Reconsidering initial Pb in titanite in the context of in situ dating

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ABSTRACT

In situ U-Pb dating of titanite, which can preserve trace-element records of various petrologic processes but also incorporates significant initial Pb, has proliferated in recent years. The widespread use of titanite data to construct tectonic P-T-t paths warrants careful assessment of the available dating techniques, as well as attention to the assumptions that underpin the U-Pb data analysis. This contribution provides the first direct comparison of the two major analytical methods [SHRIMP (SIMS) and LA-ICP-MS] for in situ U-Pb titanite dating. A set of well-characterized titanite grains from Harrisville, New York, in the Adirondack Mountains were analyzed for U-Th-Pb isotopes along the same cross-grain traverses by Sensitive High Resolution Ion Microprobe (SHRIMP) and LA-ICP-MS. Both LA-ICP-MS and SHRIMP data sets define approximately linear arrays on the Tera-Wasserburg Concordia (semi-total Pb/U) diagram and would commonly be interpreted as representing a single date population with minor scatter. However, previous studies have suggested that Adirondack titanite actually records two regionally well-defined thermal events, ~50–100 m.y. apart. When titanite data arrays are treated in detail, attempts to determine concordia-intercept ages by robust three-dimensional linear regression produce large uncertainties and/or poor fit statistics that suggest that the data are not, in fact, isochronous. Grain-by-grain analysis of U-Pb titanite data shows that different subsets of titanite (determined by additional geochemical and microstructural data) show different patterns of U-Pb data. By comparing predictions for Pb-ingrowth evolution paths in Tera-Wasserburg diagrams with observed data, it is possible to recognize both a change in initial Pb composition and Pb loss in the Adirondack titanite U-Pb data set. This study provides an example of how greater geochronologic detail can be extracted from large in situ U-Pb titanite data sets. Even when precise dates are not recovered, geological processes and events that cause data scatter can be recognized through analysis of U-Pb data patterns using the Tera-Wasserburg diagram.

Keywords: Titanite, U-Pb geochronology, initial Pb correction, LA-ICP-MS, SHRIMP

INTRODUCTION

Titanite is an increasingly popular U-Pb geochronometer and petrogenetic indicator in the study of crystalline rocks (e.g., Aleinikoff et al. 2002, 2004; Chen et al. 2016; Essex and Gromet 2000; Gao et al. 2012; Garber et al. 2017; Holder and Hacker 2019; Jung and Hellebrand 2007; Kirkland et al. 2016, 2017; Kohn 2017; Kohn and Corrie 2011; Li et al. 2010; Marsh and Smye 2017; Olierook et al. 2019; Papapavlou et al. 2017, 2018; Sciborski et al. 2019; Stearns et al. 2015; Storey et al. 2007; Timms et al. 2019). By comparison to zircon, titanite is more reactive and therefore has the potential to display a greater range of petrologic, geochemical, and microstructural variations to inform interpretations of petrogenesis and deformation (Kohn 2017). The major challenges in applying titanite as a geochronometer are its generally low U and radiogenic Pb concentrations and its tendency to incorporate substantial initial Pb (e.g., Aleinikoff et al. 2002; Frost et al. 2000; Prowatke and Klemme 2005; Tiepolo et al. 2002).

Initial Pb (Pb0) must be corrected for and that complicates accurate U-Pb geochronometry of high-Pb phases, like titanite, apatite, allanite, and rutile (e.g., Chew et al. 2014; Kirkland et al. 2017; Rubatto and Scambelluri 2003; Schoene and Bowring 2006; Wohlgemuth-Ueberwasser et al. 2017) Here, we use Pb0 to mean the Pb that is incorporated into a mineral at the time of crystallization or recrystallization, irrespective of its source and isotopic composition. Pb0 includes what is often called “common Pb,” Pb representing long-term ingrowth from actinides incorporated in the primordial Earth (Stacey and Kramers 1975). Pb0 can also include Pb acquired from nearby actinide-partitioning minerals that have ingrown Pb with a non-primordial isotopic composition. The most widely used Pb0 corrections derive from the models of Stacey and Kramers (1975) and involve assumptions about Pb0 composition based on the average, reservoir-scale geochemical behavior of Pb—i.e., assumptions about crustal evolution at the scale of an orogenic region, a crustal domain, or even bulk silicate Earth. For Pb0 corrections that employ these models to be accurate, the geochronology sample to which they are applied must be compositionally representative of the large-scale reference reservoir, a requirement that is problematic in the context of intragrain U-Pb measurements. Techniques for in situ U-Pb dating, like Secondary Ion Mass Spectrometry (SIMS), Sensitive High Resolution Ion Microprobe (SHRIMP), and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), complicate Pb0 corrections because they sample micrometer-scale intracrystalline domains (compositional zones), which may now be chemically