containing 1-100 µg/g U and relatively low concentrations of common Pb the mineral has been increasingly targeted for U-Pb geochronology by micro-beam methods to understand the timing and durations of granite related magmatic-hydrothermal systems throughout geological time. However, due to the extreme resistance of cassiterite to most forms of acid digestion, to date, there has been no method permitting the complete, closed system dissolution of cassiterite under conditions where the basic necessities of measurement by isotope dilution can be met, leading to a paucity of reference, and validation materials.

To address this a new method for the complete acid digestion utilising HBr, U and Pb purification, and low (<1 pg) Pb blank ID-TIMS U-Pb analysis of cassiterite has been developed. Dissolution rates have been experimentally evaluated under a range of conditions. A careful balance of time and temperature is required due to competing effects (e.g. HBr oxidation and PFA reactions) yet dissolution of <500 μm^3 cassiterite is readily achievable over periods comparable to zircon dissolution. Its acid resistant nature can be turned into an advantage, by leaching common Pb-bearing phases (e.g. sulfides, silicates) without disturbing the U-Pb systematics of the cassiterite lattice.

The archetypal Sn-W greisen deposit of Cligga Head, SW England, is used to define accuracy relative to CA-ID-TIMS zircon U-Pb ages and demonstrate the potential of this new method, for resolving high resolution timescales (<0.1%) of magmatic-hydrothermal systems. However, analyses also indicate that the isotopic composition of initial common Pb varies significantly, both between crystals and within a single crystal. This is attributed to significant fluid-rock interactions and the highly F-rich acidic nature of the hydrothermal system. At micro-beam precision levels, this issue is largely unresolvable and can result in significant inaccuracy (~2%) in ages. However, this new method can, for the first time, be used to properly characterise suitable reference materials for micro-beam cassiterite U-Pb analyses, thus improving the accuracy of the method as a whole.