

Timescales of granite infancy

Improvement and alternatives on plutonic geochronology

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Abstract

Radiometric geochronology is a key method to understand the formation of granite, which is the main constituent of continental crust. With increasing number of U-Pb age dating-based studies, it is important to study ways to improve zircon U-Pb dating and exploring other alternative dating methods which may cover the limitations of previous methods. In this thesis, I picked 3 common mineral phases; zircon, apatite, and titanite in I-type granite sensu lato and investigate each to discuss their reliability as a dating tool, and suggest improved methods to date granitic rocks.

Zircon U-Pb age data from the first study area Satkatbong diorite (SKD) and its mafic microgranular enclaves (MME) indicates a 30 Ma-wide of age range with ~190 Ma of weighted mean concordia age. Variabilities in Hf isotopic compositions (ϵ Hf (t): +8 to +15) were found equally from the MME and their host rock. Fractional crystallisation modelling from the same starting melt with basalt-andesitic composition shows both the SKD and MME melt could have been formed by different fractional phase combinations. The source may achieve zircon saturation in the temperature range ca. 780 – 800 °C mainly because of high water content. I suggest that this zircon saturated, long-lived source is a one type of the deep crustal hot zone (DCHZ) mush reservoir. This low-melt fraction source may explain the following characteristics of the study area: (1) antecrystic zircon accumulation on a prolonged time scale, (2) Hf isotopic variability as a result of replenishments, and (3) similar Hf isotopic systematics between the SKD and MME.

Large zircon age range (~100 Ma) were found in the second study area, Mt Stirling pluton in the Mt Buller suite. Data filtering protocol is suggested to enhance zircon age data reliability: (1) Excluding accidental inclusion by checking excessive K and Ca, (2) Trimming spots with unusual opposite core-rim age relationship (Δ (core-rim age) < 0), (3) excluding zircons with excessive non-formula elements (Al, Fe, and Mn), (4) hydrothermally altered zircon by proxy Ba/Hf > 1, and (5) potential hydrothermal zircons with V-shape REE patterns. The filtered weighted mean concordia age (402.2 ± 1.0 Ma; MSWD = 1.5) for the host rock shows improved MSWD and decreased error compared to unfiltered data (397.5 ± 1.5 Ma; MSWD = 4.8). The

filtered age indicate that the MME magma was contemporary to the host magma. The age range is reduced, yet still with a considerably long-time range of ca. 70 Ma, which exceeds analytical reproducibility ($2SE = \sim 10$ Ma).

Apatite and titanite collected from the same study area of the chapter 3 were similarly tested by trace element filtering. For apatite, (1) major element concentration Ca and P, and (2) Zr/Y and Th/U are monitored to exclude micro-inclusions or hydrothermally altered parts. Additionally, (3) age groupings are found depending on Sr and Mn concentrations. In titanite, followings are monitored: (1) major element concentrations Ca and Ti for detecting major outliers, (2) Sr/Zr and Sr/Th for excluding hydrothermal anomalies, and (3) Sr/Ca and Zr/Ti for intensive chemical exchange. Application of those filters generally enhances precisions. Apatite spots are conspicuously grouped by Sr concentration (high-, mid-, and low- Sr). The high-Sr (407 \pm 10 Ma) and mid-Sr (409 \pm 8 Ma) apatites from a host rock and MME show similar age range as titanite (404 \pm 3 Ma) and zircon (402 \pm 1 Ma), while low-Sr apatite (420 \pm 10 Ma) gives spurious older age. In addition, apatites with higher Mn content tend to be older.

This study shows that zircon age can be erroneous because of chemical reaction and possibly by the nature of zircon origin. As alternative approaches, utilising multiple geochrometers may further improve age interpretation reliability. Chemical closure must be carefully verified in any types of geochronometers by monitoring in-situ trace element concentrations.

Plain language summary

Granite is a major constituent (>70 %) of continental crust on Earth. Dating granite is therefore of great importance to understand Earth's formation. Absolute age of a material is obtained by radiometric dating technique by counting the amount of accumulated radiogenic element. Each radiogenic element has its own timescale. Many different types of chemical 'clock' thus exist depending on different minerals, and different elements in the minerals.

The aim of this study is to develop an improved mineral age-dating technique by testing different minerals and measuring additional trace elements. The results shows that the additional trace elements can improve the reliability of age data by providing additional information of chemical conditions of the chemical clock. The results of the study have broad implications in mineral age dating techniques, and can also be directly utilised in other labs by following the suggested protocols.

Publications during enrolment

• Park, J., Lim, H., Myeong, B. and Jang, Y.D., 2020. Syenite from Ulleung Island: As a window for pre-eruptive shallow alkaline magma dynamics. Lithos, 356, p.105342. https://doi.org/10.1016/j.lithos.2019.105342

• Park, J., Lim, H., Myeong, B. and Jang, Y.D., 2022. Hydrothermal mineralization of celadonite: hybridized fluid-basalt interaction in Janggi, Korea. Accepted at American Mineralogist

• Lim, H., Nebel, O., Weinberg, R. F., Nebel-Jacobsen, Y., Barrote, V. R., Cawood. P. A. Lower crustal hot zones as zircon incubators? Inherited zircon antecryts in diorites from a mafic mush reservoir. Under revision (minor) at Geological Society of London Special Publication

Thesis including published works declaration

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes one submitted publications. The core theme of the thesis is investigating improved granite dating techniques – examples from the Satkatbong diorite in Southeastern Korean Peninsula and Mt Buller in the Lachlan Fold Belt, Southeastern Australia. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the student, working within the School of Earth, Atmosphere and Environmental Science under the supervision of A/Prof. Dr. Oliver Nebel, Dr. Yona Nebel-Jacobsen and Prof. Dr. Peter A. Cawood.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.

Thesis Chapter	Publication Title	Status (published, in press, accepted or returned for revision, submitted)	Nature and % of student contribution	Co-author name(s) Nature and % of Co- author's contribution*	Co- author(s), Monash student Y/N*
2	Lower	Submitted		1) Oliver Nebel, 15%	Yes
	crustal hot			2) Roberto F.	Yes
	zones as		70%. Concept	Weinberg, 5%	
	zircon		and collecting	3) Yona Nebel-	Yes
	incubators?		data and writing	Jacobsen, 2%	
	Inherited		first draft	4) Vitor R. Barrote,	Yes
	zircon			3%	Yes
	antecryts in				

In the case of 2, 3, and 4 my contribution to the work involved the following:

	diorites from a mafic mush reservoir			5) Peter A. Cawood, 5%	
3	-	Not Submitted	70%. Concept and collecting data and writing first draft	 1) Oliver Nebel, 15% 2) Yona Nebel- Jacobsen, 10% 3) Peter A. Cawood, 5% 	Yes Yes Yes
4	-	Not Submitted	70%. Concept and collecting data and writing first draft	 1) Oliver Nebel, 15% 2) Yona Nebel- Jacobsen, 10% 3) Peter A. Cawood, 5% 	Yes Yes Yes

I have renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis.

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I hereby certify that the above declaration correctly reflects the nature and extent of the student's and co-authors' contributions to this work. In instances where I am not the responsible author I have consulted with the responsible author to agree on the respective contributions of the authors.

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Date: 31/03/2022

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People often say PhD is a marathon or long journey. With a full agreement, I would say my PhD was an epic adventure at the mysterious land, full of dangerous obstacles and fascinating figures, to achieve a humongous goal.

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Chapter 1

Introduction

1.1 Scope of the thesis

Granite sensu lato (or granitoids, including more mafic granodiorites) is a major constituent of continental crust. Understanding the petrogenesis of granitic rock is thus fundamental to understanding the formation of continental crust. Because of their plutonic origin, granitic melts are believed to considerably interact with surrounding lithologies, starting at their source and extending through to their emplacement (Taylor, 1980; DePaolo, 1981; Hildreth and Moorbath, 1988). Rheological mixing and convection at depth may alter textures of the melt (Lejeune and Richet, 1995; Wiebe and Collins, 1998) on time scales much longer compared to basaltic melts (e.g., Bateman and Chappell, 1979). Therefore, processes of granitic magma formation and associated genesis are still a matter of ongoing debate. Due to the difficulties to link granitic structures to true means of emplacement, chemical compositions are more viable to classify and to reconstruct the origin of different types of granites (Chappel and White, 1974; Frost et al., 2001).

Geochemistry also grants the capability to measure and determine timescales of granitic activity through radioactive-radiogenic isotopic analysis. Dating granitic rock has become a fundamental part of studying crust formation and evolution (e.g., Cheong and Jo, 2020), and various geochronometers have been tested and applied for decades. Except for the fission track technique, where decay damage is physically counted (Deliens et al., 1977; Meldrum et al., 1998), geochronological methods are predominantly chemical. Isotopic compositions are analysed from whole rock (bulk rock) or mineral samples. Whole rock Rb-Sr (Dallmeyer and VanBreeman, 1981; Kryza et al., 2014) or Sm-Nd (Lugmair and Carlson, 1978) isotopes were widely used. In addition to dating rocks, the Rb-Sr method can provide initial ⁸⁷Sr/⁸⁶Sr ratios, which provide source material information (Steiger and Jäger, 1977). Likewise, the Sm-Nd isotopic evolution enables the calculation of the model age for when the granitic melt was separated from the mantle (Jacobsen and Wasserburg, 1980). However, whole rock isotope dating can be inconclusive with often large error bars due to a granite's possible heterogeneity with associated initial isotope variations. An alternative dating approach is provided by abundant crystalline phases, i.e., minerals, which in parts, can be utilised for single grain isotope analysis. A variety of phases has been used for such dating.

To use a mineral phase as a geochronometer, some of the following characteristics are generally required: (1) high concentration of radioactive isotopes, (2) a general abundance that facilitates their mineral separation, and (3) that the phase remains intact and uncompromised after its initial crystallisation. For example, biotite, muscovite, and hornblende were widely used for dating using Rb-Sr, K-Ar, or Ar-Ar dating techniques, because these phases are common in granitic rocks, and include high concentrations of Rb and K (Hurford and Hammerschmidt, 1985; Kelley, 2002b). Likewise, plagioclase can be used for initial Sr isotopes (Steiger and Jäger, 1977), K-feldspar can be used for K-Ar, Ar-Ar, or K-Ca system (Hurford and Hammerschmidt, 1985; Kelley, 2002b). Actinide-enriched minerals like zircon and allanite can be used for U-Pb dating. Uranium-Pb systematics can be applied in other moderately U-bearing minerals like titanite, rutile, monazite, apatite, and Ca-garnet. Rare earth element (REE)-enriched minerals (e.g., apatite, monazite, xenotime, and garnet) can be dated by Sm-Nd (Barfod et al., 2003; Larsson and Söderlund, 2005) or Lu-Hf (Rakovan et al., 1997). However, for phosphate, U-Pb dating is preferred because of a superior actinide content. These phases are all available in rocks of granitic composition. Different phases in the same isotope system often show interesting trade-off effects because of different mineral characteristics: e.g., In K-Ar or Ar-Ar geochronology, either Ar loss or excess Ar must be carefully considered. Kfeldspar is less susceptible to include excess Ar, yet it loses Ar at relatively low temperature. Micas are susceptible to accept fluid-resolved Ar, but it is less 'leaky' (Kelley, 2002a; Kelley, 2002b). Likewise, U-Pb systematics in some U-bearing minerals can be compromised, and details of these will be discussed in later sections (1.2, 1.3, and 1.4).

In most isotope geochronometers, initial ratio measurement or an associated assumption is required. Principally, linear regression from multiple measured points on an isochron plot (e. g., ⁸⁷Sr/⁸⁶Sr vs ⁸⁷Rb/⁸⁶Sr plot in the Rb-Sr system) can calculate the initial radiogenic isotope ratio. In this isochron regression, lower parent- and higher daughter-concentration combination may estimate more precise initial ratio. Some phases incorporate near zero amounts of the daughter isotope, which allows the calculation of the initial ratio with an assumption of an initial ratio = 0. For example, in K-Ar and Ar-Ar systems, an assumption is made that the samples initially contain no radiogenic Ar (Kelley, 2002a). Similarly, zircon lattice incorporates a negligible amount of Pb, and it is assumed that most amount of analysed Pb isotopes are radiogenic. For other isotope systems with different amount of initial Pb

inherited (or 'common' lead), galena can be used to calculate initial Pb compositions if it is coexisting, because galena would not include parental U. Otherwise, the Earth-wide ²⁰⁷Pb/²⁰⁶Pb lead evolution model after Stacey and Kramers (1975) can be used to assume the initial ²⁰⁷Pb/²⁰⁶Pb ratio.

Since 'whole rock' is composed of different mineral phases, two different approaches are considered to measure concentrations of elements in a rock sample: solution analysis and mineral analysis. Whole rock isotope composition measurement is conducted by solution analysis. The most commonly applied methods for whole rock are thermal ionisation mass spectrometry (TIMS), and inductively coupled plasma mass spectrometry (ICP-MS) (Stracke et al., 2014; Schaltegger et al., 2021). To prepare the solution sample, isotope dilution (ID) is the method of choice when ultimate accuracy and precision are required (Stracke et al., 2014).

For polished thin sections, polished rock chips, and mineral mount samples that are all with solid surfaces, electron probe micro analysis (EPMA), secondary ion mass spectroscopy (SIMS), and laser ablation-ICP-MS (LA-ICP-MS) have been used. Isotopic analysis by EPMA, namely 'chemical Th-U-total Pb isochron method' (CHIME), can be applied to monazite, xenotime, and zircon (Suzuki and Adachi, 1991; Suzuki and Kato, 2008; Konečný et al., 2018). However, CHIME is in many cases not appropriate and entails a large uncertainty. In SIMS, a sample is analysed through an ion beam, and secondary ions from the ablated sample are analysed. The sensitive high-resolution ion micro-probe (SHRIMP), one of the high-resolution SIMS instruments, insures high spatial resolution and reproducibility. However, it is limited by its high price to major research institutions (Hoskin et al., 2003). Laser ablation-ICP-MS is also characterised by *in-situ* analysis like SHRIMP, but is of lower precision compared to the SIMS or ID techniques. However, LA data can be collected relatively rapidly from a larger number of zircons, is relatively cost effective, and more accessible than SIMS and ID analyses, and has therefore become the method of choice for many studies (e.g., Jochum et al., 2005).

Since granites are plutonic origin and have longer residence time than their volcanic counterparts, crystalline phases can have complicated histories that are not directly related to their crystallisation. To elucidate their origin, a temporal history is best paired with a petrological approach, which is the main focus of this study. To capture the complexity of processes in a granitic melt, different terminologies are required to describe various types of

crystals in an intrusive body (cf. Miller et al., 2007). (1) Autocryst. Autocryst defines a grain crystallised from the exact igneous body, which is similar in volcanic systems to a more familiar term, phenocryst, which is a clearly visible crystal (Fig. 1.1). (2) Xenocryst. Xenocryst are grains that are considered unrelated to the magma system. These are generally significantly older (several million years) than the hosting igneous body and may be incorporated from the country rocks during transit and emplacement of the igneous body (Fig. 1.1). (3) Antecryst. Antecryst is a grain from the same complex magmatic system, yet basically formed early, so that it has an affinity to the magma. Therefore, antecrysts may not directly be related to other phases or the melt, despite being associated with the magmatic system (Fig. 1.1). Existence of antecryst and xenocryst in a magmatic body implies a complicated, and possibly protracted, history to form an igneous body, which may involve mixing, assimilation, storage, homogenisation (MASH; Hildreth and Moorbath, 1988), and incremental growth of the body. This behaviour of the grains has conceptual affinity with the deep-seated mush reservoir model (Annen et al., 2006; Solano et al., 2012) and the cold storage model (Jackson et al., 2018), which suggest a transport of older crystals from the deeper- to upper- reservoir by reactive melt flow facilitated by replenishments.



Figure 1.1. Conceptual figure depicting different types of crystals in an intrusive body (redrawn after Miller et al., 2007). The source is deep crustal zone of mafic input, partial melting, and mixing ("MASH"). The figure is not to scale.

Closure of the system is a principal factor in geochronology, because every application of radiogenic isotope geochronology requires the system being closed for isotope exchange and accumulate daughter isotopes by decay. The concept of closure is mainly controlled by temperature in a cooling magmatic system (Fig. 1.2A); thus, it is often termed closure temperature (Table 1.1, Figs. 1.2A and 1.2C). However, although temperature is a main factor for closing systems, closure is based on sub-solidus diffusion, which is a complicated function of temperature, pressure, the element of interest, crystal lattice, and the composition of the crystal (Fig. 1.2B; Cherniak, 2010). Therefore, all of the fore mentioned factors influence the system closure. Although most of geochronological studies assume a closure of the studied grains based on reported closure temperatures (Table 1.1), open vs. closure of the system should be carefully considered based on the studied materials' other conditions together with its thermal history. Even in a simpler thermal history with constantly decreasing temperatures in a cooling igneous body, conditions of diffusion can variably change. Structural damage of crystal lattice and phase transition (i.e., melt, recrystallisation, and alteration) are important examples. Mafic replenishment, which can occur in a granitic body, is one of the heat and chemical transport means to compromise a simple closure history. In addition, if the crystal lattice is metamictised by accumulated radioactive damage, the system cannot ensure the closure. Likewise, any other chemical reactions on crystals can potentially alter the system closure. This may critically influence dating result in any geochronometer.

System	Тс (° С)	References
U-Th-Pb zircon	> 900	Dahl (1997) and Cherniak and Watson (2000)
U-Th-Pb monazite	> 750	Heaman and Parrish (1991)
U-Pb xenotime	> 650	Heaman and Parrish (1991)
U-Th-Pb allanite	650	Heaman and Parrish (1991)
U-Th-Pb titanite	650 ± 50	Cherniak (1993), Dahl (1997), and Frost et al. (2000)
U-Pb rutile	620 ± 20	Cherniak (2000), Vry and Baker (2006), and Kooijman et al. (2010)
Sm-Nd garnet	600 ± 30	Mezger et al. (1992)
Rb-Sr muscovite	500 ± 50	Jäger et al. (1967) and Jäger (1977)
K-Ar hornblende	530 ± 40	Harrison (1981)
U-Pb apatite	425 – 500	Dahl (1997) and Chamberlain and Bowring (2000)
K-Ar muscovite	350 – 425	Purdy and Jäger (1976) and Harrison et al. (2009)
Rb-Sr biotite	350	Jenkin (1997)
K-Ar biotite	310 ± 40	Harrison et al. (1985)

Table 1.1. Closure temperatures in different systems.



Figure 1.2. Conceptual explanation of closure temperature (A and C; redrawn after Kohn and Penniston-Dorland, 2017) and summary of Pb diffusion data for accessory phases (B; redrawn after Cherniak, 2010).

In this study, I investigate various minerals to discuss their reliability as a dating tool, and suggest improved methods to date granitic rocks. I firstly study zircon Hf and U-Pb systematics to investigate the source region and age of zircon. In the following projects, I use trace elements of zircon together with U-Pb isotopic compositions to compare the relation

between chemical composition and age of zircon. In the next step, I expand this approach to two different phases, apatite and titanite, to discuss chemical influences on dating results.

1.2 Zircon

Zircon U-Pb was used to date the oldest mineral on Earth and U-Pb systematics is used to date a rock's absolute age (Wilde et al., 2001). Hence, interest in zircon U-Pb dating has resulted in it becoming the most popular method for dating of geomaterials (Hoskin et al., 2003). Zircon is a common accessory phase in rocks of granitic composition. The physiochemical resilience of zircon along with high U and low common lead in its lattice have made it the go-to method for geochronology. In addition, it is a refractory mineral, and has a high closure temperature for U-Pb (Table 1.1, Fig. 1.2B; > ~900 °C; Cherniak, 2010), combined with simple, concentric zonation that is ideally suited for *in-situ* analyses. Despite these advantages, the zircon chronometer may yield erroneous age information if not carefully assessed through secondary processes, which may lead to incorrect geologic interpretations (Geisler et al., 2007; Kusiak et al., 2013). It is often reported that zircon ages in granites span over tens of millions of years for a single plutonic body or even within a hand specimen (e.g., Idaho Batholith (Gaschnig et al., 2013), Ladakh Batholith (Weinberg and Dunlap, 2000), Florida Mountains granite (Amato and Mack, 2012) See Brown and McClelland(2000) for more examples), which are unlikely to record a magmatic event. In addition, zircon can be altered by hydrothermal alteration (Geisler et al., 2007) and/or radiation-damage (Yu et al., 2021). Although common lead incorporation in zircon is not significant, this also may further contribute to spurious age result.

In this context, other mineral phases such as apatite, titanite, allanite, rutile, xenotime, and monazite have been explored as potential alternative dating tools (e.g., Kylander-Clark, 2017; Yakymchuk et al., 2017; Fisher et al., 2020).

1.3 Apatite

Apatite is common to most if not all intrusions, and has been suggested as a useful additional or alternative petro-chronometer to zircon (e.g. Engi, 2017; Kylander-Clark, 2017;

Ribeiro et al., 2020; Yu et al., 2021). Apatite is a common minor phosphate phase in wide range of rocks. It is moderately lanthanide-enriched and has extraordinarily flexible crystal structure, which can even anneal (Yu et al., 2021). This is in stark contrast to zircon, which is often affected by radioactive damages when it has high U content and is old enough to accumulate damages, in which case the zircon becomes metamict. Compare to zircon, U-Pb closure of apatite is estimated to occur at a lower temperature (~ 500 °C; Table 1.1; Fig. 1.2B; or even lower 350 – 550 °C; Chew and Spikings, 2015). Although closure temperature for this system is not precisely known and a wide range of temperatures were suggested in different studies (~350 – 650 °C; Cochrane et al., 2014; Kirkland et al., 2018, and 600 – 1200 °C; experimental study of Cherniak (2010), Fig. 1.2B), closure of apatite is near to or lower than the solidus temperature of granitic melts. This indicates apatite certainly records a lower temperaturesnapshot of the granite compared to that of zircon. Apatite incorporates a wide range of minor and trace elements, including S, Sr, U, Th, and especially lanthanide-rare earths. High concentrations of these elements in apatite are important indicators of the surrounding melt conditions at the time of apatite crystallisation. For example, Sr concentration in apatite has been shown to be a function of plagioclase fractionation of the melt during magmatic differentiation (Belousova et al., 2002a). In addition, apatite Sr content has been used for TTG - I-type - S-type granite classification (Bruand et al., 2017; Bruand et al., 2020) and as a source rock indicator (O'Sullivan et al., 2020; Ribeiro et al., 2020). Enrichment of REE or Th/U were also utilised to interpret or classify the source magma which crystallised apatite (Sha and Chappell, 1999; Yu et al., 2021). In this contribution, trace element of apatite can make a synergistic data set when combined with apatite age systematics.

1.4 Titanite

Titanite is a common accessory mineral in igneous rocks (especially in metaluminous granites). Its high U and Nd concentration can readily be utilised in geochronology (Kohn, 2017). Titanite, as commonly known as a late-stage mineral in felsic calc-alkaline plutons shows similar – higher closure temperature compared to apatite (650 °C or higher, Fig. 2B; Cherniak, 2010; 500 – 800 °C, Bonamici et al., 2015). The temperature range is sufficiently high to investigate granitic melt conditions. It has been reported that age of titanite can be

affected by the amount of common lead and lead loss, because these may result in isochron "tipping" (Kirkland et al., 2016). In addition, titanite contains high concentrations of rare earth elements (REE), which can indicate magmatic conditions of crystal growth (Kohn, 2017; Scibiorski and Cawood, 2022). Like apatite, titanite Sr can also indicate source melt characteristics (Bruand *et al.*, 2020). Titanite can also be used as a thermo-barometer (Hayden et al., 2008).

1.5 Methodology

Granitic rocks have a variety in chemical compositions and their genesis can be complex. Considering these complexities, the scope of the thesis covers granitic rocks with Itype affinity. Selected I-type granites exclude the complexity of sediment-derived zircons, at least in theory, and are thus the main case study targets in the thesis.

Laser Ablation Split Stream ICPMS (LA-SS-ICPMS) is commonly utilised as the main instrumental method in this research project. Compared to plain LA-ICPMS, split stream mode allows combinations of analysing two different isotope systems or one isotope composition plus trace element compositions, where ablated sample aerosol is split into two different mass spectrometers (Fisher et al., 2014b; Kylander-Clark, 2017). This technique offers two fundamental advantages. First, the same analytical volume is used for the measurement of two different systems, ensuring that data from both can be reliably coupled. Second, the LASS method offers a relatively rapid sampling approach with large numbers of analysis (Jochum et al., 2005; Fisher et al., 2020).

1.6 Thesis structure

Each following chapter provides brief introduction and literature reviews on topics relevant to the chapter before describing and discussing the data. Chapters 2 - 4 to deal with three main topics and have been prepared for publications as peer-reviewed journal articles. The topics are as follows:

Chapter 2: Lower crustal hot zones as zircon incubators? Inherited zircon antecryst in diorites from a mafic mush reservoir

- Hoseong Lim, Oliver Nebel, Roberto F. Weinberg, Yona Nebel-Jacobsen, Vitor R. Barrote, Peter A. Cawood
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- This chapter reports U-Pb and Hf isotope compositions from an I-type diorite in South Korea. Antecrystic origin of zircon is investigated based on largely dispersed concordia ages both from the host rock and MME. Isotopes of Hf are used for tracking source material compositions, and Zr enrichment modelling is applied to discuss zircon saturation in the lower crustal reservoir. This chapter further discusses the viable geologic conditions to form zircons with these wide ranges of age and ɛHf (t).

Chapter 3: Testing the U-Pb age reliability of hydrothermally altered magmatic zircon using trace elements: A case study from the Mt Buller I-type granitoid suite, Lachlan Fold Belt, Australia

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- In this chapter, in-situ zircon U-Pb and trace element data are reported from the Mt Buller I-type granodiorite suite, Lachlan Fold Belt. While zircon dataset shows a wide range of ages, trace elements are used as a filtering scheme to test the reliability of zircon age data. The discussion of data filtering is placed into the context of chemical closure of zircon, comparing to characteristics of other reported hydrothermally altered zircon.

Chapter 4: Apatite vs titanite dating of I-type plutons: issues and solutions, Mt Stirling pluton, Lachlan Fold Belt

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- Chapter 4 uses apatite and titanite in-situ U-Pb and trace element data to investigate their reliability as geochronometers. Similar to chapter 3, a trace element filtering protocol is suggested, which is based on mineral chemistries of apatite / titanite. I monitor ages before- and after- filtering, and discuss the difference to the zircon filtering. This chapter is concluded with discussing ages from apatite and titanite on the formation of I-type granite.

Chapter 5: Concluding remarks

• The conclusion chapter summarise results and implications from chapter 2 – 4. The zircon-apatite-titanite synthesised age is suggested and evaluate the effect of the final filtering. This chapter discusses the limitations in the studies in the thesis and suggests future works.

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Chapter 2

Lower crustal hot zones as zircon incubators? Inherited zircon antecryts in diorites from a mafic mush reservoir

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Abstract

Continental arcs are key sites of granitic magmatism, yet details of the origins of these magmas, including the role and contribution of mafic magma, the timing and location of initial zircon formation, and how zircon isotopic signatures relate to granite formation remain as challenges. Here we use U-Pb dating, trace elements, and Hf isotopic systematics of zircon in mafic microgranular enclaves (MME), from the convergent plate margin Satkatbong diorite (SKD) in Korea to understand lower arc magmatism and zircon production. The host granitic body and MME display similar major element evolutionary trends, and similar ranges of Sr, Nd, and Hf isotopes implying a cognatic relationship. Zircons show a large variability in EHf (t) (~6 units) and age (> 30 Ma). We propose that the SKD and MME originated from the same, long-lasting, lower crustal mush reservoir, enabling long and variable residence times for zircons. Prolonged zircon ages, combined with the Hf isotope variability within a single pluton (SKD and its MME) indicate that not all zircons were instantaneously crystallised in a rapidly cooling shallow magma chamber but were continuously formed in a long-lasting hot source. A low-melt-fraction mush type reservoir in a deep crustal hot zone (DCHZ) provides a viable model for the source setting. Continuous replenishment of mafic magmas acted as the main reactivator of the reservoir, and acted a critical role in spawning zircons that record a long age span, because 1) the magma adds Zr into the reservoir enabling it to reach zircon saturation, and 2) the generated zircon grains are transported upward as antecrysts by flow within the reservoir. This means antecrysts with different ages may mix with each other in the ascending magma body. The significance of this model is that a conclusive time of intrusion cannot be constrained by such zircon ages, as these antecrysts constitute inherited grains.

2.1 Introduction

Convergent continental margin granitoids range in composition from I-type intrusions, generally of mantle affinity, to S-types granites with a more evolved crustal signature. The chemical spectrum of these intrusions is the result of diverse source compositions within the lower crust, and melting reactions during partial melting. An integrated part of the lower arc crust, the regions where convergent margin granitoids originate, are so-called deep crustal hot zones (DCHZ, Annen et al. 2006; Solano et al. 2012). These are areas within the deeper

continental arc crust that act as regions with a prolonged active melt storage (Jackson et al. 2018). These mush reservoirs are assumed to be tapped and reactivated by injections of new magma batches from the underlying sub-arc mantle, and range in composition from mafic to felsic reservoirs through igneous differentiation (Jackson et al. 2018). The link between these hot zones and magmatic arc granitoids is not clear, but it is most likely that these regions represent either the source or play a key role in the development of parental melts of the high-level plutons.

The lifespan of some magmatic arc plutons can exceed millions of years (e.g. Idaho Batholith, Gaschnig et al. 2013; Ladakh Batholith, Weinberg and Dunlap 2000; Florida Mountains granite, Amato and Mack 2012), and numerous studies have shown that large plutonic bodies do not form in a single event but grow incrementally through repeated injections of new magma batches (Glazner et al. 2004; Miller et al. 2007). With long-lived DCHZ as possible sources for the magma, it is possible that some of the compositional variety in composite plutons is directly related to melt genesis at depth within the lower arc crust (e.g. Kemp et al. 2007; Hammerli et al. 2018). Conclusive evidence, however, is yet to be found.

Another prominent feature of many I-type convergent margin plutons is mafic microgranular enclaves (MME). These enclaves, which usually exhibit only slightly lower silica content than their host granites (Chen et al. 1990; Barbarin 2005), are often interpreted to represent mantle-derived juvenile influx (Barbarin 2005). They have been linked to parental melts from the source of the granites (Collins et al. 2001; Barbarin 2005), and thus may hold clues to the genesis and evolution of plutonic bodies.

Zircon is an ideal dating tool of magmatic processes and is a common accessory phase in intermediate to felsic rocks, including MME. Age information, combined with Hf in zircon can help constrain the source characteristics of rocks (Nebel et al. 2007; Roberts and Spencer 2015). Furthermore, Hf isotopes are highly stable in the zircon lattice making them resistant to diffusion, and combined with their relatively high (> 900 °C) closing temperature for Lu-Hf (Scherer et al. 2000), zircons are an ideal tool to study early stages of the magma genesis (Kemp et al. 2007). In this study, we investigate U-Pb ages and Hf isotopes of zircons from MME (~ 56 wt. % SiO2) and their host dioritic body (~ 65 wt. % SiO2; Lim et al. 2016; Lim et al. 2018), comparing them to the neighbouring Yeongdeok granite (YDG; Cheong et al. 2002; Yi et al. 2012). Previous studies implied a possible source connection between the Satkatbong diorite (SKD) and the YDG, which differ in age by ca. 60 Ma, yet exhibit similar Sr and Nd isotopic systematics (Cheong et al. 2002; Lim et al. 2018). We aim to elucidate the role of lower crust in the genesis of these plutonic bodies and the MME.

2.2 Geologic context & Previous work Geologic Setting

The Southeastern Korean Peninsula lies within the eastern margin of the Eurasian Plate. The basement of the peninsula consists of the Precambrian Yeongnam massif (YM), which resembles the South China Craton (Fig. 2.1) in radiogenic Sr-Nd-Pb isotope studies (Choi et al. 2005). The YM collided with the Gyeonggi massif (GM) in the Late Permian to Early Triassic, forming the intervening Okcheon metamorphic Belt (OB) along the suture (Fig. 2.1). During and after the collision, extensive plutonic rocks intruded the YM, formed scattered stocks that are mainly composed of alkaline or medium- to high K calc-alkaline granite to diorite. These rocks include the YDG and SKD, the study area plutons. Subsequently, the Cretaceous Gyeongsang arc system and associated volcano-sedimentary back arc Gyeongsang Basin (GB) developed along the southern segment of the Korean Peninsula (Fig. 2.1). Plutons in the study area are nonconformably overlain by the GB (Lim et al. 2016).



Figure. 2.1. Simplified geological map of the Yeongdeok area with the Yeongdeok granite (YDG) and Satkatbong diorite (SKD). GM, Gyeonggi Massif; OB, Okcheon Belt; YM, Yeongnam Massif; GB, Gyeongsang Basin (modified after Lim et al., 2018).

Yeongdeok Granite

The Yeongdeok granite (YDG) intruded into the Proterozoic Yeongnam massif. Its contacts with surrounding units are masked by a cover of Cretaceous volcano-sedimentary rocks. The granite ranges in composition from a K-feldspar megacryst-bearing biotite granite to a hornblende granite (Woo and Jang 2014). It is mainly composed of quartz, K-feldspar, plagioclase, biotite, and hornblende with accessory titanite, zircon, and apatite. Moderately enriched Rb (10–100 ppm) and HFSE (including Y and Nb) deficiency highlight its volcanic

arc granite characteristics (Cheong et al. 2002; Yi et al. 2012; Lim et al. 2018), and A/NK and A/CNK relations indicates that the YDG is a metaluminous to peraluminous I-type body (Cheong et al. 2002; Yi et al. 2012; Cheong et al. 2019). Yi et al. (2012) firstly analysed the YDG zircons and reported their age at 257 ± 2 Ma. This age indicates a post-collisional relationship with respect to the formation of the OB. The origin of the YDG has been suggested as having formed through mixing between MORB-like mantle melt and Proterozoic basement on the basis of 87Sr/86Sr (t) and ϵ Nd (t) modelling (Cheong et al. 2002). Lim et al. (2018) discussed trace element modelling and showed that the melting of a subducted eclogitic slab followed by crustal assimilation could generate the YDG magma (Cheong et al. 2019).

Satkatbong Diorite

The Satkatbong diorite (SKD) is a north-south elongated plutonic body, exposed along the coast. The SKD is a leucocratic, middle to coarse grained equigranular tonalite-quartz diorite (Lim et al. 2016) composed of plagioclase, hornblende, quartz and K-feldspar with minor titanite, apatite and zircon (Cheong et al. 2002; Lim et al. 2016). Epidote is found as a secondary phase. A U-Pb zircon age of 192 ± 2 Ma was reported for the SKD (Yi et al. 2012). This pluton is rich in MME, whose composition range from quartz diorite to diorite (Fig. 2.2A; Lim et al. 2016). The MME are also equigranular, and slightly finer grained than the host diorite and lack of cumulate textures (Lim et al. 2016). Mafic clots and acicular apatite are found in both host and enclaves on microscopic level (Lim et al. 2018). These textures indicate magma mixing between the host and MME magma (Baxter and Feely 2002; Lim et al. 2016; Lim et al. 2018), additionally supported by hybrid zones in an outcrop scale. The SKD resembles the YDG in Sr, Nd, and Pb isotope compositions but trace and rare earth element (REE) concentrations are different between the SKD and YDG (Lim et al. 2018; Cheong et al. 2019). The similar isotopic yet different REE patterns between the YDG and SKD are interpreted to indicate partial melting of similar source materials at different depths (deeper for the YDG; Cheong et al. 2002). Lim et al. (2018) however suggested both plutons could have a similar source with a similar depth if the MME magma mixing altered the source to produce the SKD.

Cumulate
In this study, we report data for an additional unit of the SKD, which has previously not been investigated. The unit, which is exposed in the northern part of the SKD, is distinct from the rest of the body in that there are no MME but the unit displays a distinctive magmatic cumulate texture (Figs. 2.2B and 2.2C). The rock suite is characterised by predominantly amphibole-plagioclase that appear aligned on an outcrop scale and also in microstructures (Fig. 2D).



Figure 2.2. Nature of the SKD complex including the main body, MME, and cumulate. (A) The leucocratic host SKD and darker melanocratic MME. Note a considerable amount of MME. (B) Magmatic layers of the cumulate sample shown by the white dashed lines. (C) Cumulate texture defined by amphiboles. (D) Photomicrograph of aligned amphiboles (white dashed line).

2.3 Samples and methodology

From the SKD complex (i.e. main body, MME, and cumulate), major and trace elements of the host rock and MME were analysed by Lim *et al.* (2018). In this study, we present an additional seven analyses of cumulates, four from the host rock, and eight from the MME. Each sample was visibly fresh, and crushed in a hydraulic press and a jaw crusher, and powdered by a tungsten carbide ball mill and an agate mortar. The samples were mixed with a flux of lithium metaborate and lithium tetraborate and then fused in an induction furnace. The melts were poured into a solution of 5 % nitric acid containing an internal standard, and mixed continuously (~45 minutes) to fully dissolve potential refractory minerals such as zircon, titanite, monazite, and chromite.

The major elements were analysed on a Thermo Jarrell-Ash ENVIROII ICP at Activation Laboratories, Canada. Calibration was performed using certified standard materials from the US Geological Survey (USGS) and the Canada Centre for Mineral and Energy Technology (CANMET). The detection limits of MnO and TiO₂ were 0.001 %, and those of the other major elements were 0.01 %. Trace elements were analysed by the Perkin Elmer Sciex ELAN 9000 ICP-MS (Activation Laboratories, Canada). The precision was estimated to be within \pm 3 % based on repeated analyses of a selected sample (15G) and international rock standards (BIR-1a, DNC-1, JR-1, NIST 694, SY-4, and W-2a).

Zircons were separated from host rock (05G, 2109, 4101) and MME (E09, E11, E12) samples (Fig. 2.1). After removal of any weathered portions, ~2–3 kg of each sample was crushed by hydraulic press, jaw crusher and then for a short period in a tungsten carbide ball mill (< 1 min). The powers were sieved through 250 μ m mesh. Water washing, panning, magnetic separation (by a hand magnet and a Frantz), and heavy liquid (tetrabromoethane; 2.97 g cm⁻³) were used to separate zircons from lighter or magnetic minerals. Zircons were then handpicked under a binocular microscope. Zircon U-Pb and Hf-isotope data were collected by the method developed for Laser Ablation Split Stream Multi-Collector Inductively Coupled Plasma Mass Spectrometry (LASS-MC-ICPMS) at the Isotopia Facility, Monash University. The isotopic data from both systems were collected simultaneously using a Resonetics S-155-LR 193 nm excimer laser coupled to a Thermo Fisher Neptune *PLUS* multicollector (Hf-isotopes) and a Thermo Fisher iCAP-TQ quadrupole mass spectrometer (U-Pb) in single

quadrupole mode (SQ). The laser aerosol was split evenly between the two instruments, and for enhanced Hf sensitivity, nitrogen gas was added to the sample line of the Neptune only, past the split junction of the ablated material at 6.0 ml min^{-1} flow rate. The laser conditions were set such that a fluence at the sample of ~4.5 J cm⁻² was obtained, with an 8 Hz frequency and 35 µm spot size. Hafnium isotopes were collected following Fisher *et al.* (2014a) with a 1 s integration time and a total of 60 s of ablation (about 30 µm depth) after a 30 s background.

Dwell times for the iCAP TQ were 10 ms for ²³⁸U and ²³²Th, 20 ms for ²⁰⁸Pb, 70 ms for ²⁰⁷Pb, 40 ms for ²⁰⁶Pb and 30 ms for ²⁰⁴Pb and ²⁰²Hg. The ablated material was carried to the mass spectrometers by combined He gas, with a flow rate of 0.55 L min⁻¹, Ar gas at ca. 1 L min⁻¹ flow rate. The U-Pb elemental fractionation, down-hole fractionation and calibration drift were corrected by bracketing measurements of unknowns with analyses of the primary zircon reference material Plešovice (206 Pb/ 238 U age = 337.13 ± 0.37 Ma; Sláma *et al.* 2008). Mud tank (176 Hf/ 177 Hf = 0.282507 ± 0.000006; Woodhead and Hergt 2005) is used as the primary reference material for Hf analysis. Secondary standards for U-Pb and Hf analyses are 91500 (Wiedenbeck et al. 1995) and GJ-1 (Jackson et al. 2004). Time resolved data was baseline subtracted and reduced using Iolite 4 (DRS after Paton et al. 2011), and the in-built data reduction schemes UPb Geochron 4 and Hf isotopes with natural abundance ratios of 171 Yb/ 173 Yb = 1.132685 (Chu *et al.* 2002) and 179 Hf/ 177 Hf = 0.7325 for mass bias correction. Mass bias of Lu was assumed identical to that of Yb (β Lu = β Yb; Fisher *et al.* 2014b). Age calculations and diagrams were constructed using IsoplotR (Vermeesch 2018). No common lead correction was made in the data reduction scheme, and model-1 discordia (Ludwig 2012) was used if a common lead regression is found. Level 5 of Horstwood et al. (2016) does not take into account systematic uncertainties. A complete list of the settings for U/Pb and Hf analyses is summarised in the supplementary material 3 (Tables S1 and S2; https://figshare.com/s/b128a2379e6ce7ec8920). Results for reference material analysis are listed in the supplementary material 1.

2.4 Results

Whole rock geochemistry

The major and trace element compositions of the YDG and the SKD are listed in table 2.1. Total Alkali vs. SiO₂ (TAS) diagram (Middlemost, 1994) indicates that the YDG samples have granodiorite–quartz monzonite–granite compositions, whereas the SKD and MME fall within a range of monzo-gabbroic diorite to granodiorite. Cumulates mostly plot in the gabbro–gabbroic diorite fields (Fig. 2.3).

The SKD has a wide range of major element values (54.1-74.2 wt.% in SiO₂, 0.31-3.61 wt.% in MgO, 1.57-4.76 wt.% in K₂O, n = 14), and the MME show a slightly more mafic compositional range in SiO₂ (51.8-64.7 wt.%, n = 17) plotting on a similar major element trend as the SKD. Compared to their host, the MME are slightly more sodic (2.86-4.60 wt.%) and potassic (1.46-3.10 wt.%) at the same silica content (Fig. 2.3). A striking feature of the rock suites is that the host rock varies substantially in silica content and extends at lower values into the region of MME silica concentrations, which could be the result of either differentiation (cumulate-melt) or mixing processes (between endmembers). Additionally, the YDG complex defines a similar linear trend to the SKD complex in Al₂O₃, K₂O, MgO, and CaO, which may indicate similar differentiation processes. The cumulates show an apparent depletion in SiO₂ and alkali elements, as can be expected from their mafic mineralogy, whereas enriched Al₂O₃, MgO, and CaO values correspond to the high proportions of amphibole and plagioclase (Fig. 2.3).



Figure 2.3. Major element Harker diagrams for Al₂O₃, MgO, Na₂O, K₂O, and CaO and the TAS diagram for the classification of plutonic rocks (Middlemost 1994). Note that the SKD shows a wide range in SiO₂.

Together with the YDG (Yi *et al.* 2012), the SKD has relatively high Sr/Y yet straddles between the adakitic and non-adakitic fields in both the Sr/Y vs. Y and La/Yb vs. Yb plots (Fig. 2.4). The MME do not show Sr/Y enrichment. These trends are also shown in the La/Yb vs. Yb diagram (Fig. 2.4). The MME plot outside of the adakitic (in this case, high-Sr/Y granite) field in both diagrams. In the REE plot, the YDG is characterised by elevated light rare earth elements (LREE) and depleted heavy rare earth elements (HREE) and lacks a negative Eu anomaly (Fig. 2.5), resulting in a relatively steep and linear slope in the REE pattern. The REE pattern for the SKD shows a less steep slope. The MME have relatively enriched HREE compared to their host rock. Negative Eu anomaly (Eu/Eu* = 0.75) of the MME indicates plagioclase fractionation during the MME magma evolution. The cumulates show, on average, lower LREE abundances than the SKD and MME and have a positive Eu anomaly (Eu/Eu* = 1.17) indicative of the accumulation of plagioclase (Fig. 2.5, Table 2.1).



Figure 2.4. Sr/Y vs. Y and La/Yb vs. Yb diagrams. Note that the YDG plots in the red area, representing high-Sr/Y granite type. Reference adakite areas are from South China Craton (Ling *et al.* 2011).



Figure 2.5. Chondrite (CI) normalised REE diagrams for the MME, SKD, cumulate, and YDG. The slope (La/Yb) of the YDG trend is steep as a typical high-Sr/Y granite characteristics, whereas the MME is less steep and the SKD is intermediate. The YDG data is from Cheong *et al.* (2002).

Zircon

A total of 82 zircons from six samples representative of both SKD and MME were systematically analysed for cores and rims (164 analyses in total) (Fig. 2.6). Zircons from the SKD and MME, as magmatic zircons, are similar in habit and chemical characteristics. Their morphologies and internal structures are similar in back-scattered electron (BSE) and cathodoluminescence (CL) images (Fig. 2.6, Fig. S2, supplementary material 2). The zircons from both SKD and MME show sector to weak oscillatory zoning, indicating relative compositional homogeneity (Fig. S2). Both rock types lack obvious inherited zircon cores (Fig. 2.6). The zircons in both rocks lack thorite microcrysts, which often occur in metamict zircons (Kusiak *et al.* 2009), highlighting their relatively unaltered condition.



Figure 2.6. Representative cathodoluminescence images of analysed zircons and ablated spots (red circle) with in-situ 206 Pb/ 238 U ages (red font ± SE) and ϵ Hf (t) values (blue font). Note zircons from the SKD and MME record indistinguishable ages.

The results of U-Pb and Hf isotope analyses are listed in the supplementary material 4 (Table S3; <u>https://figshare.com/s/b128a2379e6ce7ec8920</u>). The U-Pb and the Hf isotope data of the YDG are from Yi *et al.* (2012) and Cheong et al. (2019), respectively, and used here for comparison. Ages with more than 5 % discordance lie along a common lead contamination trend and are excluded from this study to avoid influences on either age and/or Hf values. Despite the absence of obvious core-rim textures, ages from both the SKD and MME spread by up to ~45 Ma (with MSWD = 8.2 and 12 respectively), while weighted mean concordia ages are similar at ca. 190 Ma (190.6 ± 1.4 Ma for the SKD (n = 80, 2SD = 14 Ma) and 189.7 ± 1.5 Ma for the MME (n = 90, 2SD = 18 Ma)). Ages extending over tens of millions of years are beyond analytical error (< 10 Ma of 2 SE) as confirmed by the Wetherill concordia plot together with probability density diagrams (Fig. 2.7).

Sampling locations from northern (192 ± 2 Ma, MSWD = 11, n = 63), central (188 ± 2 Ma, MSWD = 9.9, n = 71), and southern (193 ± 2 Ma, MSWD = 7.5, n = 36) parts of the pluton show no systematic variation in age (Fig. 2.7). The weighted mean ages of zircon cores are consistently older than the rim (193 ± 1 Ma core (MSWD = 6.3, n = 80) and 187 ± 2 Ma rim (MSWD = 12, n = 89; Fig. 2.7). This holds true for both the host rock core (194 ± 0.4 Ma; MSWD = 5.9, n = 37) versus rim (188 ± 0.3 Ma rim; MSWD = 9, n = 43) and the MME core (193 ± 0.3 Ma; MSWD = 6.8, n = 44) versus rim (187 ± 2 Ma rim; MSWD = 15, n = 46) zircons.



Figure 2.7. Concordia and Kernel density plots. (A) The weighted mean age is 190 ± 1 Ma (n = 80) for the SKD and MME. (B) The age distributions and variabilities in both the SKD and MME are identical. (C and D) Comparison between the standard materials and the samples in age distribution. The distribution of sample shows larger variability. (E) Core vs. rim of the

SKD rocks show the most distinct difference in the age range. (F) Spatial distribution of the sample does not explain the age variability.

Epsilon Hf values of the SKD and MME were calculated from ¹⁷⁶Hf/¹⁷⁷Hf values of each sample at the time of crystallisation (zircon ²⁰⁶Pb/²³⁸U age). The averages and ranges of ε Hf (t) are: +10.4 for the SKD, +10.9 for the MME (with ranges of +8.1 and +11.9 for sample 2109, +8.3 and +13.2 for sample 05G, and +9.1 and +12.5 for sample 4101 of the SKD; +9.0 and +13.0 for sample E12, +9.1 and +14.0 for sample E11, and +9.2 and +15.6 for sample E09 of the MME; Fig. 2.8). Both zircon populations of the SKD and MME show a wide spread of 5 to 7 epsilon units (Fig. 2.8). The average value from zircon cores is +10.6, identical to the rim. The weighted average ε Hf (t) of the MME zircons (10.7 ± 0.22) is slightly higher than that of the host rock (10.2 ± 0.21) (Fig. 2.8). The YDG has an average ε Hf (t) of +11.1 and also a relatively wide range of ~4 ε Hf (t) units (Cheong et al., 2019).



Figure 2.8. Epsilon Hf (t) vs age diagram together with Hf isotope evolution lines based on the YDG (red dashed lines). Hafnium isotope evolution lines are calculated with ${}^{176}Lu/{}^{177}Hf = 0.0093$ for felsic crust (Amelin *et al.* 1999). Depleted mantle evolution is calculated based on present-day depleted mantle values ${}^{176}Hf/{}^{177}Hf = 0.283223$ and ${}^{176}Lu/{}^{177}Hf = 0.038$ (Vervoort and Blichert-Toft 1999).

2.5 Discussion

SKD and MME formation

Plutonic systems often show a wide spectrum of zircon ages outside analytical reproducibility (e.g. Idaho Batholith (Gaschnig *et al.* 2013), Ladakh Batholith (Weinberg and Dunlap 2000), Florida Mountains granite (Amato and Mack 2012)). It has been suggested that these bodies grow incrementally and through successive magma injections (Glazner *et al.* 2004; Miller *et al.* 2007), resulting in many millions of years of activity. Age spectra are reported within single units or even hand specimens, and in the absence of evidence for substantial magma mixing, these spectra remain difficult to reconcile with the concept of incremental pluton growth.

Zircon ages of the SKD and its MME range from around 210-180 Ma. Considering an analytical error of ± 5 Ma (~2.5% of SE), this range of 30 Ma is well outside analytical scatter and thus considered to accurately represent the time span of magmatic activity. The scattering (~4% of SD) is larger than the standard error, and is a serious scale compared to lower standard errors (<~1.7% in SE) and standard deviation (<~1% in SD) in reference materials (Figs. 2.7C, 2.7D).

Considering the systematic difference in zircon core vs rim ages (Δ core-rim = average 6.3 Ma), the ca. 6 Ma of systematic difference likely indicates the time from zircon growth until the end of magmatic duration (i.e., emplacement). Notably, however, this span is not related to absolute ages, with some rim ages overlapping with core ages of other zircons, indicating that this process does not equate to a single event. A second critical observation is that these varying core-rim systematics can be observed in zircons from single samples. It is unclear how zircons in close proximity can undergo this core-rim cycle in the presence of other zircons with a similar cycle that is 10–15 Ma older.

Hafnium isotope ratios in the zircons also show a spread well beyond analytical uncertainty. A spread of ~6 ϵ Hf (t) units in zircon is an indicator for a diverse source of Hf, in this case with a considerable influence of a juvenile component (ϵ Hf (t) = +8 to +14). Such a spread in plutonic rock is not uncommon and is considered a result of juvenile-mature endmember mixing (Hildreth and Moorbath, 1988; Dungan and Davidson, 2004). This

explanation may be applicable to the SKD rocks, given the presence of more mafic MME. Petrographic mixing indicators such as mafic clots and acicular apatites in the MME and SKD indeed support magma mixing (Lim *et al.* 2018). Mixing here is best explained by chemicaland mechanical- mixing effects between MME and their host rock magma (i.e. a physical transfer of minerals between MME and host magma, Barbarin 2005). This would imply that some zircons from the MME sample could be derived from the host rock magma and vice-versa, and would explain the strong overlap in zircon ages between both suites.

Any such mixing, however, cannot explain the long timespan of zircon ages. If melts remain near their solidus for ca. 30 Ma, a physical mixing of grains requires a much higher liquid proportion, therefore higher temperatures. This may be achieved through the incremental injection of new melts, such as the MME melts. However, a viable alternative to a hot magma chamber at upper crustal levels is that the older zircons did not form within the actual magmatic body, so are not phenocrysts sensu stricto but are in fact antecrysts. In this scenario, a deep seated, lower crustal mush reservoir would be the source of the SKD and MME magmas, but at different stages of differentiation. In both cases, zircon would have already grown at depth and not in a shallow magma body.

Both, SKD and MME show similar mineralogy and identical age and Hf variabilities, and considerable overlaps in major- and trace elements (Figs. 2.3, 2.5). In a scenario in which SKD and MME magma formed in a lower crustal hot zone, the difference in magmatic composition can be achieved by different stages of fractional crystallisation (FC). While exact values for each parameter are difficult to constrain, and with this any parental magma composition, it should be possible to calculate a feasible parent to both magma compositions through reverse fractional crystallisation (eq. 1):

$$C_0 = C_L / F^{D-1} \tag{1}$$

where C_L is the concentration of the element in the residual liquid and C_0 is the initial concentration of the element, F denotes melt fraction, and D is bulk distribution coefficient.

In reality, no such hypothetical magma composition would exist, simply due to constant recharge and evacuation mechanisms of melts entering and leaving lower crustal reservoirs. However, it is imperative to test if a hypothetical magma composition can produce both melt reservoirs (SKD and MME) for the scenario proposed here to be feasible producing the zircons within a single reservoir at depth.

From the cumulate sample's mineralogy and chemistry (e.g. $Eu^* = 1.2$; Fig. 2.5, Table 2.1), plagioclase and amphibole are considered as the main fractionating phases. Setting an unknown parental liquid composition (Co), the FC modelling result indicates that the SKD and MME melt could indeed have originated from a similar source material with a simple adjustment of the amount of the amphibole fraction being removed or added from and to the system (Fig. 2.9). The MME melts fractionated less modal amphibole but more pyroxenes (10 % orthopyroxene, 80 % clinopyroxene, and 10 % plagioclase) compared to the host diorite (10 % clinopyroxene, 60 % amphibole, and 30 % plagioclase) fractional phases quote experimental result of Nandedkar et al. (2014) (starting material RN7 and RN8). Discrepancies in Ba and Sr might indicate an inaccuracy of this model in plagioclase effect. Plagioclase can be actively transferred between the MME and host rock melt, and also cumulated, which involves complexity. Even though this hypothetical parental melt is not considered a real melt composition here, the successful proof of concept further implies that amphibole is a key phase in the genesis of the melts, which is expected for I-type granitoids (Chappell et al. 2012), and a lower arc crust hydrous melt reservoir. This simple feasibility test successfully produced a hypothetical parental melt. It is, however, critical to test if any such melt would be saturated in zircon in order to produce and transport the crystals.



Figure 2.9. Fractional crystallisation modelling of the MME and SKD to check if two different magmas can be generated by different fractional phases. Sources are calculated from each resultant magma composition (Shaw 1970; Kd database McKenzie and O'Nions 1991 for orthopyroxene, garnet, and plagioclase, Foley *et al.* 1996 for clinopyroxene, Fujimaki *et al.* 1984 for amphibole). Proportions of residual phases (10% orthopyroxene, 80% clinopyroxene, and 10% plagioclase for the MME; 10% clinopyroxene, 60% amphibole, 30% plagioclase for the host rock) refers the experimental result after Nandedkar *et al.* (2014) (Starting material RN7 and RN8 therein). Note that the calculated concentration implies a nearly identical source composition dictated by amphibole proportion.

Zircon saturation

Experimentally zircon saturation in relatively mafic magma compositions is an ongoing debate. Boehnke *et al.* (2013) suggested that an unrealistically high abundance of Zr is required for basaltic melt to have autocrystic zircon, and Siégel *et al.* (2018) concluded that zircon should not be present in a melt with < 64 wt. % SiO₂, apart from some minor crystallisation in differentiated melt pockets. Experimental studies on zircon saturation in peralkaline melts demonstrate that zircon would not form because of unrealistically high levels of Zr enrichment (> 10,000 ppm) required for this to occur (Gervasoni *et al.* 2016; Shao *et al.*

2019). Borisov and Aranovich (2019) reported zircon crystallisation in the dry, near-solidus evolved basaltic melt is unlikely, while water containing condition is more plausible for the zircon crystallisation. However, zircon is found in many mid-ocean ridge (MOR) environments (basalt or gabbro; Coogan and Hinton 2006; Bortnikov *et al.* 2008; Fu *et al.* 2008; Lissenberg *et al.* 2009; Schmitt *et al.* 2011; Bea *et al.* 2020; Borisova *et al.* 2020; Aitchison *et al.* 2022), and it is often reported that zircons from a granite and MME are different from each other in their morphology and/or isotopic characteristics.

The MME zircons from our study appear to have more positive ϵ Hf (t) values (Fig. 2.8), indicating that simple grain mixing between host diorite and MME is not the only reason for the distribution of ages between both reservoirs. However, the MME are also more mafic than the host diorite so that any zircon saturation scenario in which zircons either grew or were transported must be tested for these melts. Below, we test if the MME composition could have indeed supported zircon stability through saturation calculations.

In order to assess whether zircon was stable in the MME melt compositions, we conducted Zr enrichment-zircon saturation modelling using the replenishment-evacuation-fractionation (REFC) model of Lee *et al.* (2014), the phase equilibrium calibration of Boehnke *et al.* (2013). The modelling is designed to test if an experimental primitive hydrous arc magma evolution can achieve zircon saturation (from 48.5 wt. % SiO₂ and 52 ppm Zr; after experimental petrology result, Nandedkar *et al.* 2014; and average mantle Zr content, Lee and Bachmann 2014) under mid–low crustal redox-pressure conditions (20–25 km depth and in NiNiO buffer; Nandedkar *et al.* 2014). The model is composed of 2 parts; the first part of the model investigates Zr enrichment in a recharging melt reservoir, and the second part of the model evaluates whether this enrichment is sufficient to achieve zircon saturation.

In the initial stage of any melt reservoir development, source enrichment in Zr was calculated by the REFC modelling, which implies that a parental melt undergoes fractional crystallisation (FC), yet is constantly recharged through melt replenishment with volume being controlled through melt evacuation in addition to FC. Mass balance in the magma reservoir is assumed by equal masses of FC and evacuation vs. melt replenishment. This relation is expressed in equation 2

$$\frac{C_{ch}}{c_{ch}^o} = \frac{C_{ch}/C_{ch}^o}{D\alpha_x + \alpha_e} - \left[\frac{C_{ch}/C_{ch}^o}{D\alpha_x + \alpha_e} - 1\right] \exp\left[-\Delta \overline{M}_{re}(D\alpha_x + \alpha_e)\right]$$
(2)

where C denotes concentration of a certain element in chamber/initial chamber (C_{ch}/C_{ch}^o) , α_x equals dM_x/dM_{re} and α_e equals dM_e/dM_{re} , where M means mass of fractionation (M_x) , replenishment (M_{re}) or evacuation (M_e) . Note that $\alpha_x + \alpha_e = 1$ if the mass of magma chamber M_{ch} is at steady state. In this model, number of times that the magma reservoir has recharged $(\Delta \overline{M}_{re}, \text{ cf. "overturn" Lee et al. 2014})$ is considered.

In the REFC model, the concentration of a given element (either incompatible or compatible) converges into a level of "steady state" as replenishment proceeds. In other words, the maximum enrichment for any incompatible elements (D < 1) is finite, similar to the depletion of compatible elements (D > 1) (Lee *et al.* 2014; Figs. 2.10A, 2.10B). Another significance of this model is that compatible elements (D > 1) quickly achieve a steady state compared to relatively slow enrichment of incompatible elements (D < 1) (Lee *et al.* 2014; Figs. 2.10A, 2.10B). This implies that Zr, treated here as an incompatible element (D < 1) is more enriched than other major elements, whose concentrations are more or less constant. If the initial Zr concentration in any hypothetical primitive melt is mantle-like (i.e. 52 ppm, Lee *et al.* 2014), and replenishing magma is of a similar composition, the maximum enrichment of Zr is 1037 ppm until a steady state is achieved if no evacuation ($\alpha_e = 0$) of the magma chamber is assumed (Fig. 2.10A). On the other hand, no more than 216 ppm Zr is achieved if 20 % evacuation ($\alpha_e = 0.2$) is assumed (Fig. 2.10B).

The modelling results, and with this any constraints on zircon saturation, are dependent on the bulk distribution coefficient of $Zr (D_{Zr})$. This D_{Zr} , however, is dependent on (1) magma composition, (2) fractionating phases, and (3) their weight fractions, rendering constraints on saturation strongly model dependent. To test for the effect of compatibility, we used a range of D values, from 0.05 to 2 (Figs. 2.10A, 2.10B).

Zirconium concentrations of an evolving magma were then calculated using the fractional crystallisation equation (Shaw 1970; eq 1). In this case, C_L is the Zr concentration in an evolved melt and C_0 is Zr concentration in the starting material, and F denotes melt fraction.

Each melt fraction F with corresponding temperature is quoted by experimental results from Nandedkar *et al.* (2014) The starting temperature is 1070 °C. Bulk D_{Zr} values tested in this model are 0.1 and 0.3 (Marxer and Ulmer 2019).

In the second part, zircon saturation is calculated by Boehnke et al. (2013):

$$\ln D_{Zr} = \frac{10108}{T(K)} - 1.16 \cdot (M - 1) - 1.48 \tag{3}$$

where M is a compositional parameter given by (Na+K+2Ca)/(Al·Si). From equation 3 (Boehnke et al. 2013), one can create an x-y field of Zr in melt [Zr] vs. temperature with variable M values (grey gradient lines in Fig. 2.10C). Each parabolic line may represent loss of [Zr] (i.e. zircon crystallisation) as temperature drops in a certain melt composition (M). figure 2.10C represents a combination of Zr enrichment and zircon crystallisation curves simulated by zircon saturation model of Boehnke et al. (2013) in mid-lower crustal conditions (Nandedkar *et al.* 2014) when the $\alpha_e = 0.2$ (Table S4 in Supplementary material 5; https://figshare.com/s/b128a2379e6ce7ec8920). This hypothetical value 'eruption factor' is not a real value, but an upper limit while eruption was not likely significant in this study area since no coeval volcanic unit occurs nearby. Thus, it is expected that figure 2.10C with $\alpha_e = 0.2$ could constrain the lower limit in Zr enrichment. A Boehnke et al. (2013) constrained zircon crystallisation model in the evolving basaltic hydrous arc magma (Nandedkar et al. 2014) is shown in figure 2.10C. The zircon crystallisation curve (a thick grey line with grey area of error) gradually crosses gradient lines of decreasing M values as the temperature drops, which indicates that the melt evolves into a more silicic composition at P-T-redox conditions with a lower crustal affinity (Fig. 2.10C). According to the example model, evolving melts with D =0.1 and D = 0.3 (blue and purple lines in figure 2.10C, Table S4) reach saturation points ranging from ~320-~600 ppm in 810-870 °C and 59.6-61.5 wt. % SiO₂. The implication of this model is that zircon was indeed saturated under lower crustal reservoir condition. Experimental studies of Nandedkar et al. (2014) and Marxer and Ulmer (2019) indicate zircon saturation may be achieved at low temperatures (800–830 °C) yet in a higher SiO₂ range (ca. 65–70 wt. %). The model in this study slightly underestimates SiO₂ (~ 60 wt. %) compared to those experimental studies and also to implications from Siégel et al. (2018) (~64 wt. % SiO₂) and Dickinson and Hess (1982). The essential difference is that the previous models only

considered fractionation as a Zr enrichment mechanism, while this study additionally considered basaltic magma replenishment simulated by REFC. The main implication of the Zr enrichment-zircon saturation model is that constant replenishment may provide additional Zr into a reservoir and the zircon saturation hurdle can lower for slightly less silicic magmas.



Figure 2.10. Zirconium enrichment-zircon saturation modelling for MME-like melt. (A) Various source enrichment curves are calculated by the Replenishment-evacuation-fractional crystallisation (REFC) modelling after Lee *et al.* (2014). D = 0.05 is an alternative for D = 0. Note that compatible elements take less time to reach steady state than incompatible elements. Concentration change until the steady state is not dramatic in compatible element. (B) The same graph as (A) except for $\alpha_e = 0.2$. (C) Two Zr enrichment-zircon saturation curves from

an average mantle Zr content (52 ppm; Lee and Bachmann 2014) each enriched with $D_{Zr} = 0.1$ and $D_{Zr} = 0.3$. Melt evolution follows fractional crystallisation (FC) curve. Melt fraction (F) and temperature referred experimental parameters after Nandedkar *et al.* (2014). Zircon saturation is based on Boehnke *et al.* (2013). Whole rock compositions of experimental basaltic hydrous arc melt (RN6–RN17V2 runs in Nandedkar *et al.* 2014) are used to calculate M values (Na+K+2Ca)/(Al·Si) in each temperature. Note Zircon saturation curve crosses gradient lines of decreasing M values as temperature drops, which indicates evolving melt composition in the P-T-redox conditions with a lower crust affinity. Concentration of Zr in melt enriches until zircon saturation concentration of ~320– ~600 ppm in 810–870 °C range with 61 wt. % SiO₂.

Deep crustal hot zone (DCHZ) magmatism

The similarity between SKD and MME in mineralogy, age, a EHf (t), and major- and trace element compositions, is consistent with the derivation from a common source. Their subtle differences in trace elements are mainly due to the different fractional proportions of amphibole, and this outlines the source depth where magmatic amphiboles are stable (< 18) kbar; Gill 1981). Zirconium enrichment plus zircon saturation assessment in this study indicates this less silicic source may be saturated in zircon. Even though physical mixing of zircon grains between host melt and MME cannot be excluded, a viable alternative scenario is that their common magma reservoir already contained zircons. This scenario can successfully explain the long lifespan with the observed systematic older core-younger rim pattern of zircons. The assumed source is expected to be seated at ~7.0 kbar with 810-870 °C. The temperature range corresponds to the temperature range of Marxer and Ulmer (2019) with tonalitic melt composition, which is nearly identical lithology to the SKD and MME. However, since these experimental studies (e. g., Nandedkar et al. 2014; Müntener and Ulmer 2018) indicate a more evolved magma in this temperature range, a more plausible scenario is heterogeneously distributed evolved melt pockets in the primitive reservoir. The aforementioned DCHZ mush reservoir concept (Annen et al. 2006; Solano et al. 2012; Jackson et al. 2018) already includes a similar model of a layered reservoir, where it contains more silicic melts in its upper level (Jackson et al. 2018). This is a likely source model for the SKD and MME. In analogy this can also explain the Hf isotope variability of the neighbouring (yet

older) YDG. For this, no single zircon ages are available, yet the isotope variability in ϵ Hf (t) indicates a similar situation as observed for the SKD (Fig. 2.8).

In deep-seated (18–30 km depth) reservoirs, the melt fraction is low (< 0.2) while fractional crystallisation and replenishment occur together (Jackson et al. 2018). 'Early Jurassic magma flare-ups' suggested by a regional study of Cheong and Jo (2020) could have triggered this replenishment (from Fig. 2.11A to Fig. 2.11B). Periodic replenishments of basaltic magma sporadically crank up melt fraction. Higher melt fraction is progressively segregated and moves to the upper part of the reservoir where more evolved magma resides (Jackson et al. 2018). The reservoir sporadically evacuates evolved magma when it has more melt fraction (0.2–0.35) and thus overcomes the second percolation threshold (SPT; Vigneresse et al. 1991) to obtain momentum (Fig. 2.11A, 2.11B). This evacuating magmas with basalt-andesitic composition are probably mixtures conveying both relic minerals and evolved liquid pockets which contain zircon antecrysts, and the zircon grains in it should record the timespan of the evolving mush reservoir (Fig. 2.11B). The composition of the remaining reservoir converges into that of replenishing primitive magma if it is continuously replenished (Lee *et al.* 2014). Evacuating magma in the later stage of the reservoir, therefore, is more juvenile than the previous, and mingles with the host rock, then forms the MME (Fig. 2.11C and 2.11D). Fractional crystallisation and mixing may occur at any stages in the evolution, and at any levels, of the reservoir. This occurs around the solidus temperature of ~800 °C, yet under ~900 °C (zircon closure temperature), because MME mingled at a high temperature and no "reset-ages" but prolonged ages were recorded.

The significance of the proposed model is that the exact time of an intrusion cannot conclusively be constrained by the ages of this zircon population, as these may include antecrysts, which are basically inherited. The pooling of ages in programs, such as Isoplot then indicates a single age and origin with seemingly small total error, where only elevated MSWD indicate the prolonged age spectrum. Common lead can be responsible for spreading ages. However, this study trimmed data with discordance > 5%, and the common lead effect for age-spreading in those survived spots is not significant as graphically assumed in figure 2.7A. Lead loss, on the other hand, indeed spreads ages toward younger direction, which was reported and warned by different studies (e. g., Spencer *et al.* 2016; Andersen *et al.* 2019). It is difficult to

reconcile the presence or absence of lead loss event by post-crystallisation events. The dataset in this study might not be enough to fully discuss the lead loss effect on younger ages. However, Hf isotope variability found in this study implies the age spreading is not sorely by the lead loss in zircon. The idea that zircons crystallise and achieve their Hf isotopic signature before the shallow crustal emplacement is similar to the view of Hammerli *et al.* (2018). They demonstrated that the incomplete solidification of basaltic magmas in a DCHZ (< 35–40 km) leads to the absence of garnet signature in the example from Lachlan Fold Belt I-type granites, and this may parallel the lack of enriched Sr/Y values in the SKD and MME. In addition, they proposed that zircon isotopic variabilities in intrusions likely originated by juvenile magma replenishments. Interpretation of zircon data from granitic rocks, therefore, requires care, and needs to consider conditions of zircon crystallisation across various temperatures, depths, source duration, and evidence for replenishment.



Figure 2.11. The cartoon depicting deep crustal hot zone (DCHZ) much reservoir model for the study area magmatism (not to strict scale). (A) Deep seated mush reservoir which generates the high-Sr/Y YDG magma. Consistent replenishment progressively changes the composition of the reservoir, while Zr could be kept enriched and saturated in REFC process. Note

compositional layering / gradation in the reservoir, which facilitates zircon saturation in a more silicic part. (B) Compositionally changed mush reservoir could form the less felsic SKD. Previously formed zircon could join the SKD magma. The inlet figure illustrates how the zircon saturated evolved liquids (pockets) can be captured by previously crystallised grains. (C) Consistent, or even increasing replenishment kept lowering SiO₂ in the reservoir, where MME magma were generated by different FC route compared to that of SKD. Zircons in the MME magma also have protracted ages inherited from the reservoir. (D) The SKD body achieves mechanical- and chemical equilibrium which result in overlaps between the MME and host rock. Note that mixing and fractionation may happen any time during these processes.

2.6 Conclusion

We present new LA-SS-MC-ICP-MS zircon age data and Hf isotope compositions for a diorite (SKD) and associated mafic microgranular enclaves (MME) from the Korean peninsula. The SKD shows a wide range of zircon ages, spanning ~30 Ma, with a spread of Hf isotopes (~ 6ϵ Hf units), far outside analytical reproducibility. We suggest a common parental melt for the SKD and MME, which evolved through each fractionation path towards dioritic compositions. Cumulates located towards the north of the complex represent fractionated minerals, hence mafic counterparts of the intrusion. This genetic relationship between MME and ambient diorite, which is reflected in evolutionary plots of major element compositions, can readily explain the formation of the pluton through incremental pluton growth associated with fractional crystallisation. This incremental pluton growth scenario, however, fails to explain similar zircon distribution in terms of ages and ϵ Hf (t) ranges between both rock types, notably a long timespan (~30 Ma) of zircon ages.

Based on major-trace element distributions, and in the context of proposed deep crustal hot zones, we propose that the source of both intrusion types is a lower arc crust melt reservoir. Parental melts of both intrusions are likely of basalt-andesitic composition, while one of them fractionated more amphibole forming the dioritic SKD, and the other evolved toward MME compositions through fractionation of less amphibole. We propose that a low-melt fraction mush reservoir existed, which is re-activated and tapped when hot, with mafic magma replenished from the mantle. This reservoir was probably a long-lasting zircon spawning mush, where pressure and temperature satisfy near-solidus conditions. Zirconium enrichment-zircon

saturation modelling shows that zircon formation in such a lower crustal mush reservoir is viable with consistent replenishments under hydrous (> 6 wt. % H₂O) condition.

If correct, such mush reservoirs can serve as a zircon incubator, which can explain the wide range of ages and Hf isotope signatures observed in the SKD, and possibly elsewhere. This scenario for granitoids that originate from lower crustal mush reservoirs implies that zircon ages may not indicate the true age of the intrusion. Instead, zircon Hf-isotope and age data rather record condition of the source. However, lead loss effect by post-crystallisation events might influence to the age distribution, whilst the presence or absence of the events are difficult to identify. Therefore, more researches on the zircon system closure will be required.

	Host rock (Satkatbong diorite)									
Sample	02	03	04	12	03G	05G	07G	09G	13G	15G
SiO ₂	66.29	65.92	74.22	54.13	65.75	64.67	64.92	64.87	65.13	64.19
Al ₂ O ₃	15.16	15.98	13.59	17.00	16.37	16.20	16.32	16.90	17.03	17.31
Fe ₂ O ₃ (T)	3.89	4.06	1.34	8.60	3.99	4.50	4.18	4.45	4.09	4.54
MnO	0.08	0.09	0.03	0.14	0.09	0.10	0.07	0.10	0.09	0.10
MgO	1.63	1.61	0.31	3.38	1.69	1.92	1.95	1.87	1.74	1.87
CaO	3.97	3.83	0.96	6.50	4.60	4.83	4.35	4.76	4.71	4.95
Na₂O	3.70	3.65	3.21	4.28	3.72	3.63	4.12	3.74	3.74	3.84
K₂O	2.69	2.70	4.76	1.57	2.00	2.21	2.07	2.22	2.18	1.97
TiO ₂	0.41	0.39	0.14	1.21	0.36	0.43	0.42	0.42	0.40	0.43
P_2O_5	0.09	0.11	0.03	0.23	0.12	0.13	0.12	0.12	0.10	0.13
LOI	1.47	1.86	1.51	1.79	1.99	1.41	2.23	1.27	1.61	1.62
Total	99.38	100.20	100.10	98.82	100.70	100.00	100.80	100.70	100.80	100.90
Na_2O+K_2O	6.39	6.35	7.97	5.85	5.72	5.84	6.19	5.96	5.92	5.81
FeO(I)	3.50	3.65	1.21	1.14	3.59	4.05	3.76	4.00	3.68	4.09
a/nk	1.68	1.79	1.30	1.95	1.98	1.94	1.81	1.98	2.00	2.05
a/cnk	0.93	1.01	1.12	0.83	0.98	0.94	0.96	0.98	1.00	0.99
Mg #	0.45	0.44	0.31	0.44	0.46	0.46	0.48	0.45	0.46	0.45
K/Na	0.48	0.49	0.98	0.24	0.35	0.40	0.33	0.39	0.38	0.34
I race elemer	nts (ppm)	CE.	44	200	66	70	70	70	66	74
V D-	64	65	77	209	00	73	12	/ð 005	00	14
Ва	543	514	150	361	371	550	407	635	580	555
SI	434	400	140	928	452	430	431	439	400	4/8
ř Zr	14	10	20	10	100	14	GI 111	10	104	14
	102	120	09	10	100	127	17	123	104	10
Ga Dh	77	71	14	30	58	52	67	17	10	10
Nb	3	3	5	1	3	1	3	49	49	40
Cs	48	41	42	- 17	24	21	21	19	20	16
la	43.1	8.4	26.3	29.2	22.4	14.4	18.2	10.0	9.2	24.2
Ce	77.9	18.6	52.3	55.0	43.5	29.8	34.5	21.9	20.1	45.2
Pr	7.5	24	5.5	64	4.6	3.5	3.9	2.8	2.5	4.6
Nd	22.8	10.3	18.8	25.0	17.4	13.7	15.1	12.0	10.3	16.5
Sm	3.3	2.4	3.1	5.3	3.0	2.9	3.0	2.7	2.3	3.0
Eu	0.8	0.7	0.5	1.7	0.8	0.8	0.8	0.8	0.7	0.8
Gd	2.4	2.2	2.6	4.2	2.4	2.4	2.5	2.3	1.9	2.4
Tb	0.3	0.4	0.4	0.6	0.4	0.4	0.4	0.4	0.3	0.4
Dv	1.8	2.4	2.4	3.5	2.2	2.3	2.4	2.3	1.9	2.1
Ho	0.4	0.5	0.5	0.7	0.4	0.5	0.5	0.5	0.4	0.4
Er	1.1	1.5	1.5	1.8	1.2	1.3	1.5	1.3	1.2	1.2
Tm	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2
Yb	1.1	1.7	1.6	1.6	1.4	1.5	1.5	1.4	1.3	1.4
Lu	0.2	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2
Hf	2.3	3.2	2.6	2.0	2.6	3.3	2.9	3.0	2.6	2.9
Та	0.3	0.4	0.8	0.3	0.5	0.6	0.3	0.3	0.4	0.4
Pb	11	12	29	9	10	10	8	11	11	10
Th	11.4	7.4	14.9	8.2	9.7	6.8	6.8	7.9	7.5	7.9
U	1.4	3.3	2.1	3.3	2.1	2.2	1.7	1.7	2.5	1.9
Eu/Eu*	0.9	1.0	0.6	1.1	0.9	0.9	0.9	1.0	1.1	0.9

Table 2.1. Major and trace element composition of the SKD, MME, and cumulate.

	Host rock (Satkatbong diorite)				MME					
Sample	D05	D09	D10	E09	05	06	07	11	03M	09M
SiO ₂	62.52	71.25	63.64	57.05	55.11	54.20	54.23	54.40	53.09	57.34
AI_2O_3	15.16	14.48	16.17	17.83	18.25	18.66	19.05	17.86	17.49	14.93
Fe ₂ O ₃ (T)	4.50	1.85	4.22	6.97	7.53	7.47	7.80	7.37	9.40	10.58
MnO	0.07	0.03	0.08	0.14	0.21	0.19	0.21	0.22	0.29	0.21
MgO	2.06	0.42	1.78	3.61	4.05	3.70	3.75	4.38	4.85	4.01
CaO	3.05	1.69	4.12	6.86	6.22	5.55	6.68	5.96	6.79	5.18
Na ₂ O	3.30	3.24	3.62	4.05	4.23	3.78	4.27	4.06	4.03	2.86
K ₂ O	3.37	4.71	2.77	1.67	2.28	2.39	2.10	2.06	1.84	1.72
TiO ₂	0.51	0.15	0.42	0.65	0.77	0.72	0.69	0.77	0.71	0.90
P_2O_5	0.09	0.05	0.12	0.13	0.19	0.16	0.15	0.13	0.10	0.19
	4.1/	0.90	2.18	1.69	1.36	2.24	1.75	2.05	1.92	2.77
Iotal	98.79	98.77	99.13	100.70	100.2	99.07	100.70	99.26	100.50	100.70
Na_2O+K_2O	6.67	7.95	6.39	5.72	6.51	6.17	6.37	6.12	5.87	4.58
FeO(I)	4.05	1.66	3.80	6.27	6.78	6.72	7.02	6.63	8.46	9.52
a/nĸ	1.67	1.39	1.81	2.11	1.94	2.12	2.05	2.00	2.03	2.27
a/cnk	1.04	1.07	0.98	0.85	0.88	0.99	0.89	0.90	0.83	0.93
Mg #	0.48	0.31	0.46	0.51	0.52	0.50	0.49	0.54	0.51	0.43
K/Na Trana alaman	10.07	0.96	0.50	0.27	0.35	0.42	0.32	0.33	0.30	0.40
I race elemen	its (ppm)	24	71	146	146	104	140	170	167	101
V Ro	93	24 1045	616	140	140	747	140 600	624	107	101
ва	407	1240	010	304	200	/ / 500	020	03 I 544	400	020
31 V	395	247	400	000 1E	429	523	307	21	430	300
ı 7r	130	118	1/0	08	120	20	111	24 64	40 62	20
Ga	1/	13	140	17	120	10	20	18	21	20
Rh	107	112	7/	65	71	80	68	67	50	13
Nb	3	2	3	2	4	5	6	4	6	-5
Cs	41	14	39	53	28	37	22	21	43	18
la	22.8	41.0	19.0	11 1	13.0	14.5	13.5	15.2	18.4	12.4
Ce	46.3	80.4	36.6	24.4	33.4	36.6	35.6	37.0	47.6	31.9
Pr	5.1	7.8	3.9	3.0	4.7	5.1	5.3	5.0	6.9	4.5
Nd	17.4	23.6	14.4	12.6	20.3	22.2	24.4	20.7	32.5	20.9
Sm	3.2	3.1	2.8	2.8	4.7	5.0	6.1	5.3	8.0	4.9
Eu	0.6	0.8	0.8	0.9	1.2	1.1	1.3	1.3	1.5	0.9
Gd	2.9	1.8	2.5	2.9	4.3	4.5	5.7	4.7	6.6	4.3
Tb	0.5	0.2	0.4	0.5	0.7	0.7	1.0	0.7	1.1	0.7
Dy	2.9	1.2	2.3	2.7	4.5	4.3	5.9	4.1	6.6	4.3
Ho	0.6	0.2	0.5	0.5	0.9	0.9	1.2	0.8	1.4	0.8
Er	1.7	0.8	1.4	1.6	2.6	2.7	3.6	2.4	3.8	2.5
Tm	0.3	0.1	0.2	0.3	0.4	0.4	0.6	0.4	0.6	0.4
Yb	1.8	1.0	1.5	1.7	2.8	2.7	3.7	2.7	4.2	2.6
Lu	0.3	0.2	0.2	0.3	0.4	0.4	0.6	0.4	0.6	0.4
Hf	3.3	3.1	3.5	2.5	2.9	2.5	2.9	2.0	2.2	5.0
Та	0.4	0.4	0.4	0.2	0.3	0.3	0.4	0.3	0.6	0.5
Pb	10	23	12	7	11	11	13	10	9	9
Th	6.1	18.6	8.5	4.2	4.0	3.5	2.4	5.0	5.0	8.7
U	2.0	2.3	2.1	1.0	1.0	1.6	1.9	1.5	1.8	1.7
Eu/Eu*	0.6	1.0	0.9	1.0	0.8	0.7	0.7	0.8	0.6	0.6

Table 2.1.	(Continued)
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					MME				
Sample	11M	E04	E10	E03	E07	E08	E11	E12	D06
SiO ₂	52.29	54.17	53.94	51.80	55.11	54.26	56.49	54.69	64.66
AI_2O_3	19.28	18.18	18.30	18.73	18.78	18.21	18.23	17.90	15.57
Fe ₂ O ₃ (T)	8.83	7.68	7.31	8.49	7.38	6.96	6.75	6.74	4.02
MnO	0.24	0.14	0.20	0.19	0.20	0.18	0.19	0.19	0.08
MgO	4.41	4.08	4.09	4.59	3.43	3.86	3.76	3.77	1.70
CaO	6.76	7.13	6.41	7.98	6.54	6.21	6.41	5.56	4.41
Na ₂ O	4.42	3.87	3.98	3.70	4.31	4.60	4.01	4.18	4.02
	2.05	1.46	3.10	1.65	1.94	2.41	2.25	2.11	2.46
	0.78	0.78	0.65	0.76	0.66	0.67	0.69	0.72	0.44
$P_2 U_5$	0.14	0.10	0.12	0.14	0.17	0.15	0.13	0.10	0.08
LUI Total	1.40	1.90	2.13	1.00	1.14	2.73	1.40	3.03	1.72
	6.47	99.03 5.33	7.09	99.09 5.35	99.00 6.25	7.01	6.26	99.00	99.15
$F_{0}O(T)$	7.95	5.55 6.01	6.58	7.64	6.64	6.26	6.07	6.06	3.62
a/nk	2.03	2 20	1.85	2 38	2.04	1 70	2.02	1 95	1.68
a/nk	0.89	0.87	0.85	0.84	0.89	0.85	0.88	0.93	0.90
Ma #	0.50	0.51	0.53	0.52	0.03	0.52	0.50	0.53	0.30
K/Na	0.31	0.25	0.51	0.02	0.30	0.34	0.37	0.33	0.40
Trace element	nts (ppm)	0.20	0.01	0.20	0.00	0.01	0.07	0.00	0.10
V	181	179	139	179	133	152	165	140	82
Ba	520	505	553	389	587	296	551	594	444
Sr	399	544	498	465	494	389	426	435	309
Y	29	17	30	17	22	29	23	23	21
Zr	103	65	20	98	98	60	86	84	129
Ga	21	19	18	20	20	19	19	19	15
Rb	71	43	127	50	71	138	75	66	84
Nb	6	3	5	4	4	5	5	5	3
Cs	2.7	2.5	3.5	1.0	3.9	6.4	2.7	3.9	2.6
La	17.1	11.9	17.9	17.4	18.6	12.7	10.8	16.2	11.6
Ce	42.2	26.6	45.5	39.3	40.5	34.2	27.7	38.2	25.1
Pr	5.9	3.3	6.1	4.7	5.1	5.1	4.1	5.0	3.3
Nd	25.8	13.7	24.1	18.0	21.2	22.3	18.3	21.3	13.2
Sm	6.2	3.3	5.3	3.7	4.9	5.3	4.4	4.9	3.2
EU	1.3	1.0	1.2	1.2	1.3	1.1	1.1	1.2	0.7
Ga Th	5.0	3.4	4.9	3.4	4.3	5.0	4.4	4.0	3.2
	0.0	0.5	0.0	0.5	0.7	0.9	0.7	0.7	0.5
Dy Ho	4.0	3.3 0.7	5.0	3.3 0.7	5.9	5.1	4.3	4.2	3.3 0.7
Fr	1.0	1.9	3.2	2.0	23	3.2	2.6	2.5	2.0
Tm	0.5	0.3	0.5	0.3	0.4	0.2	0.4	0.4	0.3
Yh	3.1	1.8	39	2.2	25	3.6	27	27	2.1
lu	0.5	0.3	0.6	0.4	0.4	0.6	0.4	0.5	0.3
Hf	27	17	12	2.6	24	2.0	24	2.3	34
Та	0.5	0.2	0.5	0.3	0.3	0.4	0.4	0.7	0.4
Pb	12	8	8	7	7	7	12	12	7
Th	3.0	4.3	5.6	2.2	3.9	3.0	4.7	7.4	6.8
U	1.0	1.1	2.5	0.7	0.8	2.5	1.3	3.0	2.2
Eu/Eu*	0.7	0.9	0.7	1.0	0.9	0.7	0.7	0.8	0.7

Table 2.1.	(Continued)
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	М	ME				Cumulate			
Sample	D12	D15	01	08	09	10	D04	E01	E02
SiO ₂	64.55	61.19	67.10	58.45	51.46	48.85	48.77	52.64	53.15
AI_2O_3	15.42	16.62	15.19	17.89	18.94	18.94	21.75	19.12	18.75
Fe ₂ O ₃ (T)	4.03	6.00	3.84	6.51	8.08	9.59	8.09	8.60	8.29
MnO	0.07	0.10	0.08	0.12	0.17	0.17	0.11	0.15	0.22
MgO	1.79	2.96	1.71	2.99	5.21	5.17	3.64	4.89	5.23
CaO	4.93	5.99	4.51	6.80	8.48	10.52	10.38	9.38	8.72
Na₂O	3.88	3.23	3.84	3.37	2.85	3.64	2.52	2.78	3.77
K ₂ O	2.33	1.95	1.84	1.33	1.30	0.92	1.00	0.91	0.69
TiO ₂	0.45	0.67	0.43	0.65	0.73	0.81	0.82	0.80	0.89
P_2O_5	0.09	0.14	0.09	0.14	0.11	0.24	0.08	0.05	0.14
LOI	2.31	1.38	1.77	1.07	2.48	1.35	1.86	1.35	0.80
Total	99.85	100.20	100.40	99.32	99.80	100.20	99.03	100.70	100.70
Na_2O+K_2O	6.21	5.18	5.68	4.70	4.15	4.56	3.52	3.69	4.46
FeO(T)	3.63	5.40	3.46	5.86	7.27	8.63	7.28	7.74	7.46
a/nk	1.73	2.24	1.83	2.56	3.11	2.71	4.16	3.44	2.70
a/cnk	0.86	0.91	0.92	0.92	0.88	0.73	0.90	0.85	0.82
Mg#	0.47	0.49	0.47	0.48	0.56	0.52	0.47	0.53	0.56
K/Na	0.40	0.40	0.32	0.26	0.30	0.17	0.26	0.22	0.12
I race elemer	its (ppm)						0.15	004	004
V	82	147	69	146	229	232	315	234	221
Ba	314	402	483	343	1/4	318	257	222	192
Sr	260	403	544	491	513	854	658	518	483
Y Z-	17	21	13	16	16	11	11	12	13
Zr	115	99	121	95	62	23	40	70	61
Ga	15	10	10	18	18	17	20	18	18
	92	52	54	37	43	22	40	22	14
	3 22	10	3	2 1 0	27	1	1	∠ 1 2	3
	2.3 12.3	1/ 3	1.0	1.0	3.7 7.5	3.1 10.1	2.0	1.3	1.0
La	12.3	14.3	0.9	14.1	17.5	21.1	12.0	1.0	11.4
Dr	20.0	33.0	2.1	20.0	2.4	21.1	13.9	17.2	22.2
Nd	13.3	4.2	2.1	12.0	2.4	2.5	7.8	2.2	2.0
Sm	2.0	3.0	1.8	2.9	9.0 2.5	2.2	2.0	2.2	2.5
Eu	2.5	0.9	0.8	2.0	2.5	2.5	2.0	0.9	2.5
Gd	27	3.8	17	24	2.6	21	2.1	23	2.5
Th	0.4	0.6	0.3	0.4	0.4	0.3	03	0.4	0.4
Dv	2.8	3.9	1.6	2.6	2.6	2.0	2.2	2.3	2.6
Ho	0.6	0.8	0.3	0.5	0.5	0.4	0.4	0.5	0.5
Fr	17	2.2	1.0	14	1.5	1.0	12	1.3	1.5
Tm	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Yh	1.8	2.2	1.0	1.5	1.6	1.0	1.2	1.5	14
lu	0.3	0.3	0.2	0.2	0.3	0.2	0.2	0.3	0.2
Hf	3.1	2.6	2.9	2.5	17	0.7	1.3	1.8	1.5
Та	0.3	0.3	0.4	0.2	0.1	< 0.1	0.2	0.2	0.2
Pb	7	8	9	8	< 5	11	7	5	7
Th	12 2	78	57	30	19	16	19	33	27
U	1.4	2.2	2.6	1.2	0.7	1.6	1.2	1.0	0.9
Eu/Eu*	0.7	0.7	1.3	1.1	0.9	1.3	1.2	1.2	1.2

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Chapter 3

Testing the U-Pb age reliability of hydrothermally altered magmatic zircon using trace elements: A case study from the Mt Buller I-type granitoid suite, Lachlan Fold Belt, Australia

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3.1 Introduction

From the dating to investigating the petrogenesis of plutons, the number of studies using zircon geochronology has significantly increased over the last decades, so that zircon has become the most commonly used accessory mineral for dating plutons (Hoskin et al., 2003; Hermann and Rubatto, 2014; Spencer et al., 2016). Dating plutons is conducted by either isotopic dilution (ID) or laser ablation (LA) analysis. The latter is characterised by *in-situ* analysis, but is of less precision compared to the ID technique. However, LA data can be collected relatively rapidly from a larger number of zircons, is relatively cost effective, and more accessible than ID analyses, and has therefore become the method of choice for many studies (e.g., Jochum et al., 2005).

Zircon is a common accessory phase in rocks of granitic composition. The physiochemical resilience of zircon together with high U and low (common) Pb in its lattice have made it the gold-standard for geochronology. In addition, it is a refractory mineral, and has a high closure temperature (> ~900 °C; Cherniak, 2010) and combined with simple, concentric zonation that is ideally suited for *in-situ* analyses (Ireland and Williams, 2003). However, despite its robustness, the zircon chronometer may yield erroneous age information if secondary processes are not carefully assessed, which may lead to incorrect geologic interpretations (Geisler et al., 2007; Kusiak et al., 2013). It is not uncommon that zircon ages in granites span over tens of millions of years for a single plutonic body or even within a hand specimen (e.g., Idaho Batholith (Gaschnig et al., 2013), Ladakh Batholith (Weinberg and Dunlap, 2000), Florida Mountains granite (Amato and Mack, 2012), Satkatbong diorite (2nd chapter)), which are unlikely to record a single magmatic event. In addition, zircon is not completely free from common lead contamination, and often vulnerable to hydrothermal alteration (Geisler et al., 2007) and/or radiation-damage (Yu et al., 2021), which may further contribute to spurious age information.

Previous studies have indicated the role of late-stage hydrothermal fluids in altering zircons and their U-Pb systematics, especially in the context of hybridised granitic suites that contain abundant microgranular mafic enclaves (MME; Kusiak et al., 2009). A number of different publications have proposed various methods to filter and assess zircon data (Geisler et al., 2007; Fu et al., 2009; Spencer et al., 2016; Bell et al., 2016; Zhong et al., 2018; Bell et al., 2019). These will be used, extended and combined in this study.

Here, I present zircon analyses from an I-type granodiorite (termed "host" hereafter) and its mafic microgranular enclaves (termed "MME" hereafter) from the Mount Buller suite in the Lachlan Fold Belt, Southeastern Australia. The age of the intrusion is derived from U-Pb dating of zircon and coupled with in-situ trace element data utilising laser ablation split-stream mod (LASS). The combined data is used to assess the age of the suite, and to discuss influences of chemical alteration.

3.2 Geological setting

The Lachlan Fold Belt (LFB) is part of the Paleozoic Tasmanides, which formed part of an accretionary orogenic system on the margin of Gondwana. Orogenic activity along the margin produced granites (and associated volcanic rocks) with a range of I-type to S-type compositions over a period of ca. 300 Ma (Chappell et al., 1988; Kemp et al., 2009).

The general framework of the Lachlan Fold Belt is an extensive succession of early to mid-Palaeozoic marine sedimentary formations and associated igneous rocks. The southern Lachlan Fold Belt is commonly divided into three sections, from west to east: the Western, Central, and Eastern section (Richards and Singleton, 1981). In the central section, near Melbourne, Devonian – Carboniferous granitic bodies intruded the Early-Ordovician to Mid-Ordovician sedimentary country rock. In this region, muscovite granites, biotite granites, and granodioritic bodies are widespread. These plutons correspond to S-type or I-type in major element chemistry. Granitoids in the east margin of central section are generally late Devonian and post-date the Tabberabberan orogenic phase (Richards and Singleton, 1981).

Mount Buller

The Mount Buller suite is one of the post-Tabberabberan intrusions with a reported K-Ar age of 381 ± 7 Ma (Richards and Singleton, 1981) in the central section. The suite is composed of three main bodies, the Mt Stirling, Mirimbah, and Howqua intrusions. Homogeneous, hornblende-bearing fine- to coarse- grained granodiorite mainly comprises the Mt Stirling and Mirimbah intrusions, with the latter also including a mafic unit of gabbroic composition (Fig. 3.1). The Howqua intrusion, also known as the Howqua mafics, comprises gabbro-norite, quartz diorite, and tonalite, with minor granodiorite and granite. Granitic rocks are cut by dacitic, andesitic, and basaltic dykes. Compositional boundaries between rock types within the intrusions are transitional. The three intrusions commonly include MME, which range in size from few centimetres to metres, with lower silica content and higher proportions of mafic minerals than their host. Three component mixing is the most recent proposed model for the Mt Buller suite rocks (Collins, 1996; Keay et al., 1997; Soesoo, 2000) involving mantle, Cambrian greenstone, and Ordovician sedimentary rock endmembers.

Mt Stirling, of particular interest in this study, is composed of three lithological subunits: (1) Slightly brighter, medium- to coarse-grained hornblende granodiorite (HGD), (2) darker, fine- to medium-grained porphyritic hornblende granodiorite (FGD), and (3) MME included in the HGD and FGD. The HGD and FGD show nearly the same mineral assemblages, but grain sizes and mode (e.g., finer and slightly more mafic minerals in FGD) are the main differences between these two units. The unit FGD shows resorbed plagioclase crystals.

The HGD and FGD have previously yielded 87Sr/86Sr (i) values in the range of 0.7037 – 0.7071, and ϵ Nd (t) values of +3.4 to +5.6, with similar values in the MME (Soesoo, 2000). These isotopic compositions in the host rock and MME do not correlate with SiO2 concentrations. Soesoo (2000) proposed a fractional crystallisation model for the mafic and felsic Mt Buller rocks with minor mixing or crustal assimilation, so called incestuous mixing (i.e., mixing of earlier solidified crystals with the same, but more evolved, magma).



Figure 3.1. A geologic map (modified from VandenBerg, 1997) of the Mount Buller Suite composed of main three plutons (the Mt Stirling, Mirimbah, and Howqua). The sampling site is located in the south western part of Mt Stirling pluton.

3.3 Sample description

Samples were collected from an outcrop at the Mount Buller alpine village, located at the southwestern part of the Mt Stirling pluton, and include both HGD and FGD and MME. The host granodiorites are massive and relatively homogeneous (Fig. 3.2A), and in some places mildly porphyritic in texture. They are composed of quartz, plagioclase, amphibole, biotite, with accessory K-feldspar, apatite, titanite and zircon. The predominant phenocrystic phases are plagioclase and hornblende with less abundant biotite. Zircon and apatite are euhedral and equally distributed in groundmass and as inclusions in phenocrysts (Fig. 3.2B, 3.2C, and 3.2D). Zircons are relatively clean yet often contain both stubby and acicular apatite inclusion (Fig. 3.2E, 3.2F, and 3.2G). Some of zircons from the host rock and most of zircons from the MME show resorption (Fig. 3.2G). Euhedral titanite is rare in thin section, while anhedral titanite exsolution occurs in contact with ilmenite. Finer grained part of the host rock show resorbed plagioclases.

Darker grey colour MME are also massive and homogeneous, whilst they are porphyritic to equigranular with finer crystals than those of the host rock. Major and minor phases are identical to the host rock. Fine-grained opaque oxide minerals, accessory minerals and early mafic phases are distributed evenly and later larger grained phases (plagioclase, K-spar, and quartz) capture them. The MME contains quartz ocelli (quartz mantled by fine-grained hornblende crystals) and mafic hornblende clots. It contains resorbed plagioclase phenocrysts as the finer grained part of the host rock.

Contact between the host rock and MME is generally sharp, but sometimes boundaries show gradual transition. This is mainly because the boundary is defined by different proportions of mafic minerals but with both phases having an overall identical mineralogy. On the host rock side of the granodiorite-MME boundary, megacrystic or coarser grained plagioclase shows resorbed texture. Amphibole and plagioclase xenocrysts which transferred from the MME melt are observed.



Figure 3.2. Hand, thin section and BSE images of analysed samples. (A) Hand specimen which includes both host rock (h2; HGD) and enclave (m1). (B) Zircon crystal captured by interstitial quartz (h3). (C) Euhedral zircon in feldspathic framework in transmitted light (h3). (D) same

as C but under crossed polars. (E) A back scattered electron (BSE) image of a representative zircon from the host rock with weak concentric compositional zoning. (F) Euhedral zircon from the host rock. Apatite inclusions are common. (G) BSE image of a representative zircon from the MME, which shows apatite inclusions and resorption texture. (H) BSE image of a representative zircon from the MME, which shows relatively homogeneous composition. Qtz: quartz; Zrn: zircon; Ap: apatite; Kfs: K-feldspar; Pl: plagioclase.

3.4 Analytical procedures

Zircons were collected from five host rock (h2z, and h3z from the HGD, h1z, h4z, and h5z from the FGD) and two MME samples (m1z and m2z). Weathered parts of rock samples were removed prior to crushing in a hydraulic press, with big chips going through a big and then a small jaw crusher. Pebble size (~2 cm) chips were ground to ~sand size in a disc mill. The samples were then sieved through a 180 μ m fabric sieve. After washing to remove fine dust from the sample, and drying, magnetic phases were separated from the <180 μ m grain fraction initially by a neodymium hand magnet bar and then a Frantz magnetic separator. Tetrabromoethane (TBE) was used for heavy liquid separation. Washed and dried heavy (> 2.97 g/cm³) grains were then picked for zircon.

A scanning electron microscope (FEI Qanta 600 MLA, W-filament source) attached with Delmic Jolt Cathodoluminescence (CL) detector at the school of Earth, Atmosphere, and Environment (EAE), Monash University was used for back-scattered electron and cathodoluminescence images. Operating voltage and emission current were 20.0 kV and 40 – 100 μ A, respectively. Laser ablation split stream mode (LASS) was used for simultaneous U-Pb isotopes and trace elements collection. ASI-RESOlution ArF 193 nm excimer laser ablation system, ThermoScientific iCapTM TQ ICP-MS, and ThermoScientific iCAPTM Q ICP-MS in the Isotopia Laboratory, Monash University, were used for laser ablation, U-Pb, and trace element analyses, respectively. Laser (1.04 kV with 5.5 mJ) frequency was 10 Hz with 30 second ablation time, and each spot diameter was 30 μ m. Glass NIST 610 was used as a primary reference material, and NIST 612, ATHO, BCR2, and BHVO2 were used as secondary was 152300 ppm. Plesovice was used as a primary reference material for U-Pb analysis, and 91500 and GJ-1 were used as secondary reference materials.

Both core and rim of zircons were analysed. The primary standards were analysed after every 20 unknown spots, and secondary reference materials after every 40 unknown sample. The analyses were completed in two sessions, 19th of February and 17th of March, 2021. Software Iolite 4 (Paton et al., 2011) was used for data reduction, which mainly creates a primary standard spline and propagates errors of unknowns based on offsets of the spline. Age calculation and plots were conducted by the IsoplotR (Vermeesch, 2018). Secondary reference material concordia ages from the two different sessions (601.3 ± 2.9 Ma for GJ-1 and $1059 \pm$ 5 Ma for 91500) corresponded to the respective reference values for each zircon (602 Ma for GJ-1 (Jackson et al., 2004) and 1064 Ma for 91500 (Wiedenbeck et al., 1995)). Chi-squared test to GJ-1 and 91500 (0.58 and 0.57) and MSWD (0.93 and 0.94) shows a good quality of fit (Fig. 3.3). Common lead correction in this study is after the 2-stage lead growth model of Stacey and Kramers (1975).



Figure 3.3. Concordia diagrams and Kernel density plots for the reference material GJ-1 (Jackson et al., 2004) and 91500 (Wiedenbeck et al., 1995)

3.5 Results

Trace element analysis

In-situ trace element concentrations of zircon are listed in supplementary material 6 (Table S5; <u>https://figshare.com/s/b128a2379e6ce7ec8920</u>). Zircons from the host rock and MME have an average Th/U = 0.65 (n = 232). Concentration of Y in zircon generally correlates with ambient magma composition (Belousova et al., 2002b). Yttrium contents in the Mt Buller zircons lie within the intermediate – felsic magma range (ca. 300 - 3000 ppm; Belousova et al., 2002b). Total REE + Y abundance (Σ REE+Y) of the total zircons from the host rock and MME

shows a typical crustal zircon range (Hoskin and Schaltegger, 2003) (1225 ppm in average, n = 232) (Fig. 3.4). Potassium concentrations range from below the detection limit to a maximum of 6851 ppm, yet high-K spots (>1000 ppm) potentially indicate outliers; most spots are below 400 ppm (average: 79 ppm and 346 ppm, for the host rock and MME respectively) (Fig. 3.4). Calcium shows a similar trend: mostly in the 1000 - 2000 ppm range, yet outliers (e.g., > 10000 ppm points in figure 3.4; note the y-axis is log scale) reach wt. % range (Fig. 3.4). Iron concentration is generally not higher than 1000 ppm with a few wt. % level outliers. Concentrations of Sr, Ba, and Pb are generally below 100 ppm with some outliers (less than ten points) over hundreds of ppm level (Fig. 3.4; Pb is not stated). This concentration range from the study area ranges from similar to 2 - 3 orders of magnitude higher compared to the level of the standard zircons (GJ-1 and 91500). Aforementioned elements show no clear correlation with Hf or REE. While trace element concentrations in both the host rock and MME are largely variable, most of elements show similar patterns in both the host rock and MME zircons (e.g., 1.95 – 393 ppm and 2.00 – 209 ppm Ti in the MME and host zircons). The exceptions are LREE; ~four orders of magnitude variations are observed in both the host rock and MME in LREE (La - Nd), Sm and Eu (Fig. 3.5). The spread of Ce positive anomaly (Ce/Ce*) is large, from 0 to ~100, and Eu anomaly (Eu/Eu*) ranges from 0.4 to 1 with the exception of 6 points with a positive Eu anomaly. Rare earth element patterns of both the host rock and MME zircons are likely composed of mixtures of distinct REE patterns. The distinct patterns show generally more enriched LREE overall than that of HREE (Fig. 3.5).



Figure 3.4. Trace elements of the zircons from host rock and MME from the Mt Stirling intrusion. Elements presented in this figure (Ca, K, Fe, Sr, and Ba) are non-formula elements for zircon, which are suggested as index elements in hydrothermal alteration of zircon. Note that the concentration of these element ranges from similar to 2 - 3 orders of magnitude higher compared to the level of standard zircons (GJ-1 and 91500).



Figure 3.5. C1 Chondrite (McDonough and Sun, 1995) normalised REE plot for host rock and MME zircons. Note the similarity between the host and MME zircons.

U-Pb dating

Isotope compositions of U-Pb and associated ages are listed in the supplementary material 6 (Table S5; <u>https://figshare.com/s/b128a2379e6ce7ec8920</u>). Weighted mean of common lead corrected age of the host rock is 398 ± 1 Ma (n = 240) and that of the MME is 382 ± 7 (n = 62). However, zircon ages form a wide range from $\sim 350 - \sim 450$ Ma in the host rock with a MSWD = 4.8, and $\sim 300 - \sim 450$ Ma in the MME with a MSWD = 16 (age plots in Fig. 3.6). A probability density diagram with kernel density estimation (KDE) of the host rock zircon shows a main peak and a shoulder and tail extending towards younger ages. Weighted mean age of the peak is ca. 400 Ma (Fig. 3.6). The density diagram of the MME shows a less pronounced peak age with considerable scatter and thus fails to fit a Gaussian distribution (density plots in Fig. 3.6). This spread of ages either side of the peak in both the host and MME, especially the pronounced tail on the younger side of the peak, contributes significantly to uncertainties and a larger MSWD.



Figure 3.6. Wetherill and Tera-Wasserburg type age plots and kernel density diagrams for the host rock and MME. Note spread of error circles and high MSWD, hence indicating overdispersion. Ages are common lead-corrected (Stacey and Kramers, 1975).

3.6 Discussion

Zircon age filtering

The zircon age range of the granodioritic host and MME samples records a large scatter over more than 100 Ma. Even if some age outliers (i.e., tails in the density diagram) are excluded, the remaining age group still spreads over nearly 100 Ma. This extreme range of ages cannot plausibly be interpreted in a geological sense if the ages represent an igneous intrusion event. This is a common, yet important issue, because many papers trim zircon data but few of them focus on the logics of the trimming criteria (e.g., discarding datasets based on an arbitrary discordance threshold; Spencer et al., 2016). In this study, the reliability of these ages is tested by the means of additional chemical analyses that were collected in conjunction with the age data. The methodology of this approach is outlined below.

In a first step, I use excessive amounts of Ca or K to identify individual analyses that do not represent an igneous age. High amounts of either element are not present in a zircon matrix and likely represent inclusions of other minerals, such as apatite or fluid inclusions within the zircon. We thus excluded analyses with weight percent-levels of Ca and K.

Following this initial filtering step, I used core-rim age differences as a measure of unreliable age data. For the vast majority of data, a core-rim pair were analysed, allowing a calculation of the age difference between both spots, termed here Δ (core-rim) value. Negative values indicate a rim that is older than its respective core, which for concentric growth zoning of zircon is geologically not possible. Age plots (Wetherill and Tera-Wasserburg style) in figure 3.6 and 3.10 indicate which analyses have been trimmed using this method. The reason for the difference in ages remain elusive but are likely to be analytical in nature. Younger core age might indicate laser mistargeting because of indistinctive zoning in some zircons. Invisible micro- crack or hole, and fluidal interaction through the crack or hole can also induce lead loss and spurious younger core age.

Following these basic filtering steps, the age distribution is still too large to record one single igneous event. In light of reported possible hydrothermal alteration of zircons during syn- or post-emplacement, I undertook further filtering using related geochemical proxies. It is well known that Th/U = 0.1 is a proxy for separation between igneous (> 0.1) and metamorphic (< 0.1) zircon (e.g., Kirkland et al., 2015). Although this is a guideline rather than an absolute criterium (Belousova et al., 2002b), we can still use it for an early stage skimming tool. Similarly, more than 1 wt% of $\Sigma REE + Y$ can be used for an early trimming criterion, since it may be indicative of a severely altered zircon composition (Figs 3.4 and 3.8; Hoskin and Schaltegger, 2003), thus zircon data with this range need to be excluded.

The remaining data after this filtering may further be assessed for fluid alteration by checking fluid mobile element abundances. For igneous zircon, high amounts of fluid mobile elements like Ba, K, and Sr potentially indicates unwanted hydrothermal alteration. Here we use a fluid mobile trace element vs. an immobile element to monitor extreme enrichment of fluid mobile elements. Following the approaches of Geisler et al. (2007) and Kusiak et al. (2009), and because K had been used to filter for inclusions earlier, Ba/Hf = 1 is used as a criterion, with samples exceeding this value being excluded from the dataset. The point with Ba/Hf > 1 may indicate excessively abundant Ba compared to naturally abundant Hf in zircon. A total of 24 out of 291 with Ba/Hf > 1 (after previous filtering is applied) (Fig. 3.7A), indicating that ~10 % of zircons can be hydrothermally altered, which were not detected in the previous proxies. Other non-formula elements like Ca, Al, Fe, and Mn were also suggested for proxies of zircon alteration if one of them is higher than a weight percent (Geisler et al., 2007).



Figure 3.7. Zircon data trimming scheme using trace elements (A) and REE (B – E). (A) Comparing non-formular and fluid mobile element (Ba) to formular element (Hf) can be a proxy to detect severely altered zircons (out for 1 > Ba/Hf). (B) Lambda (λ 1 vs. λ 2) plot after O'Neill (2016) to separate two different REE patterns (the group N and V). Note that the point of inflection separates the group N and V. The inlet figure depicts zircon's temperature range of 600 – 900 °C (Ti in zircon thermometry, Watson et al., 2006). (C) Nd/Sm versus Eu anomaly, (D) Ce anomaly, and (E) (Sm-Nd)_N (= tilting in Sm-Nd). The group V invariably shows higher Nd/Sm values than that of the group N, which indicates tilts of REE pattern at the group N and V are distinct. Cerium anomaly may separate two groups sharply compared to Eu anomaly.

Note that Ba/Hf trimming scheme may not similarly work in the REE trimming scheme. (F) A conceptual diagram describing the filtering scheme.

The large compositional spectrum of zircon further extends towards REE, especially in LREE or Nd/Sm, which are distinct in hydrothermal vs. magmatic zircons (Fu et al., 2009; Bell et al., 2016; Zhong et al., 2018). Zircons from the Mt Buller host rocks and MME show a range of distinct REE patterns and this distinction can potentially be used as an additional filter. While conspicuous differences in Nd/Pr or Nd/Sm are shown in both the host and MME zircons (Fig. 3.5 and 3.9), a REE pattern comparison scheme with focus on shape and steepness of the pattern (O'Neill, 2016) can be applied to quantify the differences and to find more cryptic differences. Lambda 2 against lambda 1 relations, as defined by O'Neill (2016) are distinguished into two groups of zircons depending on quantified shape factors (i.e., average, degree, and curvature of the REE pattern) (Fig. 3.7B).

Based on this separation, zircons were separated into two groups, with reference to their REE shape. One is termed "V-shape" and the other "N- (Normal-) shape" in relation to the shape in a chondrite-normalised REE pattern. V-shape group zircons are generally characterised by higher LREE and Nd/Sm, negative Δ (Sm-Nd) (= tilting in Sm-Nd in REE diagram), and lower Ce positive anomaly (Ce/Ce* \approx 1.8) than N-shape (Ce/Ce* \approx 11; Figs. 3.7C, 3.7D, 3.7E and 3.8). These features in V-shape zircons may be associated with hydrothermal overprint, because LREE are preferentially enriched in hydrothermal fluids and their interaction with zircon can lead to an incorporation into the crystal lattice (Belousova et al., 2002b; Fu et al., 2009; Bell et al., 2016). Therefore, chemical composition of V-shape group zircons implies higher probability of hydrothermal alteration, and thus the need to separate from unambiguously magmatic zircons. This is the fourth filter I applied.



Figure 3.8. Trimmed zircon trace elements concentrations after the trace element- and REEdata trimming test



Figure 3.9. Various zircon REE patterns. Zircons from both the host rock and MME shows both N- and V-shape zircons equally. V-shape zircons are featured by generally higher LREE, smaller Ce/Ce*, and descending trend from Nd to Sm. Note the interesting point of REE pattern (B), in that many of these severely altered -thus supposed to be deleted in the previous trimming step- would have normal-like REE pattern.

The exclusion of V-shape group zircons results in a more defined and narrower age span compared to that of the total (raw or ungrouped) ages (Fig. 3.10). Indeed, kernel density diagrams of the N-shape group zircons show a clearer Gaussian distribution (Fig. 3.11). The same effect can be observed for the MME's distribution, yet with a less pronounced distribution compared to the host granite, probably because of a smaller number of laser spots than that of the host (Figs. 3.11B, 3.11D, and 3.11F).

An interesting feature about the V-shape and N-shape zircon groups is that both host rock and MME display evidence for the hydrothermal overprint, indicating that this REE pattern separation is not attributed to the difference between the host and MME magmas, and that the hydrothermal overprint affected both rock types equally.

An important implication of the various types of filtering is that some outliers in one step may survive in other steps, so that only the combination of all will produce an age that most likely represents the igneous formation age. For example, some zircons with Ba/Hf >1 (Fig. 3.9B) have N-shape REE patterns. This indicates that undertaking the entire sequence of steps is important.

It is critical here that the trends in the Ba/Hf (Fig. 3.7A) and REE (Fig. 3.9; also Nd/Sm, Fig. 3.7D) are a continuous trend so that filtering at a certain threshold needs to be defined. This indicates that the hydrothermal alteration process, which effects zircon is a gradual process, and in turn implies that any cut-off threshold for these trimming schemes may not to be evaluated individually. For the current dataset, however, the proposed threshold yields the most robust results, tested through an iterative approach of filtering and zircon age MSWD.



Figure 3.10. Tera-Wasserburg age plots after data trimming process. Trimmed ages show narrower range than previous hence lower MSWD. Note that MSWD is still higher than 1 in both the host rock and MME, which indicates dispersion still remains.



Figure 3.11. Probability density diagram by kernel density estimation (KDE). (A - B) Unfiltered age distribution of the host rock and MME zircons. (C - D) Density plots for the v-shaped zircons from the host and MME zircons (E - F) Trimmed age data shows clearer normal

distribution compared to the untrimmed age data. Note MME's normal distribution is less clear, probably due to fewer number of points than that of the host rock zircons.

Implications for dating I-type magmatism

The fact that V-shape zircons, which are indicative for hydrothermal influence, yield different U-Pb results than the N-shape zircons, implies that the U-Pb system was not closed in these zircons (29% and 34% filtered out from the respective host and MME). This, however, was not apparent from CL imaging alone. Even though their age range (430 - 250 Ma) is similar to the N-shaped group zircons (Fig. 3.11), their exclusion clearly enhances the precision of the dating. Considering that large amounts of zircons used for a mean age calculation can also significantly reduce the error on a calculated age (albeit high MSWD), combined with a different mean age, this can result in false geologic interpretations. For example, even though the host rock ages before and after the filtering are near identical, the MME ages differ significantly. Before the filtering, the difference in mean age and associated uncertainty between host rock and MME indicates two different events, with mafic enclaves being injected into a seemingly still crystalline mush of host rock ca. 15 Myrs after emplacement of the granite. The filtering, however, clearly shows a contemporaneous origin of both rock types, which is geologically much more feasible.

A remaining issue, despite trace element filtering, is the age range of the N-shape zircon group (\sim 70 Ma in both the host rock and MME; 440 – 370 Ma), exceeds analytical reproducibility (2SE = \sim 10 Ma). Accordingly, the sample has still a high MSWD (1.5 for the host rock and 2.9 for the MME). The analyses of standard zircons (Fig. 3.3) indicate that this age difference is real and not an analytical artefact.

These zircons may simply indicate a long range of formation in the source of the melts (cf. chapter 2). According to the Ti in zircon thermometer (Hayden et al., 2008), the majority of zircons formed in a temperature range of 600 - 900 °C (inlet diagram in Fig. 3.7B). This is a feasible temperature range for I-type magma (Collins et al., 2020b). The temperature range might delineate the upper and lower limit temperatures; regarding the closure temperature of Pb in zircon (~900 °C) as an upper limit of the expressed zircon age, and regarding ~600 °C of granodioritic melt solidus as a lower limit. This temperature range is also wide, while no temperature difference is found in either core-rim or the major age (peak age) and other minor

age (tail ages) bandwidths. Therefore, zircons from the host rock and MME were likely formed over a long-time range of 70 Ma, and over a variously changing temperature range of 600 - 900 °C. The temperature variability may be dictated by mafic magma replenishments (cf. chapter 2)

Previously reported K-Ar ages of Mt Stirling pluton are 385 ± 14 Ma for biotite and 379 ± 13 Ma for hornblende (Richards and Singleton, 1981). These ages are $\sim 15 - 20$ Ma younger than the weighted mean zircon ages in this study. These hornblende – mica age however, may correspond to some younger fractions of zircon ages or even hydrothermal zircon ages. Regarding low-T formation in hornblende and biotite (300 - 500 °C hydrothermal transition from hornblende to biotite; Brimhall et al., 1985) together with their lower closure temperature (Tc _{Hn} = 530 and Tc _{Bt} = 310 °C; Harrison, 1982; Harrison et al., 1985) compared to that of zircon, these probably indicate hydrothermal overprint ages during or after the later stages of emplacement. This interpretation corresponds to that the zircons with younger ages in this study are suspected to be hydrothermally altered.

Most of the reported Lachlan Fold Belt granite ages are K-Ar ages from amphibole or biotite or whole rock Rb-Sr ages. Ages of other Victorian granitoids in the Lachlan Fold Belt range from ~365 to ~412 Ma based on whole rock Rb-Sr isochron ages (Gray, 1990), and 348 Ma (min) – 392 Ma (max) (average 370 Ma) from K-Ar (biotite, muscovite, and hornblende ages; Richards and Singleton, 1981). Similar younger K-Ar age – older zircon U-Pb age relationship has reported from the Lachlan Fold Belt, Wilsons Promontory Batholith (391 ± 14 and 379 ± 15 Ma with K-Ar ages; Richards and Singleton, 1981, and 395 ± 4 Ma with U-Pb zircon; Elburg, 1996). If zircon age indicates high-PT conditions of a primitive reservoir, zircon ages of the rest of the central LFB may shift older 10 – 20 million years to older than ~400 Ma, when potential hydrothermal ages were successfully trimmed out.

Investigation of the origin of the MME remains unclear because the MME and host rock are not distinct in zircon, then it is hard to separate their origins. This may be partly ascribed to mechanical grain mixing between the host rock and MME melts. However, the main reason for the similarity is probably that zircons formed prior to the generation of the host and MME magmas. Regarding similar morphology (Fig. 3.2) and similar Rb-Sr and Sm-Nd isotopic systematics between the host rock and MME (Soesoo, 2000), it is expected that these two magmas shared both common source and zircons. Thus the zircons were already

crystallized in the source and extracted into the host and MME magmas. This means the source of the host and MME magmas were already saturated in zircon (cf. chapter 2).

3.7 Conclusion

This study reports zircon U-Pb and trace element LASS data from the Mt Stirling pluton, Lachlan Fold Belt in southeastern Australia. Both trace elements and age data display a large spread of values in both the granodioritic host and MME. We suggest that trace elements and REE of zircons should be tested prior to the age determination. A scheme is proposed to filter data of zircon analyses that are either compromised by inclusions or through late-stage hydrothermal alteration. The proposed order of filtering is as follows: (1) Accidental inclusions by checking excessive K and Ca, (2) Comparing core and rim ages to exclude Δ (core-rim age) < 0, (3) zircon with excessive non-formular elements (Al, Fe, and Mn), (4) hydrothermal zircon by Ba/Hf > 1, and (5) potential hydrothermal zircons based on different REE patterns.

The filtered weighted mean age of the Mt Stirling pluton is $402 \text{ Ma} \pm 1 \text{ Ma}$, and this places the Mt Buller suite towards an earlier phase in the LFB granites. If this is true for other igneous suites, this could indicate a much more defined time of events in the LFB evolution. Zircon ages containing potentially hydrothermal altered grains may return spurious, younger ages. Therefore, caution must be applied when trying to date bodies with evidence for hydrothermal alteration.

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Chapter 4

Apatite vs titanite dating of I-type pluton: issues and solutions, Mt Stirling pluton, Lachlan Fold Belt

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4.1 Introduction

Establishing precise ages of granitic rocks is a fundamental requirement in understand crustal formation processes. The age of granites is often interpreted by analysing U-Pb isotopic composition of its magmatic zircons. Zircon, as a common and refractory mineral phase in granitic rock has high U and low Pb content with a relatively high closure temperature of > 900 degrees Celsius (Cherniak, 2010). These characteristics make this mineral the most used tool to constrain the U-Pb age of a crystallising granitic body (Košler and Sylvester, 2003; Paton et al., 2011; Spencer et al., 2016). However, an increasing number of studies have highlighted inconsistencies in zircon geochronology. In addition, some zircon data indicate biasing of ages consequent to significant common lead (Pb) or Pb loss (Spencer et al., 2016; Yu et al., 2021), even within a single hand specimen (cf. chapters 2 and 3). In these cases, the "age" of the zircon population of interest fails to yield a reliable age for the intrusion. In part this can be ascribed to inhomogeneity in radiogenic Pb (Kusiak et al., 2013), but may also relate to the presence of inherited zircons from the source of the intrusion (chapter 2), or alteration of zircon (chapter 3). As such, even though being one of the most reliable dating tools, zircon dating does not come without challenges.

In this context, other mineral phases such as apatite, titanite, allanite, rutile, xenotime, and monazite have been explored as potential alternative dating tools (e.g., Kylander-Clark, 2017; Yakymchuk et al., 2017; Fisher et al., 2020). Whilst titanite (or sphene), allanite (a group of REE-rich silicates) and rutile (TiO₂) are more common in more mafic plutons, such as I-type granitoids, xenotime and monazite (REE phosphates) are more prevalent in felsic plutons, especially those bodies with an S-type character.

Apatite (Ca₅(PO₄)₃(F, Cl, OH)) is common to most, if not all intrusions, and has been suggested as a useful additional or alternative petro-chronometer to zircon (e.g., Engi, 2017; Kylander-Clark, 2017; Ribeiro et al., 2020; Yu et al., 2021). It is moderately lanthanideenriched and has an extraordinarily flexible crystal structure, which can be annealed (Yu et al., 2021). This is contrast to zircon, which is often affected by radioactive damage when it has high U content or is old enough to accumulate damage, in which case the zircon becomes metamict (Yu et al., 2021). Apatite includes a wide range of minor and trace elements, such as S, Sr, U, Th, and REEs. These incorporated elements in apatite may provide a record of magmatic conditions at the time of the crystallisation. Titanite (CaTiSiO₅) is a common accessary mineral in igneous rocks (especially in metaluminous granites). In contrast to allanite and rutile, however, its high U concentration can readily be utilised in geochronology. In addition, titanite contains high concentrations of rare earth elements (REE), which can indicate magmatic conditions of crystal growth (Kohn, 2017; Scibiorski and Cawood, 2022). Titanite can also be used as a thermo-barometer (Bruand et al., 2020).

In the same study area of chapter 3, the I-type Mt Buller suite in the Lachlan Fold Belt, Southeastern Australia, both apatite and titanite are abundant compared to other REE-rich minerals. Here I study the U-Pb and trace element systematics of apatite and titanite from an Itype granodiorite and its mafic microgranular enclaves in order to better understand their use as an alternative geochronometer to zircon.

A complex cooling history can make apatite age interpretation confusing (Kirkland et al., 2018), but the study area has a relatively simple igneous origin, and U-Pb systematics of zircon are readily available for comparison (chapter 3). Therefore, the Mt Stirling granodioritic pluton is an ideal case study to test the reliability of apatite and titanite dating. We collect insitu U-Pb ages together with trace elements using laser ablation split-steam mode (LASS), so that we can interpret age data coupled with trace element chemistry.

4.2 Sample description

Apatite and zircon are euhedral and equally distributed in groundmass and phenocrysts (apatite grain in Fig. 4.1D) – acicular or stubby apatite often captured by euhedral zircons (Fig. 4.1C). Both apatite from the host rock and MME are nearly identical in shape and size, and they are similarly homogeneous in back scattered electron (BSE) image (Figs. 4.1E and 4.1G). Euhedral titanite is rare in thin section, while anhedral – subhedral titanite exsolution are often found in contact with ilmenite (Figs. 4.1B and 4.1D). Titanite and apatite formation was prior to amphibole and K-feldspar formation (Fig. 4.1D). Some titanite crystals show characteristic two cleavages in a grain scale BSE image (Fig. 4.1F), yet the typical sector zoning or any other compositional zoning is ambiguous. Most of titanites are rather homogeneous (Figs. 4.1F and 4.1H).



Figure 4.1. Hand, thin section and BSE images of analysed sample. (A) Hand specimen which includes both host rock (h2) and enclave (m1). (B) Titanite crystals contiguous to an ilmenite grain. (C) Acicular and stubby apatites captured by a euhedral zircon grain from the host rock

sample. (D) Thin section back scattered electron (BSE) image for the FGD sample. Apatite and titanite are captured by hornblende. Note a titanite exsolution from the ilmenite. (E) BSE image of a representative FGD apatite, and (F) titanite from the same sample. The typical cleavages are recognized yet the difference in the brightness is rather due to topography. (G) Apatite BSE image of the MME sample, with clear and homogeneous section, and (H) a titanite grain from the same sample. Ttn: titanite; Zrn: zircon; Ap: apatite; Hbl: hornblende; Ilm: ilmenite; Grt: garnet; Pl: plagioclase.

4.3 Analytical procedures

Apatite and titanite were collected both from the host (h1, h2, h3, h4, and h5) and MME (m1 and m2) samples. Any weathered parts were removed prior to being crushed by a hydraulic press, with big chips passing through first a large and then a small jaw crusher. Pebble size grains were ground to ~sand size by a disc mill. The ground sample then were sieved through a 180 μ m fabric sieve. After washing and drying the < 180 μ m fraction, magnetic phases were separated by a neodymium magnet bar and then a Frantz ® magnetic separator. Tetrabromoethane (TBE) was used for the heavy liquid separation after. Washed and dried heavier (> 2.97 g/cm³) portions were picked for apatite and titanite.

A scanning electron microscope (FEI Qanta 600 MLA, W-filament source) attached with Delmic Jolt Cathodoluminescence (CL) detector at the Monash University, Australia, was used for back-scattered electron and cathodoluminescence images. Operating voltage and emission current were 20.0 kV and $40 - 100 \mu$ A, respectively. Apatite and titanite U-Pb isotope and trace element data were collected by the method developed for Laser Ablation Split Stream Inductively Coupled Plasma Mass Spectrometry (LASS-ICP-MS) at the Isotopia Facility, Monash University. The isotope and trace element data were simultaneously collected by a Resolution S-155-LR 193 nm excimer laser coupled to a ThermoScientific iCapTM TQ ICP-MS (U-Pb isotopes; single-quad mode), and ThermoScientific iCAPTM Q ICP-MS (trace elements). The laser aerosol was split evenly between the two instruments at 0.15 L min⁻¹ each carrier (He) flow rate. The laser conditions were set such that a fluence at the sample of ~4.8 J cm⁻² was obtained, with a 10 Hz frequency and 25 μ m (30 μ m for titanite) spot size.

Dwell times for the iCAP TQ were 10 ms for ²³⁸U and ²³²Th, 20 ms for ²⁰⁸Pb, 70 ms for ²⁰⁷Pb, 40 ms for ²⁰⁶Pb and 30 ms for ²⁰⁴Pb and ²⁰²Hg. The ablated material was carried to the mass spectrometers by He gas, with a flow rate of 0.55 L min⁻¹, with auxiliary Ar gas at ca.

0.8 L min⁻¹ flow rate. The U-Pb elemental fractionation, down-hole fractionation and calibration drift were corrected by bracketing measurements of unknowns with analyses of the primary monazite reference material Madel ($^{206}Pb/^{238}U$ age = 511.0 ± 1.3 Ma; Payne et al., 2008) for apatite analysis and the BLR-1 titanite (1047.1 \pm 0.4 Ma; Aleinikoff et al., 2007). Time resolved data was baseline subtracted and reduced using Iolite 4 (DRS after Paton et al., 2011), and the in-built data reduction schemes 'UPb Geochron 4' and 'Trace Elements'. Age calculations, common lead correction, and diagrams were constructed using IsoplotR (Vermeesch, 2018). Common lead correction in this study is after the 2-stage model in Stacey and Kramers (1975). A complete list of the settings for U/Pb and trace element analyses is summarised material 6S in the supplementary 7 (Tables and S7; https://figshare.com/s/b128a2379e6ce7ec8920).

Secondary reference material ages for apatite (530.72 ± 6.38 Ma for 401Ap and 494.61 ± 11.56 Ma for MAD; Thomson et al., 2016; Fig. 4.2) are in a good agreement with the reference ages for 207 Pb/ 206 Pb anchored ages (Stacey and Kramers, 1975). Secondary reference material ages for titanite (318.96 ± 4.11 Ma for Mud Tank and 95.09 ± 1.18 Ma for CKHB; Fisher et al., 2020) correspond to the reference values (Fig. 4.2). Trace elements analyses for both apatite and titanite refer NIST 610 NIT612as a primary standard



Figure 4.2. Tera-Wasserburg age plots for the reference apatites 401 Ap (Thompson et al., 2016), MAD (Thomson et al., 2012), and reference titanites Mudtank (Fisher et al., 2020) and CKHB (Fisher et al., 2020). They show good agreements to the reference values when anchored to modelled (²⁰⁷Pb/²⁰⁶Pb)o by Stacey and Kramers (1975).

4.4 Results

Trace element analyses

Apatite. In-situ trace elements concentrations of apatite are listed in supplementary material 8 (Table S8; <u>https://figshare.com/s/b128a2379e6ce7ec8920</u>). Both, average Th (57 ppm) and U (53 ppm) concentrations in the host rock apatite (63 and 64 ppm in the MME

apatite, respectively) are not as high as zircon, allanite, or titanite. The ratio of Th/U of the host rock and MME similarly ranges from 0.38 to 3.81 (Fig. 4.3). Concentration of Y ranges from 204 – 1290 ppm in the host rock, and from 234 – 749 ppm in the MME (Fig. 4.3), except two spots of > 3000 ppm. The host rock apatite Sr concentration ranges from 217 to 640 ppm except for outliers (392 ppm on average) and Sr in the MME ranges from 284 to 401 ppm (321 ppm on average). Strontium content of the apatite conspicuously separates samples based on rock type, and forms three clusters of high-Sr (400 – 600 ppm, FGD), mid-Sr (~300 ppm, MME), and low-Sr (~250 ppm, HGD) groups. The range of Mn content ranges from 379 – 949 ppm (694 ppm on average) in the host rock (except three outliers), and 340 – 780 ppm in the MME (638 ppm on average). Concentration of Zr is relatively low at ca. 0.05 - 1 ppm in both the host rock and MME, yet outliers exist with 10 – 3000 ppm level. The sum of light rare earth elements (LREE, La – Sm) ranges from 1590 – 10400 ppm and from 3140 – 9630 ppm in the host rock and MME, respectively. The two Y outliers are > 24000 ppm in $\Sigma LREE$.

The high-Sr apatites and low-Sr apatites are not separable in other elements (Fig. 4.3). In a REE diagram normalised to C1 Chondrite, both patterns of host rock and MME apatite have a negative slope with La/Yb = 30.8 and 47.1, respectively, and consistently show negative Eu anomalies (0.28 and 0.48 for the host rock and MME) (Fig. 4.8). Apatites from the host rock vary in their Ce anomaly (Ce/Ce*). While two different groups may likely be separated by Ce/Ce*, the anomaly ranges from 0.95 to 1.19 and changes gradually (Figs. 4.3, and 4.8A).

Titanite. Trace element concentrations of titanite are listed in supplementary material 8 (Table S9; <u>https://figshare.com/s/b128a2379e6ce7ec8920</u>). In titanite, Y content or (Ce+Nd)/Y (a proxy for LREE) can be used to distinguish different origins of titanite (McLeod et al., 2011; Hu et al., 2017). The Y values range from 80.2 - 4150 (average 1240) ppm in the host rock and 72.2 - 4090 (average 947) ppm in MME (Fig. 4.4). The ratio of (Ce+Nd)/Y shows similar variability in the host rock and MME. The host rock and MME titanites contain ca. 10 - 50 ppm Sr, and ca. 100 - 2000 ppm Zr, while some grains show outliers out of this range (Fig. 4.4). Total concentration of all LREE ranges 932 - 28500 ppm in the host rock and MME have similar REE C1 chondrite normalised patterns (Figs. 4.8C and 4.8D). These two ratios do not correlate with Y concentrations. The ratio Nb/Zr can be used to distinguish titanite from granitic (felsic) melt from more mafic melt as shown in the study of McLeod et al. (2011).
The host rock and MME titanites share similar Nb/Zr values except \sim 6 outliers of Nb/Zr > 10 (Fig. 4.4).

The REE concentration of the host rock titanite (C1 Chondrite normalised) forms a similarly inclined pattern (La/Yb = 19; Fig. 4.8C) with different degrees of enrichment (Σ REE range 1025 – 31630 ppm). The same pattern and enrichments are found in the MME titanite (La/Yb = 20, Σ REE range 1037 – 23510 ppm). Both the host rock and MME titanites show large variabilities in Eu anomalies (Eu/Eu*) from negative to positive (0.3 – 3.3 in the host rock and 0.5 – 3.4 in the MME; Figs. 4.8C and 4.8D). The MME titanites show a high proportion of positive Eu anomalies (23 of 30). Overall, REE patterns of the host rock and MME are similar in range and shape.



Figure 4.3. Apatite trace elements of the host rock and MME. A great difference is shown between different rock units in Sr; thus the host rock unit is further separated into high-Sr (FGD) and low-Sr (HGD). Rare earth elements (REE) and Ce anomaly show no separation but a similar range in each unit.



Figure 4.4. Titanite trace elements of the host rock and MME from the Mt Stirling. Concentrations of (Ce+Nd) and Y strongly correlate. A similar range in LREE and Dy/Yb is shown by both the host rock and MME titanite. The mixing indicator Nb/Zr also show similar range between the host rock and MME except few anomalies.

U-Pb dating

Isotope compositions of U-Pb and calculated ages are listed in the supplementary material 8 (Tables S8 and S9). Apatite U-Pb data in a Tera-Wasserberg diagram form an

apparent mixing array between the radiogenic samples and a common lead component, which equates to an inverse isochron with a best-fit regression. The calculated inverse isochron ages for the host rock and MME apatites are 415.98 ± 5.77 Ma (n = 210, MSWD = 0.59) and 409.31 ± 8.25 Ma (n = 82, MSWD = 0.57) (Fig. 4.5), respectively. Two sigma error ellipses are greater than those of zircon or titanite because of lower U concentration. These are older than respective zircon ages of the same rocks outside analytical uncertainty (cf. chapter 3).

The host rock titanite ages in the Tera-Wasserburg plot also show variable amounts of common-Pb content. For the host rock, an isochron can be defined by the best-fit linear regression which also defines a mixing endmember with initial 207 Pb/ 206 Pb, yielding an age of 403 ± 3 Ma (n = 122, MSWD = 4.8) (Fig. 4.5). MME titanite data also show an isochron along the common lead mixing array, with an isochron age of 389 ± 6 Ma (n = 33), and a similar scatter (MSWD = 3.4) (Fig. 4.5). Of all calculated ages, only the host rock titanite data yields an age in agreement with the calculated zircon age of the intrusion (ca. 402 Ma).



Figure 4.5. Tera-Wasserburg diagrams for the apatite (lefthand side) and titanite (righthand side). Note both minerals show common lead contamination trend, yet the degree of contamination is varying. Error ellipses are rather close to the concordia curve. A few outliers are found in both the host rock and MME, and apatite and titanite.

4.5 Discussion

Age data filtering

Although apatite and titanite are less susceptible to metamictisation by radioactive damage, there are potential other influences that can make the interpretation of determined ages difficult: mineral inclusions, alterations, zoning, diffusion, and recrystallisation. Since apatite and titanite incorporate various trace elements and REE, monitoring the chemistry linked to U-Pb age data may be a powerful protocol to obtain a reliable age.

Apatite. The major elements in the crystal lattice of apatite, P and Ca, should be monitored. In case of significant variations, it is plausible to ascribe this to inclusion or epoxy being hit by the laser spot. In the initial dataset, there were 2 spots with only ~300 ppm P. These spots have been excluded. The outliers in this stage were not presented in Figure 4.3

Checking excessive Zr (> 100 ppm) is the next step in the filtering of poor-quality apatite analyses. Since Zr is not readily incorporated into the apatite lattice, excessive Zr compared to other incompatible, but commonly abundant element in apatite (e.g., LREE, HREE, or Y) can detect large anomalies, preferentially on a log scale. Zircon micro-inclusions can be detected by this proxy. The proxy Zr/Y indicate that a number of outliers exist in the dataset (Fig. 4.6A). Low Th/U is another factor to be filtered. Since low Th/U (< 0.5) is a typical indication of peraluminous S-type granite apatite (Sha and Chappell, 1999; Chu et al., 2009), it is not expected to have formed in an I-type rock (ASI = ~1 in the host rock and ~0.8 in the MME) such as the Mt Buller suite. The Th/U diagram (Fig. 4.6A) shows two discrete groups. The group with Th/U < 0.5 has been disregarded in the age determination. Figures 4.6C and 4.6D show outlier distribution in Zr and LREE concentration. Interestingly, some outliers of Th/U and Zr/Y are not outliers in Zr and LREE, and this shows obvious Th/U and Zr/Y outliers would not simply be filtered by Zr or LREE contents. Based on a Zr/Y vs Th/U plot (Fig. 4.6A), the apatite age changed from 415.98 ± 5.77 Ma (n = 210; MSWD = 0.59) to 413.37 ± 7.19 Ma (n = 181; MSWD = 0.44) in the host rock. The changed age indicates lower MSWD and is slightly younger, yet largely overlap with the unfiltered age. The MME apatite does not have anomalous spots in this filter.



Figure 4.6. Apatite (A - D) and titanite (E - F) age data trimming scheme using trace elements. (A) The proxies Th/U and Zr/Y (x 10000) can detect outliers in apatite which potentially suffered hydrothermal alteration. (B) A significant apatite Sr distinction is shown in rock units.

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(C - D) Outlier distribution in Zr and LREE. Outliers likely correspond to Zr and LREE anomalies, although some are in the main population. (E - F) Outliers in Sr/Zr and Sr/Th may indicate hydrothermally suffered spots. (G - H) Anomalies in Sr/Ca and Zr/Ti indicate abrupt change in cation exchange, break of crystal lattice, or influences by micro-inclusions.

Titanite. Similar to Ca and P in apatite, Ca and Ti are major constituents in titanite, and should be monitored for anomalies. Significant deficient Ca or Ti spots in titanite likely imply micro-inclusions, altered-, flawed crystal, or epoxies. The raw dataset included three spots with only hundreds – thousands of ppm in Ca or Ti. These outliers were not presented in the Figure 4.4.

If an analysed spot shows a peak in Sr in titanite, this may indicate alteration of the crystal lattice given that excessive Sr can be introduced by hydrothermal fluid (Nebel, 2018). In addition, anomalies in Sr may indicate different origins of the given titanite grains as Sr in titanite is known for its capability to effectively discriminate magma type (Bruand et al., 2020). Figure 4.6E shows titanite in the host rock and MME marks Sr/Zr anomalies. These outliers indicate excessive amount of Sr compared to Zr as a general indicator for alteration. The ratio Sr/Th can also be used because Th is a source enrichment indicator, a fluid immobile element, and also a competing element with Sr in the decahedral-site. Five spots with Sr/Zr- or Sr/Th-anomalies were excluded.

The following step can additionally filter age spot that experienced an abrupt change in cation exchange behaviour. In a titanite crystal lattice, Sr^{2+} replaces Ca^{2+} and Zr^{4+} replaces Ti^{4+} (Kohn, 2017). Pit profile in lasering shows this trade off relationship between Sr and Ca, and Zr and Ti: The higher the Sr (or Zr) concentration detected, the lower the Ca (or Ti) concentration is (Fig. 4.7). The doped Sr and Zr against Ca and Ti probably indicate a coupled substitution in the crystal structure, and abrupt element replacement may imply a crystal system opened, which causes Pb loss. Spots with these anomalies in Sr/Ca or Zr/Ti can be excluded if the anomalies form a significantly different trend to the main trend. The proxy Sr/Ca and Zr/Ti plots with reference titanites BLR and OLT show five anomalies apart from the main trend (Figs. 4.6G and 4.6H). Note that reference titanites show a narrow range of the proxies although each one of them may have variable levels (e.g., ~2 – 4 for the BLR and ~5.5 for the OLT Sr/Ca; Fig. 4.6G). Therefore, significant offsets in this plot may represent unreliable ages as monitored in the trace element chemistry, and are excluded in the following age estimation. Filtered age does not shift to a significant amount for the host rock (from 403 ± 3 Ma to 404 ± 3 Ma). However, MME age shifts from 389 ± 6 Ma to 397 ± 4 Ma.



Figure 4.7. Titanite pit profile for T60 with four elements (Ca, Ti, Sr, and Zr). Trade-off relationships between Ca and Sr, and Ti and Zr were shown in pit profile. It is often difficult to



exclude these parts by just adjusting time selection because of shortage of total ablation time (upper) or subtle and less obvious anomalies (lower).

Figure 4.8. Apatite (upper) and titanite (lower) REE diagrams. Trace element-filtered spots are depicted in grey colour. (A) Host rock apatite REE patterns. Negligible difference is shown between the high-Sr and low-Sr groups. (B) MME apatite REE patterns. Slightly smaller Eu negative anomaly is the minimal difference between the host rock and MME apatites. (C) The host rock titanite and (D) MME titanite also shares similar REE patters while MME titanites show more Eu positive anomalies.

Age determination

Apatite. The trace element-filtered apatite age plot on the Tera-Wasserburg diagram shows a more defined isochrons without obvious outliers (Figs. 4.5 and 4.9). However, because of relatively large error ellipses (because of the low U concentration) and poorly defined linear regression because of dispersed error ellipses distribution, the calculated isochron age has a

larger error compared to that of titanite or zircon. This implies that a larger number of apatite spots would generally be required to obtain a smaller error.

Note that reference material ages were accurate and precise when anchored to a common lead ratio corrected by Stacey and Kramers (1975). Likewise, the anchored inverse isochron can help in reducing the size of the error for the unknown apatites. It can be assumed that apatite and zircon in the magma reservoir were both of magmatic origin and thus formed contemporaneously. Stacey and Kramers (1975)'s two-stage isotope evolution model can constrain the initial lead ratio (207 Pb/ 206 Pb)₀ using the concordia age derived from the Mt Stirling zircons. This model using the host rock zircon age (402.15 Ma) yields a (207 Pb/ 206 Pb)o = 0.8632, which anchors the y-axis of the Tera-Wasserburg age plot. However, with Stacey and Kramers (1975) two-stage common lead correction, the apatite age shifts towards an even older (from 413.37 ± 7.29 Ma to 417.01 ± 3.31 Ma in the host rock, from 409.31 ± 8.25 Ma to 413.13 ± 4.11 Ma in the MME), yet with ~ two-fold smaller errors. However, it is unrealistic for apatite to have an older age than that of zircon with respect to the high closure temperature of zircon and considering a constantly decreasing temperature in a cooling igneous body. In light of this discrepancy, we will further evaluate the chemistry of apatite to elucidate what causes this age difference.

Strontium in apatite is one of the most characteristic elements often used for a source indicator in detrital grains, because its variability strongly reflects the chemical characteristics of the parental rock (Belousova et al., 2001; Chu et al., 2009; Bruand et al., 2017; O'Sullivan). Concentrations of Sr in each sample are considerably different in this study (Fig. 4.3). Three groups of Sr concentrations are defined here: low-, mid-, and high-Sr groups (400 – 600 ppm of FGD, ~300 ppm of MME, and ~250 ppm of HGD). These Sr groups in apatite correspond to the sample lithologies, reinforcing the relationship of Sr-in-apatite and host rock chemistry. Low-Sr apatites are from medium- to coarse-grained hornblende granodiorite (HGD), mid-Sr apatites are from MME, and high-Sr apatites are from fine- to medium-grained porphyritic granodiorite (FGD). Interestingly, REE patterns do not show a distinction between these lithologies or Sr groups, except for minor differences in Eu anomalies (Eu/Eu* =0.33, 0.48, and 0.24, respectively for low-, mid-, and high-Sr; Fig. 4.8). The difference in Sr, however, seems to be reflected in age differences when individual groups are used to calculate ages. The host rock apatite age without Sr distinctions (i.e., HGD + FGD) is 413 ± 7 Ma (n= 181, MSWD

= 0.44). The low-Sr apatite is 420 ± 10 Ma (n = 75, MSWD = 0.44) and high-Sr is 407 ± 10 Ma (n = 106, MSWD = 0.41) (Fig. 4.9). Common lead anchored ages show smaller difference between the low- and high- Sr groups (420 ± 5 Ma and 415 ± 4 Ma, respectively) with smaller errors. These ages are still not aligned with the zircon ages, except for the high-Sr apatite. However, the fact that the latter seems to approach the zircon age indicates that a magmatic or post-magmatic process is responsible for the discrepancy in ages.



Figure 4.9. Tera-Wasserburg plots after data trimming process for the apatite (lefthand side) and titanite (righthand side). Empty ellipses indicate filtered out data. Both apatite and titanite data are freer from outliers to the main trend, which indicate trace element filtering worked correctly. Apatite U-Pb ages are varied between isochron age and anchored age, whilst titanite ages do not show a significant difference.

In light of these findings, we employ another factor for distinguishing between multiple ages: the Mn content. Kirkland et al. (2018) found that apatite U-Pb analysis results show multiple isochrons corresponding to different Mn concentrations. It is not fully understood why Mn content corresponds to U-Pb age, but Mn differently behaves in magmatic or hydrothermal environment (Le Roux et al., 2011; Hawthorne et al., 2012), and the difference is likely able to indicate different geologic events. Indeed, the high-Sr apatite group shows a decrease in calculated age when spots are cut off based on their Mn content from the highest to the lowest (Figs. 4.10E and 4.10F). If the top 30 % are cut off, the age changed from 407 \pm 10 Ma to 399 \pm 14 Ma. Intriguingly, the MME apatite group follows the same trend.

Hence, using the Sr-Mn criteria, apatite ages can be grouped into different ranges of mean ages, although overlapping within error. It is inferred that the uncorrected 413 Ma (total population host rock apatite) is a "blurred age"

The reason for this "age effect" is difficult to reconcile with magmatic activity, as closure temperatures and time scales of apatite formation would not allow for a spread of several millions of years. Instead, it is speculated here that the higher Mn and lower Sr concentrations reflect interaction of apatite with late-stage fluids. The phosphate structure of the mineral possibly allows a dissolution-reprecipitation of crystals (similar to monazites, cf. Weinberg et al., 2020) with the incorporation of higher-Mn lower-Sr contents that would be enriched in late-stage liquids as opposed to early melts. This process likely lasted for several million years, causing a partial reset of U-Pb systematics of affected grains. This effect is similar to that affecting zircon. The result is a "mixing effect" of ages by merging more than one "generation" of apatite; i.e., igneous and hydrothermally altered ones.

If correct, caution is advised for the hydrothermally altered apatites with respect to the use of a common lead anchored isochron. It would lose its rationale for those apatites because different apatite generations may have different initial lead ratios. Alternatively, the fluids are circulating in a closed system within the pluton, and the common Pb would still remain applicable. Either way, Pb loss/reset millions of years after formation of the apatites, coupled with new common Pb incorporation can cause a clock-wise rotation of the isochron in a Tera-Wasserburg diagram, which evidently yields older apparent ages. This counter intuitive effect

- a younger event leading to older calculated ages might make it difficult to detect in other igneous system for which no reference age is available.

In this study, the high-Sr host rock apatite age with unanchored regression is closed to the zircon reference age compared to the low-Sr apatite age or the anchored age (Fig. 4.11); a bizarre effect of the isochron rotation in a Tera-Wasserburg diagram. However, the use of Sr and Mn concentrations in apatite might prove a useful filter for future apatite dating approaches in other I-type plutons.



Figure 4.10. High-Sr apatite (A and C) shows younger age trend compared to that of low-Sr group apatite (B and D), either in isochron or anchored ages. (E and F) Apatite still shows age variabilities in Mn concentrations which is probably a reason for less precisely focused apatite ages.

Titanite. Titanite trace element data filtering allows removing outliers and potentially erroneous data points (Fig. 4.9). These 'outliers' might be easily recognisable without trace

element data if they are large anomalies in the age plot. However, Figure 4.9 shows these outliers are often cryptic in the age plot. Therefore, we recommend to remove those points based on trace element systematics as these elements allow us to recognise laser mistargeting or flawed crystal. The titanite isochron age after filtering allows host rock and MME titanite ages that align with the age of zircons (Fig. 4.11). The filtered ages show lower MSWD for both the host rock (from 4.8 to 3.4) and the MME (from 3.4 to 1.8).

In a similar approach to apatite, Stacey and Kramers (1975) 2-stage common lead correction was applied to anchor the (207 Pb/ 206 Pb)o to 0.8632. Common lead corrected ages and unanchored isochron ages of titanites were virtually indistinguishable (Fig. 4.9): Common Pb corrected age of the host rock is 405 ± 2 Ma (n = 110, MSWD = 3.5), and that of the MME is 397 ± 4 Ma (n = 28, MSWD = 2.4). Both ages correspond well to the zircon 206 Pb/ 238 U age and to each other. This agreement may indicate that titanite is less affected by hydrothermal fluids circulating in plutons compared to apatite and surprisingly zircon.

Implications in the Mt Stirling magmatism

The very existence of MME can be used to constrain temperature conditions of the magmatic reservoir at Mt Stirling. As mingling between the MME and host magma is evident from field relationships, both magmas would share a similar temperature evolution. Since zircon, apatite, and titanite geochronometry depends on their respective U-Pb closure temperature (T_c), we can assume that the MME and the host rock age difference between chronometers would reflect any such T_c relationship as a function of late-stage fluids and cooling. In this study, unfiltered MME titanite age data were younger than that of the host, which was identical to U-Pb zircon ages, whereas apatite was older. After the trace element filtering, however, these age differences were reduced to negligible differences and all seem to align with each other. It is thus apparent that a late-stage fluid affected all phases (cf. also chapter 3).

To understand the mineral crystallisation history in the Mt Stirling pluton and to obtain an absolute age for the intrusion, a holistic approach consideration of zircon, titanite and apatite age data is advised. When considering these mineral ages, it is noted here that the zircon age is a concordia age, which is a cluster of single grain ages, whereas the titanite and apatite ages are anchored / unanchored isochron ages that are reported as single ages. The effect of filtering may thus affect the calculated ages differently, which in turn is reflected in the MSWD. Larger errors may even promote a better MSWD, which on its own should not be used as a measure for the reliability of ages.

In the age compilation (Fig. 4.11), the titanite ages (404 Ma) are identical to the weighted mean concordia zircon age (402 Ma). Filtered apatite ages overlap with this age range. Regarding the highest Pb closure temperature in zircon (~900 °C), followed by titanite (500 – 800 °C Fisher 2020) and apatite (~350 – 650 °C or higher; Fisher 2020), and zircon's grainscale individual age ranges (Fig. 4.10), it appears that the intrusion cooled quickly. The age of 404 Ma may constrain the true crystallisation age in this lower crustal magma reservoir. As an I-type granite the temperature ranges around 780 to 800 °C (Lee and Bachmann, 2014; Collins et al., 2020b), and it is expected that all phases passed their closure temperature rangel.

The fact that all phases include compromised grains that fall off this age and create different ages, indicates that their respective closure temperature be regarded as an only magmatic T_c , but that hydrothermal processes below this threshold indeed have the capacity to affect these chronometers. Notable is that the "protracted" age range towards 380 Ma that corresponds to mica and hornblende K-Ar ages that have been previously reported as the "true" age of the Mt Buller suite (Richards and Singleton, 1981), which may indeed reflect a 15 Myrs hydrothermal alteration event that partially affected the grain populations studied here.

Apatite ages show a larger error than that of zircon or titanite. This may simply be ascribed to lower U concentrations in apatite, but Sr and Mn variabilities imply that some apatite grains were significantly affected. It is widely known that acicular apatite formation is triggered by mafic and felsic magma mixing (Baxter and Feely, 2002). Both acicular and stubby apatites occur in the Mt Stirling pluton, although most of acicular apatites could not be analysed in this study because of their small size. Although the host rock and MME apatite ages are nearly identical, their large errors (~20 Ma of 2SE) might indicate mixture of different types of apatite with the apatite population influenced by different factors; new element addition, alteration, or re-crystallisation. It is thus concluded that zircon and titanite are superior to the phosphate apatite for age determinations. In turn, apatite may however be useful to constrain

hydrothermal histories of rocks, probably in conjunction with Sr isotopes or Rb-Sr systematics of micas. Further work is needed though to substantiate this proposition.

The revision of the absolute age of the Mt Stirling suite places the pluton towards the older range of ages of granites in the Lachlan Fold belt (Richards and Singleton, 1981; Collins et al., 2020a). Since many of the older ages are K-Ar ages, and some are simply pooled zircon ages, then based on the finding of this study, revision and careful re-evaluation of other granite ages of the LFB is advised.



Figure 4.11. Age compilation in the Mt Stirling granodiorite. Note zircon ages are concordia ages, and apatite and titanite ages are isochron- or common lead anchored- ages. Titanite and zircon ages well correspond. Apatite ages show large errors except when anchored. However, anchored age indicates ~420 Ma which is older than most of zircon concordia ages. The

variabilities in Sr and Mn show the potentially different age components in the apatite group, and probably higher Sr and lower Mn apatites are more reliable in age determination.

4.6 Conclusion

This study reports apatite and titanite U-Pb and trace element LASS data from the Mt Stirling pluton, Mt Buller suite, Lachlan Fold Belt in southeastern Australia. Both minerals in the host rock and MME show no systematic differences in trace element chemistry between these reservoirs, while apatite shows a great variability in Sr. Trace element concentrations are suggested as "proxies" to filter out unreliable age data: In apatite, (1) major element concentration Ca and P, and (2) Zr/Y and Th/U should be monitored for excluding zircon micro-inclusions or hydrothermally altered parts. In titanite we suggest to monitor (1) major element concentrations Ca and Ti first, and (2) Sr/Zr and Sr/Th for excluding hydrothermal anomalies, and (3) Sr/Ca and Zr/Ti for excluding unwanted abrupt ion exchanges. Common lead anchoring further improved the precision of ages. After applying those filters, age data show smaller errors and MSWD.

Low U concentration is the fundamental problem in apatite geochronology, inducing bigger error or variabilities in calculated ages. In this study, it is observed that Sr and Mn variabilities correspond to the age spread, which is ascribed to dissolution-reprecipitation reactions during hydrothermal alterations. In contrast, titanite ages from the host rock and MME show a good agreement with zircon ages. Titanite age results do not show the same level of age drift in filtering data or different plotting techniques compared to apatite. Therefore, titanite appears a more stable alternative to zircon for dating I-type granites.

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Chapter 5

Conclusion

5.1 Summary and holistic age interpretation

The aim of the thesis is to report radiogenic age data from I-type granitoids, to address potential limitation on the widely-applied zircon dating method for these rocks, to suggest an improved, applicable zircon dating protocol and to investigate other, alternative dating methods. In the first case study (chapter 2), zircon U-Pb and Hf isotope systematics are investigated to understand the temporal history and source information preserved in zircon in an I-type granitoid from the Korean peninsula. In a second study area (chapters 3 and 4), first zircon trace element data is collected together with U-Pb data to evaluate the reliability of zircon U-Pb ages. Plutonic samples from the Mt Buller suite in the Australian Lachlan Fold Belt were used to test the existing K-Ar ages and possible discrepancies introduced by this dating method. In a subsequent study, apatite and titanite from the same rock samples were then compared with the zircon ages, and their age information was put to the test (chapter 4).

Zircon U-Pb age data from the Korean pluton host diorite and its mafic microgranular enclaves (MME) show an extensive range over 30 Ma in both rock types. Epsilon Hf values range from ca. +8 to +15 over ~7 units, both in the host rock and MME. This range in age and Hf isotope composition is larger than the analytical reproducibility of the laser ablation method applied here, as tested against reference materials. Compositional variabilities among the samples within the pluton, i.e., host rock vs. MME, can be best explained as result of melt evolution mainly by fractional crystallisation: more amphibole- and less olivine- fractionation in the host. The Zr enrichment – zircon saturation modelling in a replenishment, evacuation and fractional crystallisation (REFC; Lee et al., 2014) system can explain that both rock types have been zircon saturated, despite their low Si content. This led to a model in which the U-Pb age variability is consequent to zircon inheritance. To explain the wide range of age in zircon spawning pool'. The deep-seated hotter reservoir may allow longer time range of zircon formation, and a wide range of ε Hf (t) can be achieved by numerous replenishments through time. This concept introduces an inheritance of zircons in I-type granites.

Even larger zircon age range (~100 Ma) in a host rock and its MME were found in the second study area at the Mt Stirling pluton in the Mt Buller suite. However, in this suite of rocks, a different approach to the zircon age spread is investigated. A step-by-step age data filtering scheme is applied to enhance zircon age data reliability: (1) Accidental inclusions by

checking excessive K and Ca, (2) trimming spots with unusual opposite core-rim age relationship (Δ (core-rim age) < 0), (3) excluding zircons with excessive non-formula elements (Al, Fe, and Mn), (4) hydrothermally altered zircon by proxy Ba/Hf > 1, and (5) potential hydrothermal zircons with V-shape REE patterns (Table 5.1). Indeed, unfiltered age data of the host rock (397.5 ± 1.5 Ma; MSWD = 4.8) and MME (382.4 ± 7.4 Ma; MSWD = 16) show not only wide range in ages but also large errors and MSWDs. The MME age is ~10 Ma younger than the host. The filtered weighted mean age, however, is 402.2 ± 1.0 Ma (MSWD = 1.5, ~20% of spots filtered out) for the host rock, and 398.8 ± 3.9 Ma (MSWD = 2.9, ~25% of spots filtered out) for the MME. The filtering results in smaller errors and MSWDs and indicate the MME magma was contemporary to the host magma. The age range of individual grains is reduced, yet still with a considerably long-time range of ca. 70 Ma, which exceeds analytical reproducibility (2SE = ~10 Ma).

Combined, chapter 2 and 3 thus indicate that a filtering process for hydrothermally altered zircon is probably required for some samples, yet the process proposed in chapter two further contributes to the variability in age data of igneous zircon. As such, the zircon age archive with all its robustness may not be suitable for this kind of dating.

A test for this is then carried out using other accessory phases. Apatite and titanite were collected from the same rock sample for which U-Pb isotopes and trace elements were analysed. Using a similar approach to the zircon age data filtering, apatite and titanite age data are filtered by trace elements. For apatite, (1) major element concentration Ca and P, and (2) Zr/Y and Th/U are monitored to exclude outliers as potential micro-inclusions or hydrothermally altered parts. In addition, (3) Sr and Mn should be monitored if they form distinct age groups (Table 5.1). In titanite, the following proxies are monitored: (1) major element concentrations Ca and Ti for detecting major outliers, (2) Sr/Zr and Sr/Th for excluding hydrothermal anomalies, and (3) Sr/Ca and Zr/Ti for excluding unwanted abrupt ion exchanges (Table 5.1). After applying those filters, passed age data show smaller errors and MSWD. Common lead anchoring slightly improves the precision of titanite ages and considerably improves that of apatite. However, common lead anchored apatite age indicates older apatite than zircon, which is unrealistic considering the lower closure temperature of apatite compared to that of zircon. Apatite spots are conspicuously grouped by Sr concentration (high-, mid-, and low- Sr). The high-Sr (407 \pm 10 Ma) and mid-Sr (409 \pm 8 Ma) apatites from a host rock and MME show similar age ranges

corresponding to titanite $(404 \pm 3 \text{ Ma})$ and zircon $(402 \pm 1 \text{ Ma})$, while low-Sr apatite $(420 \pm 10 \text{ Ma})$ from another host rock indicates spurious older age. In addition, apatites with higher Mn content tend to be older. The implications are that additional age data can be obtained by titanites, apatites less so, unless zircon age data is available. In this iterative approach applied here, the combination of zircon-titanite ages plus trace elements has yielded a true age of the intrusion, notably 15 Myrs older than previously thought based on K-Ar ages. It is suggested that a similar approach elsewhere will yield true and accurate age information for I-type granitoids.

Table 5.1. Summary of trace element filtering protocols for zircon, apatite, and titanite chronometers.

Steps	Filtering target	Zircon	Apatite	Titanite
1	Major outliers, accidental inclusions	K or Ca > wt %	Ca and P deficiency and distinct Zr/Y outliers	Ca and Ti deficiency
2	Laser spots mistargeted (in relation to zoning)	Δ (core-rim age) < 0	-	-
3	Significant hydrothermal alteration	ΣREE + Y > 1 wt%, Th/U < 0.1, Al, Fe, and Mn > 1 wt% (Geisler et al., 2007)	Th/U (<0.5) (Sha and Chappell, 1999; Chu et al., 2009)	-
4	Cryptic fluid alteration	Ba/Hf >1	-	Sr/Zr and Sr/Th > 1
5	Potential fluid alterations, unusual ion- exchange, or distinct chemical groups	Nd/Sm > 3 or (Sm-Nd)N < 0	Sr or Mn (distinct groups)	Sr/Ca, Zr/Ti (distinct outliers compared to reference materials)

Chapter 2's zircon age and Hf isotope variabilities report an example of inconclusive protracted zircon age which is similarly found also in the zircon age in chapter 3. In the second study area, a holistic approach merging all zircon, apatite, and titanite age data is conducted. In a Tera-Wasserburg plot with three minerals, the filtered host rock mineral age converges to 403 ± 1 Ma (n = 387; MSWD = 2.1), and that of the MME is 397 ± 3 Ma (n = 151; MSWD = 2.1) (Figs. 5.1A and 5.1B). Filtered-out data in the host rock and MME displays significantly



dispersed, inconsistent distribution and generally younger character than the ages of filtered data (Figs. 5.1C and 5.1D).

Figure 5.1. The holistic consideration of zircon, apatite, and titanite age data. (A) Filtered ages from the host rock and (B) the MME. (C) Remaining age data after the filtering, from the host rock and (D) from the MME.

5.2 Conclusion and implication

The final age from the total dataset indicates a ca. 400 Ma age for Mt Buller and its contemporary MME. This age shifts the Mt Buller suite towards an earlier phase in the LFB granites. If this trend is conformed in other igneous suites in the LFB following a similar

protocol, this could indicate a slight tuning on the time of events in the LFB evolution. Most of reported LFB granite ages are K-Ar ages from biotite or hornblende, and ~380 Ma is reported for the Mt Buller suite age (Richards and Singleton, 1981). This age range roughly corresponds to younger tail ages in the zircon or hydrothermal zircon and apatite ages. Regarding the lower closure temperature of mica and hornblende U-Pb systems (310 °C for biotite and 530 °C for hornblende), these younger ages of ~380 Ma may indicate later stage hydrothermal overprinted ages. This scenario implies 1) that refractory minerals from other granitoids may indeed have older ages than the reported K-Ar ages and 2) the importance of considering chemical (hydrothermal) as opposed to thermal (igneous) closure in various chronometers. As confirmed in the chapter 3, zircons in a sample can contain potentially hydrothermal altered grains which may return spurious, younger ages. Therefore, caution must be applied when trying to date bodies with evidences of hydrothermal alteration.

Examining U-Pb, Hf, and trace element of zircon in the two study areas indicate complicated and prolonged zircon origin in a small volume of sample from an igneous pluton. Even though the trace element filter managed to trim hydrothermal zircons, zircon ages in both study areas are still widely ranged beyond analytical reproducibility. If this is not an analytical issue, a new zircon saturation model would be required because shallow and low temperature in the upper crust cannot explain the prolonged zircon crystallisation.

Therefore, it is important to investigate detailed histories of plutons in different settings. Apatite petro-chronometry by U-Pb and trace element analysis shows that it is susceptible to be blurred by hydrothermal low temperature events. Low U content in apatite compared to zircon or titanite causes larger error ellipses, which also contribute to inconclusive age determination. Larger number of apatite spots would therefore be required to improve precision. Trace element examination can enhance the accuracy of apatite, and especially Sr content should be carefully monitored if it records distinct fluid records.

Titanite geochronology result from the host rock and MME show a good agreement with zircon ages. Titanite age data do not significantly drift while filtering data or by different plotting techniques compared to apatite. This phase therefore appears to be a more stable alternative to zircon for dating I-type granites. In overall perspective, trace element monitoring is important to investigate chemical influences to closure of the Pb isotopic system. Trace element filtering protocol may improve accuracy and precision of apatite, titanite, and especially zircon ages. In addition, utilising multiple geochronometers and crosschecking each other may further improve age interpretation reliability.

5.3 Outlook and future studies

Radiometric age dating is one of the fundamental tools in solid earth sciences. However, this technique bears significant complexity and flexibility depending on different analytical methods, chronometers, and assumptions. This thesis conducted a fundamental study on geochronology, and suggested a filtering concept to improve dating techniques. Reliabilities in zircon, apatite, and titanite geochronometer will be more improved if following expected objectives are fulfilled:

1) The age filtering schemes suggested in the thesis are generally based on principles of diffusion, distribution coefficient, and ion exchange. However, theoretical backgrounds for the chemical behaviour in specific mineral-element pairs are as of today not fully understood. With more case studies, more quantitative guidelines for each filtering step will be required to improve the filtering scheme. Chemical proxy thresholds (e.g., Ba/Hf = 1 in the zircon age data trimming) can be potentially redefined in future because currently they were defined empirically for this study only.

2) Since diffusion and closure are complicated function of temperature, pressure, the element of interest, crystal lattice, composition, and size of crystal, various physical condition should be tested to understand the correct closure temperature of a studied phase. Investigation on these conditions and closure of systems will provide improved reliability in age dating results and further in interpretation of igneous systems.

3) Zircon saturation and survival in mafic magma remains elusive. More case studies on the zircon occurrence from mafic rocks are required. Theoretical backgrounds for zircon in mafic melt can be investigated by studying solubility, diffusion kinetics, and rate of dissolution. With an improved understanding in the nature of zircon crystallisation, the nature of prolonged zircon age should be then re-evaluated. More case studies associated with higher precision SIMS or TIMS analyses are required to verify the age variability.

4) The nature of titanite zonation (mainly sector zoning) and relating it to trace element distribution is still poorly understood. While trace element concentration holds a potential key to understand this issue, a geochronological approach can accompany any such attempts to achieve a better understanding of titanite.

5) Finally, it remains a matter of ongoing investigation as to why zircon ages spread out over such a long time, despite clearly reliable and accurate reference zircon dating. If the age spread in a normal distribution is indeed a geologic feature, as proposed here, a tailing towards younger ages remains mysterious and needs to be further investigated in future studies.

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Supplementary material 1: Reference material results

The primary reference material was Plesovice of reported ${}^{206}\text{Pb}/{}^{238}\text{U}$ age = 337.13 ± 0.37 Ma (Slama et al. 2008). Secondary reference materials were GJ1 (609 Ma, Jackson et al., 2004), 91500 (1065 Ma, Wiedenbeck et al. 1995) and Mud Tank (732 Ma, Woodhead and Hergt 2005) for U-Pb. Ages determined from the secondary reference materials show good agreements with reference ages (Fig. S1).

The ¹⁷⁶Hf/¹⁷⁷Hf of secondary reference material values are: 0.282000 ± 0.000011 with 0.682 MSWD for GJ1 (¹⁷⁶Hf/¹⁷⁷Hf = 0.282000, Morel et al. 2008), 0.282300 ± 0.000015 with 0.918 MSWD for 91500 (¹⁷⁶Hf/¹⁷⁷Hf = 0.282313, Fisher et al. 2014), and 0.2824767 \pm 0.0000035 with 0.748 MSWD for Plesovice (¹⁷⁶Hf/¹⁷⁷Hf = 0.282484, Slama et al. 2008). The results are in agreement with reference values. Ratio of non-radiogenic, stable isotope ratio (¹⁷⁸Hf/¹⁷⁷Hf) was monitored for other sources of fractionation (Spencer et al. 2020) (Fig. S1).

Supplementary material 2: Scanning electron microscope images

Representative cathodoluminescence (CL) and back-scattered electron (BSE) images for the host rock and mafic microgranular enclaves (MME) are shown in figure S2. Note both the host rock and MME zircons show magmatic textures, with weak oscillatory zonings in BSE signal. This indicates a lack of significantly older inherited cores and hydrothermally altered parts. Embayment textures are slightly more often in the MME.



Figure S1. Reference material U-Pb dating and ¹⁷⁸Hf/¹⁷⁷Hf QA/QC. (a – b) Individual ellipses correspond to 2SE uncertainty. Mean ages are given with 2SE uncertainty level. (c) Reference zircon ¹⁷⁶Hf/¹⁷⁷Hf analysis results. (d) Natural ¹⁷⁸Hf/¹⁷⁷Hf ratio values in total laser points $1.46688 < ^{178}$ Hf/¹⁷⁷Hf < 1.46746 represents the acceptance limit in ¹⁷⁸Hf/¹⁷⁷Hf relative to the expected natural abundance according to Spencer et al. (2020). (e – f) Data quality and effectual

corrections of interfering elements were assessed using ϵ Hf (t) vs. ¹⁷⁶Lu/¹⁷⁷Hf and ϵ Hf (t) vs. ¹⁷⁶Yb/¹⁷⁷Hf. There is no apparent correlation between ϵ Hf (t) and ¹⁷⁶Lu/¹⁷⁷Hf or ¹⁷⁶Yb/¹⁷⁷Hf, which suggests isobaric corrections for the interference of Yb on Hf are effective.



Figure S2. Representative cathodoluminescence (CL) and back-scattered electron (BSE) images for the host rock (a and c) and mafic enclaves (b and d).

Supplementary material 3 – 8

Please visit <u>https://figshare.com/s/b128a2379e6ce7ec8920</u> to access Supplemental Material 3 – 8.