Earth-Science Reviews 176 (2018) 87–116

Contents lists available at ScienceDirect

Earth-Science Reviews

journal homepage: www.elsevier.com/locate/earscirev

Use and abuse of zircon-based thermometers: A critical review and a recommended approach to identify antecrystic zircons

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ARTICLE INFO

Keywords:
Zircon
Magmatism
Autocryst
Antecryst
Geothermometry
Granite petrogenesis

ABSTRACT

Zircon- and bulk-rock Zr-based thermometric parameters have become fundamental to petrogenetic models of magmatism, from which broader geochronological and tectonic implications are being made. In particular, petrogenetic models have become increasingly reliant on Ti concentration in zircon geothermometry (T_{ZircTi}) and zircon saturation temperature ($T_{Zircsat}$). A feature of many of these studies is an implicit assumption that all zircons present in the host igneous rock are autocrystic, that is, crystallised from the surrounding melt. However, it has long been recognised that zircons present in an igneous rock can be inherited either from the surrounding country rock or source region (xenocrysts), or from earlier phases of magmatism or the magmatic plumbing system (antecrysts). Distinguishing these different origins for zircon crystals or domains within crystals is not straightforward.

Here, we first review the utility and reliability of zircon-based thermometers for petrogenetic studies and show that $T_{Zircsat}$ is a theoretical temperature and cannot be used to constrain magmatic or partial melting temperatures. It is a dynamic variable that changes during magma crystallisation, and essentially increases as fractional crystallisation proceeds, whereas true magmatic temperatures (T_{Magma}) decrease. Generally, in Temperature-SiO_2 space, the cross-over point of these two temperatures is magmatic system dependent, and also affected by the type of calibration used for the $T_{Zircsat}$ calculations. Consequently, each magmatic system needs to be evaluated independently to assess the validity and usefulness of $T_{Zircsat}$. A fundamental conclusion of $T_{Zircsat}$ and T_{Magma} relationships assessed here is that new zircon generally only crystallises in silicic (granitic/rhyolitic) melt compositions, and thus autocrystic zircons should not be assumed to be present in igneous rocks with bulk compositions < 64 wt% SiO_2, although inherited and minor zircons crystallising from late-stage differentiated melt pockets can be present. This highlights the importance of discriminating autocrystic from inherited zircons in igneous rocks.

We then review techniques available to discriminate autocrystic from inherited zircons, and propose a new methodology to assist in the identification of autocrystic zircons for emplacement age determination and separate evaluation of inherited zircon components. The approach uses two strands of data: 1) zircon data such as zircon morphologies, textures, compositions and U-Pb ages, and 2) whole-rock data, in particular SiO_2 and coupled geothermometry ($T_{Zircsat}$ and T_{Magma}) to estimate whether the magma was zircon-saturated or undersaturated. To test this new protocol, we use as examples, several Phanerozoic granitic rocks intersected by drilling in Queensland where contextual information is limited, and show how antecrystic and xenocrystic zircons and monazites can be distinguished. In contrast, where zircons are metamict (for example, high U and Th-rich zircons), much of the ability to discriminate is impacted because such zircons have suffered Pb loss and have modified compositions (e.g., higher T_{ZircTi}). We recommend an integrated approach incorporating whole-rock chemistry, independent geothermometric constraints, zircon composition, textures and ages obtained by routine cathodoluminescence and LA-ICP-MS or ion microprobe analysis to provide increased confidence for the discrimination of inherited zircons from autocrystic zircons and determination of the emplacement age.

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http://dx.doi.org/10.1016/j.earscirev.2017.08.011
Received 2 February 2017; Received in revised form 29 July 2017; Accepted 18 August 2017
Available online 30 August 2017

1. Introduction

Zircon is a key mineral for geological studies due to its occurrence in a wide range of rock types, its geochemical resilience in a range of geologic environments and conditions, and lack of incorporation of common Pb during crystal growth facilitating radiometric dating. Zircon is commonly used to: 1) determine the emplacement ages of igneous rocks thereby providing chronostratigraphic constraints with application to the definition of geologic time boundaries, terrane histories and correlations, regional tectonics, plate reconstructions and supercontinent cycles (Li et al., 2002; Kamo et al., 2003; Ramezani et al., 2007; Hawkesworth et al., 2010; Cramer et al., 2015; Faleiros et al., 2016; Sheppard et al., 2016), 2) define timescales of magma generation and eruption, with implications for the understanding of volcanic hazards (e.g., Reid et al., 1997; Brown and Fletcher, 1999; Charlier et al., 2005; Turner and Costa, 2007), 3) constrain sediment provenance (e.g., Thomas, 2011; Gehrels, 2014), 4) evaluate the conditions of granite petrogenesis (e.g., Hogan and Sinha, 1991; Chappell et al., 1998; Miller et al., 2003; Kemp et al., 2005; Bea et al., 2007; Collins et al., 2016), including Hadean conditions of silicic magma generation (e.g., Peck et al., 2001; Harrison et al., 2008), and 5) unravel the nature and evolution of crustal sources (Hawkesworth and Kemp, 2006; Kemp et al., 2006). Despite the use of zircon geochemistry and geochronology to constrain many problems in Earth Sciences, much debate exists over the use and interpretation of zircon-based information. Such debates include whether for igneous rocks the spread of ages along concordia represents magma residency, Pb loss, inheritance or incremental assembly (Reid et al., 1997; Brown and Fletcher, 1999; Charlier et al., 2005; Campbell et al., 2006; Miller et al., 2007; Moser et al., 2009; Berra et al., 2014; Barboni et al., 2015; Buret et al., 2016); what significance and reliance can be placed on zircons present in mafic rocks (Fu et al., 2008; Kaczmarek et al., 2008; Rioux et al., 2012; Belousova et al., 2015); and the robustness and meaning of Ti-in-zircon thermometry and zircon saturation temperature (Hanchar and Watson, 2003; Harrison and Schmitt, 2007; Harrison et al., 2007; Fu et al., 2008). More recently, petrogenetic models of granitic magmatism have become increasingly reliant on Ti concentration in zircon geothermometry and zircon saturation temperature (Chappell et al., 1998; Miller et al., 2003; Watson and Harrison, 2005; Liu et al., 2013; Moecher et al., 2014; Weinberg and Hasalová, 2015; Collins et al., 2016). These models have then been extrapolated to base reinterpretations of the tectonic setting of granitic magmatism. A feature of many of these studies is an implicit assumption that all zircons present in the host igneous rock are autocrystic; that is, the zircon crystals or outer zones of crystals have crystallised from the host magma, whereby all zircons can be used to provide information on the emplacement age, and the chemical characteristics of the zircons are reflective of their host magmatic environment (Miller et al., 2007).

It has long been recognised, however, that zircons present in an igneous rock may not always be autocrystic and that instead they can be inherited either from the country rock or from the source region (xenocrysts; restitic), or are related to older phases of similar magmatism such as being sourced from the magmatic plumbing system (antecrysts; e.g., Miller et al., 2007; Claiborne et al., 2010a; Jerram and Bryan, 2015). In some cases, inherited zircons may form domains within crystals or form the entire population in the igneous rock (e.g., Charlier et al., 2005; Bryan et al., 2008; Ferrari et al., 2013). Xenocrystic zircons generally have distinct cathodoluminescence responses, age, chemical and isotopic contrasts making them relatively straightforward to recognise and separate. The distinctly older ages of xenocrysts cannot be explained by any prolonged magma residency in the crust (Miller et al., 2007). In contrast, antecrystic zircons often have a much more subtle age and chemical distinction that can often be undetectable or unresolvable by being within analytical error of autocrystic zircons. The age differences between antecrystic and autocrystic phases can be as little as 10–100's years or up to several million years, a resolution that can only be achieved by very small analytical uncertainties (Charlier et al., 2005; Walker et al., 2007; Bryan et al., 2008; Schaltegger et al., 2009; Leuthold et al., 2012; Schoene et al., 2012; Barboni et al., 2015).

A fundamental goal in geochronology is to be able to constrain the emplacement age of an igneous rock. Given that antecrystic and xenocrystic crystals or crystal domains can yield significantly older age information and differing chemical attributes recording different magmatic environments, it is critical that analysis is confidently carried out on autocrystic components. The objective of distinguishing inherited from autocrystic zircons is thus twofold: first, to facilitate interpretation of complex geochronological data thereby better constraining the emplacement age and last magmatic environment that the zircons experienced, and second, to use the antecrysts to illuminate the preceding magmatic history related to pluton or erupted magma volume construction. This paper first reviews the utility and reliability of commonly used zircon-based information for petrogenetic studies. We then review existing approaches to identify inherited zircon (antecrysts/xenocrysts) following which, a new methodology is described for identifying the presence of inherited zircon, and tested with granitic rock examples.

2. Zircon- and bulk-rock Zr-based thermometric parameters used in igneous petrogenetic and tectonic studies

Temperature is a fundamental parameter that affects the rheological behaviour and crystallisation history of magmas as well as the partial melting conditions of source rocks. A variety of mineral-based geothermometers (e.g., Fe-Ti oxides, Ti-in-quartz, plagioclase-hornblende, pyroxene-hornblende or two-pyroxene) have traditionally been used to estimate magmatic temperatures (see Anderson et al., 2008 for a review). However, such thermometers have limitations in their applicability due to mineral susceptibility to subsolidus re-equilibration, mineral pairs not being in equilibrium (Bacon and Hirschmann, 1988), hydrothermal alteration, metamorphism and weathering that can affect the primary compositions of igneous minerals, or the lack of co-existing mineral pairs. As a result of the low diffusivity of Ti in zircons, zircon resistance to weathering, alteration and metamorphism, and the great ease in analysing Ti-in-zircon, particularly by LA-ICP-MS, many studies are increasingly reliant on the Ti-in-zircon thermometer (Watson and Harrison, 2005; Moecher et al., 2014; Collins et al., 2016) for temperature constraints in igneous rocks. Similarly, the routine acquisition of bulk-rock composition in petrogenetic studies promotes the application of zircon saturation thermometry based on Zr concentration and major element composition (Watson and Harrison, 1983) to understanding igneous petrogenesis. Reinforcing this point is in a survey of articles published since 2013, only 14 results were obtained for a search of “Fe-Ti oxide thermometer” versus 262 results for “Ti-in-zircon thermometer”, and 282 for “zircon saturation temperature” (retrieved 24th July 2017 using Google Scholar). The following sections review these two geothermometric approaches and highlights several issues in their applicability to igneous petrogenetic studies.

2.1. Ti-in-zircon geothermometry

Due to the isovalent substitution of Si by tetravalent Ti, and the relatively well-constrained chemical potential of Ti in crustal rocks, Ti content of zircon is attributed to changes in intensive variables (Watson et al., 2006). Specifically, Ti content in the zircon structure is dependent on temperature, independent of pressure, and assuming Ti activity is known, Ti in zircon can be used to estimate the magma temperature at the time of zircon crystallisation (Watson et al., 2006; Ferry and Watson, 2007). Consequently, the application of the Ti-in-zircon thermometer (T_{ZircTi}; [Eq. (1); Watson et al., 2006]) to petrogenetic studies has steadily increased over the last 10 years, and has become central to a debate on the thermal state and dynamics of the early crust, as based on Ti-in-zircon thermometry on Archean and Hadean zircons (Coogan