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On the Age-Old Problem of Dating a Granite: Combined Zircon, Apatite, and Titanite Petrochronology in an I-Type Granite from Mt Stirling, Australia

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To address the limitations of current dating methods, it is crucial to not only enhance existing techniques like U-Pb zircon dating but also explore alternative tools. This study focuses on three common mineral phases-zircon, apatite, and titanite-in an I-type granite. The goal is to assess their reliability as dating tools and propose improved methods for dating granitic rocks. In the case study of the Mt Stirling pluton within the Mt Buller igneous suite in Southeastern Australia, significant variability in laser ablation U-Pb zircon ages (around 100 million years) was observed. To improve the reliability of zircon age data and reduce non-magmatic-related variabilities, a data filtering protocol is applied. This protocol involves several steps such as trimming zircons with excessive K and Ca, excluding zircons with unusual core-rim age relationships, removing zircons with excessive non-formula elements (Al, Fe, and Mn), identifying hydrothermally altered zircons, and applying a 10% discordance threshold. The filtered Concordia Age (406 ± 1 Ma; mean square weighted deviation (MSWD) = 0.7, n = 80) of the host rock exhibits improved precision and reduced error compared to the unfiltered data (399 ± 2 Ma; MSWD = 9.3, n = 240). The filtered individual dates show less scatter and a mean that is different (i.e. outside statistical uncertainty), noting that their total still spans a considerable time range of ~50 million years, exceeding the individual zircon analytical reproducibility of 2 standard errors (~15 million years of 2 SE). Caution is advised when using the proposed error for the pooled analyses as a definitive precision. Similarly, trace element filtering approaches were applied to apatite and titanite samples from Mt Stirling, two phases that arguably cannot be inherited. For apatite, monitoring Ca and P as well as Zr/Y and Th/U ratios, along with identifying age groupings based on Sr concentrations, was effective in eliminating outliers and enhancing dating precision. In the case of titanite, monitoring Ca and Ti, Sr/Zr and Sr/Th ratios, and Sr/Ca and Zr/Ti ratios successfully enhanced dating precision. Notably, apatite and titanite grains were grouped in distinct Sr concentrations (high-, mid-, and low-Sr), with these groups corresponding to different date groups: high-Sr apatite and high- and low-Sr titanite returned c. 403 Ma, while low-Sr apatite and mid-Sr titanite returned c. 420 and 393 Ma, respectively. The spuriously younger or older dates may indicate an open system and influences from various common-Pb sources. The 403 Ma date coincides with the filtered zircon data, placing further confidence in the coupled approach, and is interpreted here as the igneous intrusion age. Notable is that this age is 25 Myr older than previously reported K-Ar age data, thus far considered to be the age of the intrusion. This study underscores the potential for erroneous zircon dates due to cryptic chemical influences. To enhance the reliability of age interpretation using laser ablation analyses, employing a petrochronological approach using split-stream combined age and trace element data is recommended in addition to the combination of multiple geochronometers. In the case of Mt Buller, it has proven crucial to carefully verify chemical closure of all applied geochronometers by monitoring concomitant trace element concentrations. Applied to other intrusions, petrochronology can play a critical role in obtaining reliable age information, even for igneous rocks that appear pristine. With this, we emphasise the importance of a careful approach towards individual age data interpretation, which can be produced fast and in abundance with modern analytical approaches.

Key words: petrochronology; zircon; apatite; titanite; granite petrogenesis

INTRODUCTION

Establishing precise ages of granitic rocks is a fundamental requirement in understanding crustal formation processes. The age of granites is often interpreted by analysing U–Pb isotopic compositions of magmatic zircons (Hoskin et al., 2003; Hermann & Rubatto, 2014; Spencer et al., 2016). Zircon, as a common and

refractory mineral phase in granitic rock, has high U and low Pb content with a relatively high closure temperature (T_C) of >900 °C (Cherniak, 2010). These characteristics make this mineral the most used tool to constrain the U–Pb age of a crystallising granitic body (Košler & Sylvester, 2003; Paton et al., 2011; Spencer et al., 2016).

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However, an increasing number of studies have highlighted inconsistencies in zircon geochronology. For example, zircon in batholiths often record a range of dates that extend over tens of millions of years (e.g. Idaho Batholith (Gaschnig et al., 2013), Ladakh Batholith (Weinberg & Dunlap, 2000), Tynong Province (Regmi et al., 2016), Florida Mountains granite (Amato & Mack, 2012), see Brown & McClelland (2000) for more examples), far beyond what can plausibly be related to an intrusion event, even considering incremental pluton growth (Glazner et al., 2004; Schaltegger & Davies, 2017). In addition, some zircon data indicate biasing of dates consequent to significant common lead or Pb loss (Spencer et al., 2016; Yu et al., 2021), even within a single hand specimen (e.g. Weinberg & Dunlap, 2000). In these cases, the 'dates' of the zircon population of interest fail 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 (Kemp et al., 2007; Hammerli et al., 2018), alteration of zircon (Geisler et al., 2007; Fu et al., 2009; Kusiak et al., 2013; Bell et al., 2016), Pb loss (Amelin & Zaitsev, 2002; Gelcich et al., 2005; Schoene & Bowring, 2006), and matrix mismatch (Sylvester, 2008; Thompson et al., 2016). As such, even though being one of the most reliable dating tools, zircon dating does not come without challenges.

In this context, two feasible approaches to solve the problem are as follows: (1) To improve the zircon U–Pb dating result and (2) to find alternative methods. Previous studies have highlighted the role of late-stage hydrothermal fluids in altering zircons and their U–Pb systematics (Tichomirowa et al., 2019), especially in the context of hybridised granitic suites that contain abundant mafic microgranular enclaves (MME; Kusiak et al., 2009). Chemical abrasion of zircon was suggested and developed as a high-precision tool to overcome the chemical alteration of zircon (Crowley et al., 2014). It is a slow process and thus requires a considerable amount of time. 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; Zhong et al., 2018; Tian et al., 2022). These methods will be used, extended, and combined in this study to test their impact on age accuracy and precision.

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). In igneous rocks, titanite (or sphene), allanite (a group of rare earth element (REE)-rich silicates), and rutile (TiO₂) are more common in plutons with mafic influx (e.g. I-type granite), whilst xenotime (an REE phosphate) and monazite (a phosphate mineral) are more prevalent in more felsic plutons, especially those bodies with an S-type character.

Apatite ($Ca_5(PO_4)_3(F, Cl, OH)$) 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 lanthanide enriched and has an extraordinarily flexible crystal structure, which can be annealed (Yu et al., 2021). This differs from zircon, which can become metamict (radioactively damaged) when it has high U content or is old enough to accumulate damage (Allen & Campbell, 2012; Yu et al., 2021). Apatite incorporates a wide range of minor and trace elements, including S, Sr, U, Th, and lanthanide–REE. These elements incorporated 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 REE, which can indicate magmatic conditions of crystal growth (Kohn, 2017; Scibiorski & Cawood, 2022). Titanite can also be used as a thermo-barometer (Bruand et al., 2020).

Here, we present zircon, apatite, and titanite analyses from an I-type granodiorite (referred to as 'host' hereafter) and its mafic microgranular enclaves (referred to as 'MME' hereafter) from the Mount Buller suite in the Lachlan Fold Belt (LFB), Southeastern Australia. As a case study, the dates are compared to each other and to reported biotite and hornblende K-Ar dates (Richards & Singleton, 1981). In this study, the age of the intrusion is derived from U-Pb dating and coupled with in situ contemporaneous trace element data utilising a laser ablation split-stream (LASS) method. The combined data are used to assess the age of the suite, and respective implications are discussed with respect to possible fluid alteration. The I-type Mt Buller suite includes abundant apatite and titanite compared to other REE-rich minerals. The U-Pb and trace element systematics of these minerals from the host and its MME may be investigated to understand their use as an alternative geochronometer to zircon.

A complex cooling history can make apatite age interpretation confusing because it can be reset easily (c. 350 °C of T_c, Cherniak, 2010; Kirkland et al., 2018), but the study area has a seemingly relatively simple igneous origin (Soesoo, 2000), and U–Pb systematics of zircon are readily available for comparison. Therefore, the Mt Stirling Granodiorite is an ideal case study to test the reliability of apatite and titanite dating. By collecting *in situ* U–Pb ages with trace elements using the LASS method, this study aims to interpret age data alongside trace element chemistry to draw more reliable conclusions.

GEOLOGIC SETTING

The 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 c. 300 Ma (Chappell et al., 1988; Kemp et al., 2009). The general framework of the LFB is an extensive succession of early to mid-Palaeozoic marine sedimentary formations and associated igneous rocks. The southern LFB is divisible from west to east into three sectors: the Western, Central, and Eastern that extend across Victoria (Richards & Singleton, 1981). On the boundary between the Central and Eastern sectors, 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 the central sector are generally late Devonian and post-date the Tabberabberan orogenic phase (Richards & Singleton, 1981) (Fig. 1).

Mount Buller suite

The Mount Buller suite is one of the post-Tabberabberan intrusions with a reported K–Ar date of 381 ± 7 Ma (Richards & Singleton, 1981). The suite is composed of three main bodies, namely the Mt Stirling, Mirimbah, and Howqua intrusions. Homogeneous, hornblende-bearing fine- to coarse-grained granodiorite mainly constitutes the Mt Stirling and Mirimbah intrusions, with the latter also including a mafic unit of gabbroic composition. The Howqua intrusion, also known as the Howqua mafics, comprises gabbro-norite, quartz diorite, and tonalite, with minor



Fig. 1. A geologic map (modified from VandenBerg, 1997) of the Mount Buller suite composed of three main plutons (the Mt Stirling, Mirimbah, and Howqua). The sampling site is located in the southwestern part of Mt Stirling pluton.

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 a few centimetres to metres, with lower silica content and a higher proportion of mafic minerals than their host. Three-component mixing is the most recently 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.

The Mt Stirling Granodiorite, the target of this study, is subdivided into three units: (1) slightly brighter, medium- to coarse-grained hornblende granodiorite (HGD), (2) darker, fineto medium-grained porphyritic hornblende granodiorite (FGD), and (3) MME included in the HGD and FGD. Whilst the HGD and FGD show nearly the same mineral assemblages, they differ in grain size and mode (e.g. finer and slightly more mafic minerals in FGD). The unit FGD also shows resorbed plagioclase.

The HGD and FGD have previously yielded ⁸⁷Sr/⁸⁶Sr (i) values in the range of 0.7037–0.7071, and ϵ Nd (390 Ma) values of +3.4 to +5.6, with similar values of the MME (Soesoo, 2000; based on the K–Ar dates after Richards & Singleton, 1981). These isotopic compositions in the host rock and MME do not correlate with SiO₂. Soesoo (2000) proposed a fractional crystallisation model for the mafic and felsic Mt Buller suite rocks with minor mixing or crustal assimilation, the so-called incestuous mixing (i.e. mixing of earlier solidified crystals with the same, but more evolved, magma).

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 included both HGD and FGD phases and MME (the same outcrop with 'sample numbers 101154–101160' in Bagaric, 1994). Three samples (h1, h4, and h5) from the HGD, two samples (h2 and h3) from the FGD, and two samples (m1 and m2) from the MME were collected. The host rock HGD and FGD are massive and relatively homogeneous (Fig. 2a), and in some places mildly porphyritic in texture. They are composed of quartz, plagioclase, amphibole, biotite, and opaque oxide minerals with accessory K-feldspar, apatite, titanite, and zircon. The predominant phenocrystic phases are plagioclase and hornblende with less abundant biotite. The anorthite number is 30–38 (Bagaric, 1994).

Darker grey MME are also massive and homogeneous, and 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 finegrained homblende crystals) and mafic homblende clots. It contains resorbed plagioclase phenocrysts as the finer grained part of the host rock.

Contact between host rock and MME is generally sharp, but sometimes boundaries show a 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. Mineral transfer between the host rock and MME is implied, indicating mingling of two coeval magmas.

Apatite and zircon are euhedral and equally distributed in groundmass and phenocrysts (apatite grain in Fig. 2b)acicular or stubby apatite often captured by euhedral zircons (Fig. 2c and d). 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 (Fig. 2g and h). Euhedral titanite is rare in thin section, while anhedral—subhedral titanite growth is often found in contact with ilmenite (Fig. 2b). No significant difference was found between titanites from the host rock and MME. When handpicking, titanites were seen to be pale to thick brown in colour, and often showed conchoidal fractures. Titanite and apatite formation was probably prior to amphibole and K-feldspar formation (Fig. 2b). Some titanite show characteristic two cleavages in a grain-scale BSE image, yet the typical sector zoning or any other compositional zoning is ambiguous. Most of the titanites are rather homogeneous (Fig. 2e and f).

ANALYTICAL METHOD

Zircon, apatite, and titanite ('z', 'a', and 't' as each sample name code) were collected both from the host (h1, h2, h3, h4, and h5) and



Fig. 2. Hand specimen, thin section, and BSE images of analysed sample. (a) Hand specimen that includes both host rock (h2) and enclave (m1). (b) Thin section BSE image for the FGD sample. Apatite and titanite are enveloped by hornblende. Note subhedral titanite growth around ilmenite. (c) Acicular and stubby apatites enclosed in a euhedral zircon grain from the host rock sample. (d) Host rock zircon and MME zircon comparison. Note the similarity. (e–f) BSE images of representative FGD and MME titanites. The typical titanite cleavages are recognised yet the difference in the brightness is rather due to topography. (g–h) BSE images of representative FGD and MME apatites with clear and homogeneous sections.

MME (m1 and m2) samples. Weathered portions of the whole rock 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 approximately sand size by a disc mill. The ground samples 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 was used for the heavy liquid separation after. Washed and dried heavier (> 2.97 g/cm³) portions were picked for zircon, apatite, and titanite.

A scanning electron microscope (FEI Qanta 600 MLA, Wfilament source) attached with Delmic Jolt Cathodoluminescence (CL) detector at the Monash University, Australia, was used for BSE and cathodoluminescence images. Operating voltage and emission current were 20.0 kV and 40–100 μ A, respectively. Apatite and titanite U-Pb isotope and trace element data were collected by the method developed for laser ablation splitstream inductively coupled plasma mass spectrometry (LASS-ICP-MS; Kylander-Clark et al., 2013) 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 iCAP™ TQ ICP-MS (U–Pb isotopes; single-quad mode) and ThermoScientific iCAP™ Q ICP-MS (trace elements). The ablated material was carried to the mass spectrometers by combined He gas, with a flow rate of 0.55 l min⁻¹. Make-up Ar gas was at c. 1 l min⁻¹ flow rate each instrument, split evenly after a Y-shape tube. The laser conditions were set such that fluence at the sample of $\sim 4.8 \text{ Jcm}^{-2}$ was obtained, with a 10 Hz frequency, 30- μ m spot size, and c. 10- μ m pit depth for zircon and titanite (25 μ m for apatite).

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 U–Pb elemental fractionation, down-hole fractionation, and calibration drift were corrected by bracketing measurements of unknowns with analyses of the primary reference materials Plesovice for zircon (²⁰⁶Pb/²³⁸U age=337.13±0.37 Ma; Sláma et al., 2008), apatite 401Apt for apatite (530.3±1.5 Ma; Thompson et al., 2016), and the BLR-1 for titanite (1047.1±0.4 Ma; Aleinikoff et al., 2007). The primary reference materials for trace elements in each session is the glass NIST 610, and secondary reference materials are NIST 612, ATHO, BCR2, and BHVO2. The fixed ²⁹Si values for the internal standard were 152300 ppm for zircon and 142000 ppm for titanite, and 393600 ppm of ⁴³Ca for apatite.

Time-resolved data were reduced using Iolite 4 (data reduction scheme '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). The raw data were initially plotted on the Tera-Wasserburg concordia plot, and concordia intercept dates were estimated when data showed a linear regression.

The DRS VizualAge_UcomPbine (Chew et al., 2014) was used to utilise the 401Apt as a primary reference material, by correcting the 401Apt for common Pb prior to downhole fractionation correction. A complete list of the settings for U/Pb and trace element analyses is summarised in the electronic supplementary material 1 (ESM1; Table S1 and S2).

The result of reference material analyses is summarised in Table S3. Zircon secondary reference materials 91500 and GJ-1 show an agreement with the reference concordant ages (Table S3). Secondary reference material ages for titanite (319 ± 4.0 Ma for Mud tank and 95.1 ± 1.2 Ma for CKHB; Fisher et al., 2020) correspond to the reference values (Table S3). Concordia Age of the

A_MAD (478.8 \pm 8.9 Ma as a secondary apatite reference material; Thomson et al., 2012; Table S3) is in good agreement.

RESULTS

Trace element analyses Zircon

In situ trace element concentrations of zircon are listed in ESM2 (Table S4). Zircons from the host rock and MME have an average Th/U = 0.69 (0.26–2.33; n = 345). Generally, concentration of Y in zircon correlates with ambient magma composition (Belousova et al., 2002). Yttrium contents in the Mt Stirling zircons lie within the intermediate-felsic magma range (c. 300-3000 ppm; Belousova et al., 2002). Total REE + Y abundance (Σ REE + Y) of the zircons from the host rock and MME shows a typical crustal zircon range (Hoskin & Schaltegger, 2003) (1225 ppm in average; 1211 ppm in median, n = 232) (Fig. 3). 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: 79.3 (0.72 median) ppm and 346 (17.9 median) ppm, for the host rock and MME, respectively) (Fig. 3). Calcium shows a similar trend: mostly in the 1000-2000 ppm range, yet outliers (e.g. > 10000 ppm points in Fig. 3; note the y-axis is log scale) reach wt % range (Fig. 3). 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 10 points) over hundreds of ppm level (Fig. 3; 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 except Ca correlates with light REE (LREE). While REE concentrations in both the host rock and MME are largely variable, most of the elements show similar patterns in both the host rock and MME (e.g. 1.95–393 and 2.00–209 ppm Ti in the MME and host zircons; Table S4; Fig. 3). Large variabilities are shown in LREE; ~4 orders of magnitude variations are observed in both the host rock and MME in LREE (La–Nd), Sm and Eu (Fig. 4a and b). 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. REE patterns of both the host rock and MME are likely composed of mixtures of two distinct REE patterns. One of the distinct patterns show generally more enriched LREE and low Ce anomaly (Fig. 4a and b).

Apatite

In situ trace elements of apatite are listed in ESM2 (Table S5). Averages of 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. 5). Concentration of Y ranges from 204 to 1290 ppm in the host rock and from 234 to 749 ppm in the MME (Fig. 5), 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 Mn content ranges from 379 to 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 approximately 0.05–1 ppm



Fig. 3. 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).

in both the host rock and MME, yet outliers exist with 10–3000 ppm level. The sum of LREE (La–Sm) ranges from 1590 to 10400 ppm and from 3140 to 9630 ppm in the host rock and MME, respectively. The two Y outliers are >24000 ppm in Σ LREE.

The high-Sr apatites and low-Sr apatites are not separable in other elements (Fig. 5). In an REE diagram normalised to C1 chondrite, both patterns of host rock and MME apatite have a negative slope with $(La/Yb)_N = 19.8$ and 32.0, respectively, and consistently show negative Eu anomalies (0.28 and 0.48 for the host rock and MME) (Fig. 4c and d). 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 4c and 5).

Titanite

Trace element concentrations of titanite are listed in ESM2 (Table S6). 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 to 4146 (average 1241) ppm in the host rock and 72.2 to 4089 (average 947) ppm in MME (Fig. 6). The ratio of (Ce + Nd)/Y shows similar variability in the host rock and MME. The host rock and MME titanites contain c. 10–50 ppm Sr and c. 100–2000 ppm Zr, while some grains show outliers out of this range (Fig. 6). Strontium content of the titanite separates samples, and it corresponds to rock types, which is like the apatite case, yet slightly less deviation than apatite. The three clusters are high-Sr (24–46 ppm, FGD), mid-Sr (~22 ppm, MME), and low-Sr (~16 ppm, HGD). Total concentration of all LREE ranges from 932 to 28500 ppm in the host rock and 957 to 21400 ppm

in the MME. Ratios like La/Sm and Dy/Yb show that both the host rock and MME have similar REE C1 chondrite normalised patterns (Fig. 4e and f). 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 by McLeod et al. (2011). The host rock and MME titanites share similar Nb/Zr values between each other, except ~6 outliers of Nb/Zr > 10 (Fig. 6).

The REE concentration of the host rock titanite (C1 chondrite normalised) forms a similarly inclined pattern (La/Yb = 19; Fig. 4e) with different degrees of enrichment (Σ REE range 1025–31630 ppm). The same pattern or 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; Fig. 4e and f). 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.

U–Pb dating Zircon

Isotope compositions of U–Pb and associated dates are listed in the ESM2 (Table S4). The 206 Pb/ 238 U date of the host rock is 399 ± 2 Ma (n = 240) and that of the MME is 387 ± 10 Ma (n = 62). However, zircon dates form a wide range from c. 350 Ma to c. 450 Ma in the host rock with a large MSWD value of 9.3 and ~300 to ~450 Ma in the MME with an MSWD of 26 (Fig. 7). A probability density diagram with Kernel density estimation (KDE) of the host



Fig. 4. (a and b) C1 chondrite (McDonough & Sun, 1995) normalised REE plot for the host rock and MME zircons. Note the similarity between the host and MME zircons. (c and d) Apatite and (e and f) titanite REE diagrams. Trace element-filtered spots are depicted in grey colour. (c) Negligible difference is shown between the high-Sr and low-Sr groups. (d) Smaller negative Eu anomaly is the minimal difference between the host rock and MME apatites. (e) The host rock titanite and (f) MME titanite share similar REE patters while MME titanites show more positive Eu anomalies.

rock zircon shows a main peak and a shoulder and tail extending towards younger dates (Fig. 7). The weighted mean date of the peak is c. 400 Ma, although the density diagram of the MME shows a less pronounced peak age with considerable scatter and thus fails to fit a Gaussian distribution (Fig. 7). This spread of dates on either side of the peak in both the host and MME, especially the pronounced tail on the younger side of the peak, contribute significantly to errors and a larger MSWD.

Apatite

Apatite U–Pb isotopic compositions and calculated dates are listed in the ESM2 (Table S5). Apatite U–Pb data in a Tera-Wasserberg concordia plot form an apparent mixing array between the radiogenic samples and a common lead component, which intercepts to the concordia with a best-fit regression. The calculated concordia intercept dates (alias., inverse isochron dates) for the host rock and MME apatites are 417 ± 4 Ma (n = 206, MSWD = 1.3) and 408 ± 4 Ma (n = 82, MSWD = 0.99) (Fig. 8a and 8b), respectively. Two sigma error ellipses are slightly greater than those of zircon or titanite because of lower U concentration. The result indicates c. 10 Myr older apatite dates compared to zircon. Although the apatite data apparently have well-defined regression (i.e. with ~1 of MSWD), they still include anomalously large error spots.

Titanite

The host rock titanite dates in the Tera-Wasserburg concordia plot also show variable amounts of common-Pb content. For the host rock, the best-fit linear regression, which also defines a mixing



Fig. 5. Apatite trace elements of the host rock and MME. A clear distinction is shown in Sr between different rock units; thus, the host rock unit is further separated into high-Sr (FGD) and low-Sr (HGD). REE and Ce anomaly show no separation but a similar range in each unit.

endmember with initial ²⁰⁷Pb/²⁰⁶Pb, yields a concordia intercept date of 403 ± 3 Ma (n = 120, MSWD = 4.7) (Fig. 8c). MME titanite data also show a common-Pb mixing trend, with a concordia intercept date of 389 ± 6 Ma (n = 33), and a similar scatter (MSWD = 3.4) (Fig. 8d). Both the host rock and MME titanite data yield similar dates compared to the zircon dates out of the host rock and MME, while the titanite dates are slightly older within error ranges (399 ± 2 vs 403 ± 3 Ma for the host rock zircon vs titanite and 387 ± 10 vs 389 ± 6 Ma for the MME zircon vs titanite) and high MSWD.

DISCUSSION Age data filtering Zircon

The range of zircon dates from 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 individual spot still spreads over nearly 30–40 Ma. This extreme range of dates cannot be explained only by a duration of an intrusive event or size of analytical error of the LA-ICP-MS method. Regarding the size of error in the method is c. 5% at

the 2 sigma level (cf. Chang et al., 2006), it is plausible to describe this as a combination of uncertainties of multiple factors. It is difficult, however, to estimate the amount of contribution made by which factor. Simple, currently popular statistical methods for trimming data (e.g. discarding datasets based on different discordance thresholds; Spencer et al., 2016) may not be enough to explain the reasons for the spreading, and an understanding of factors contributing to the scatter (e. g., geological variations) that justifies a trimming scheme is essential. In this section, the reliability of these dates is tested by the means of additional geochemical analyses that were collected in conjunction with the age data. The methodology of this approach is outlined below.

In a first step, we employed high concentrations of Ca or K beyond trace element levels to identify individual analyses that may be chemically affected and thus do not represent an igneous age. High concentrations 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, we used core–rim age differences as a measure of unreliable age data. For the vast majority of data, a core–rim pair was analysed, allowing a calculation of the age



Fig. 6. Titanite trace elements of the host rock and MME from the Mt Stirling. Concentrations of (Ce + Nd) and Y strongly correlate. Both the host rock and MME titanite show a similar range in LREE and Dy/Yb. The source indicator Nb/Zr also shows a similar range between the host rock and MME except for a few anomalies, implying an identical source for these magmas, substantial mixing between each other, or both.

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 in Fig. 7 (Tera-Wasserberg and KDE) display data after the first and second steps. The detailed reason for reverse Δ ages remains elusive but is likely to be analytical in nature. A younger core date might indicate laser mistargeting because of indistinctive zoning in some zircons. Invisible microcracks and fluid interaction through the crack can also induce lead loss and spurious younger core date.

Following these basic filtering steps, the age scattering is still too large to record one single igneous event. In light of reported possible hydrothermal alteration of zircons during syn- or post-emplacement, we 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 criterion (Belousova et al., 2002), we employ it here for an early stage skimming tool. Similarly, more than 1 wt % of Σ REE + Y can be used for an additional early trimming criterion, since it may be indicative of a severely altered zircon composition (Fig 3; Hoskin & Schaltegger, 2003); thus, zircon data above this threshold is excluded.

The remaining data after this filtering may further be assessed for fluid alteration by testing for elevated fluid-mobile element abundances. For igneous zircon, high amounts of fluid-mobile elements like Ba, K, and Sr potentially indicate hydrothermal alteration. Here we use a fluid-mobile trace element vs an immobile element to monitor 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, 1000*Ba/Hf = 1 is used as a threshold proxy, with samples exceeding this value being excluded from the dataset. The value of 1000*Ba/Hf > 1 is thus used as an indicator for excessively abundant Ba compared to naturally abundant Hf in zircon. A total of 24 out of 291 analyses display 1000*Ba/Hf > 1 (after previous filtering is applied) (Fig. 9a), indicating that \sim 10% of zircons are hydrothermally altered, which were not detected in the previous proxies. We note here that other non-formula elements like Ca, Al, Fe, and Mn were also suggested for proxies of hydrothermal alteration if higher than a weight percent (Geisler et al., 2007).

The large compositional spectrum of zircon can further be inspected in REE, especially in LREE or Nd/Sm, which are distinct in hydrothermal vs magmatic zircon (e.g. Fu et al., 2009; Bell et al., 2016; Zhong et al., 2018). Zircons from the Mt Stirling host rocks and MME show a range of distinct REE patterns, and this



Fig. 7. Tera-Wasserburg concordia plots (²⁰⁶Pb/²³⁸U dates) and kernel density diagrams for the host rock and MME zircon. Note spread of data and high MSWD, indicating overdispersion.

distinction can be used as an additional filter. While conspicuous differences in Nd/Pr or Nd/Sm are shown in both the host and MME zircons (Figs 9 and 11), an 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. 9b).

Based on this separation, zircons were separated into two groups, with reference to their REE shape. One is termed 'Vshape' 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*≈1.8) than N-shape (Ce/Ce*≈11; Figs 9c, e, and 11). 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 incorporation into the crystal lattice (Belousova et al., 2002; Schulz et al., 2006; Fu et al., 2009; Bell et al., 2016). Therefore, the chemical composition of V-shape group zircons implies a higher probability of hydrothermal alteration, and thus the need to separate these from unambiguously magmatic zircons. This is the fifth filter we applied.

The exclusion of V-shape group zircons results in a more defined and narrower span of dates compared to that of the total (unfiltered) dates (Fig. 12). Indeed, kernel density diagrams of the N-shape group zircons show a clearer Gaussian distribution (Fig. 12). The same effect can be observed for the MME's distribution, yet with a less pronounced Gaussian distribution compared to the host granite, probably because of a smaller number of laser spots than that of the host (Fig. 12b, d, and f). 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 but to the hydrothermal influence over both rock types equally.

Even after filtering erroneous spots based on different trace elements and REEs criteria, a few discordant data still remain. In this study, the rest of discordant data is trimmed based on 10% degree of discordance threshold (Figs 12g, h, and 13e, f). After processing the 10% discordance filtering, 30% of the host rock and 17% of the MME data remain, respectively. Both the newly calculated host rock and MME ages (406 ± 1 Ma and 410 ± 6 Ma, respectively) increased slightly, although MME data are based



Fig. 8. Tera-Wasserburg concordia plots for the apatite (a–b) and titanite (c–d) and their concordia intercept dates. Both minerals show common-Pb mixing lines between initial and radiogenic Pb, but many data spots represent low degrees of contamination (i.e. error ellipses close to the concordia curve), taking advantage in intercepting on the concordia. A few outliers are found in both the host rock and MME for both apatite and titanite.

on a considerably smaller number of data (Fig. 13e and f). These outcomes are interpreted here such that the filtered final dates represent the igneous zircon crystallisation ages.

An important observation of the different types of filtering is that many Ba/Hf and Nd/Sm outliers have low degrees of discordance (<10%; Fig. 13a, b, and d). As such, datasets that are based solely on a discordance threshold (either 5% or 10% of discordance) would still include such potentially altered zircon analyses. Indeed, these outliers with conspicuously anomalous Ba/Hf or Nd/Sm often have significantly younger or older ages (Fig. 13a, b, and d). Failing to remove these outliers from the final dataset may cause inaccurate age determination.

It is important to note that some outliers in one step may survive in other steps, so that only the combination of all steps will produce an age that most likely represents the igneous formation age. For example, some zircons with Ba/Hf >1 (Fig. 11b) have N-shape REE patterns. This indicates that processing the entire sequence of steps is important.

We acknowledge that any trends in Ba/Hf (Fig. 9a) and REE (Fig. 11; also Nd/Sm, Fig. 9d) are continuous, so the filtering threshold can be defined differently on an individual basis. This indicates that the hydrothermal alteration, affecting zircon is a gradual process, and in turn implies that any cut-off threshold for these trimming schemes cannot be defined by a single value. For the current dataset, however, the proposed threshold yields the most robust results, tested through an iterative approach of filtering and zircon date MSWD.

Although apatite and titanite are less susceptible to metamictisation by radioactive damage, their ages may also be affected by other potential factors that compromise accurate ages determined: mineral inclusions, alterations, zoning, diffusion, and recrystallisation. Both apatite and titanite however incorporate various trace elements and REE equally or more so than zircon. Monitoring trace element chemistry linked to U–Pb age data similar to the zircon filtering may thus be as effective to obtain a reliable age.

Apatite

Apatite's major elements in the crystal lattice, P and Ca, should be monitored in a first step. Significant variations in these elements could indicate that inclusions or epoxy was hit by the laser spot. In the initial dataset, two spots had only about 300 ppm of P, leading to their exclusion. The outliers at this stage were not included in Figs 5 and 14.

The next step in filtering poor-quality apatite analyses involves checking for excessive Zr (> 100 ppm). Since Zr is not readily incorporated into the apatite lattice, excessive Zr compared to other common incompatible elements abundant in apatite (such as light and heavy REE (LREE, HREE), or Y) can detect zircon micro-inclusions, typically discerned on a logarithmic scale. The Zr/Y used here indicates that 15 outliers exist in the dataset (Fig. 14a). The following step involves filtering based on low Th/U ratios. Given that low Th/U (< 0.5) is a typical characteristic of peraluminous S-type granite apatite (Sha & 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 Stirling Granodiorite. Standard apatites 401Ap and Mud Tank exhibit narrow ranges in Zr/Y (Fig. 14a), but the Mt Stirling apatite



Fig. 9. Zircon data trimming scheme using trace element ratios (a) and REE patterns (b–e). (a) Comparing non-formula and fluid-mobile element (Ba) to formula element (Hf) can be a proxy to detect severely altered zircons (outliers for 1 < 1000 Ba/Hf). (b) Lambda ($\lambda 1 \text{ vs } \lambda 2$) plot, based on O'Neill (2016) to separate two different REE patterns (the group N and V). Note that the point around the inflection (marked by an arrow) separates the group N and V. The inset figure depicts zircon's temperature range of 600–900 °C (Ti in zircon thermometry, Watson et al., 2006). (c) Nd/Sm vs Eu anomaly, (d) Ce anomaly, and (e) (Sm–Nd)_N (=tilting between Sm and Nd in the chondrite normalised REE diagram). The group V invariably shows higher Nd/Sm values than those of the group N, which indicates tilts in Nd–Sm are opposite in the group N and V. The Ce anomaly may separate two groups more distinctly than the Eu anomaly. Note that Ba/Hf trimming scheme may not work in the same way as the REE trimming scheme. (f) A conceptual diagram describing the filtering scheme.

yields variable and discrete groups in Th/U and Zr/Y values. Groups with Th/U < 0.5 or Zr/Y (×10000) > 60 have been discarded for age determination. Fig. 14b shows Tera-Wasserburg concordia plot with only the first (P and Ca) filtering, while Fig. 14a shows trace element ratios with this filtering. Fig. 14c and d indicates the second step in filtering. These filters successfully excluded outliers including the spot with the largest error, yielding a slightly younger date and smaller MSWD (from 417 ± 4 Ma, MSWD = 1.3 to 414 ± 5 Ma, MSWD = 1.2; Fig. 14b and d). Fig. 14e and f displays the outlier distribution in Zr and LREE concentrations. Notably, the MME apatite does not exhibit anomalous spots with this filter.

Interestingly, some outliers of Th/U and Zr/Y are not outliers in Zr and LREE, indicating that some large outliers in Th/U and Zr/Y might not be filtered solely by checking Zr or LREE concentrations.

The trace element-filtered apatite age plot on the Tera-Wasserburg concordia plot shows more defined isochrons without apparent outliers (Fig. 14b and d). However, due to relatively large error ellipses (caused by low U concentration), the concordia intercept date comes with a larger error compared to those for zircon or titanite. This implies that a greater number of apatite spots are generally needed to obtain a smaller error margin (e.g. c. 3% in 2 SE recorded in this study with N = 181).



Fig. 10. Concentrations of trimmed zircon trace elements after the trace element and REE data trimming test

Properly anchored inverse isochrons can help reduce the error for unknown apatite samples (Chew et al., 2011; Thomson et al., 2012; Kirkland et al., 2018). To determine common-Pb (²⁰⁷Pb/²⁰⁶Pb)_i ratios, we applied the iterative process (Chew et al., 2011; Thomson et al., 2012; Kirkland et al., 2018) using the two-stage model in Stacey & Kramers (1975) and zircon Concordia Age. It needs an assumption that the target mineral phase and zircon shared the same common lead pool (i.e. the same $^{\rm 207}{\rm Pb}/^{\rm 206}{\rm Pb}$ composition) when the zircon crystallised. The Stacey & Kramers (1975) twostage isotope evolution model constrains the initial lead ratio (²⁰⁷Pb/²⁰⁶Pb)_i using the Concordia Age derived from the Mt Stirling zircons. The model with the host rock zircon age (406 Ma) yields a $(^{207}Pb/^{206}Pb)_i = 0.8634$, which can be used as an anchor on the y-axis of the Tera-Wasserburg concordia plot. Once the initial anchored age is obtained, we then use the age to retrieve another (²⁰⁷ Pb/²⁰⁶ Pb)_i for iterative trial. We repeated this until ages converge (Thomson et al., 2012).

However, the Stacey & Kramers (1975) two-stage commonlead anchoring output in this study not only poorly fits to actual common-Pb mixing array (Fig. 15a and b) but also returns a spuriously older date (445 \pm 4 Ma, MSWD = 3.1) compared to the concordia intercept date (414 \pm 5 Ma, MSWD = 1.2) and the zircon date (406 \pm 1 Ma). It is unrealistic for the apatite concordia intercept date to be the same as, or older than, the zircon dates, given zircon's higher T_C and a continuously decreasing temperature in a cooling igneous body. Therefore, this filter proved to be unsatisfactory for the host apatite data, as it returned a spuriously older date compared to the host zircon date (Fig. 15a).

Strontium in apatite is one of the most characteristic elements often used as 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 et al., 2020). The Sr concentrations in apatite in each sample vary significantly in this study (Fig. 5). Three groups of Sr concentrations are defined: low-, mid-, and high-Sr groups (c. 250, c. 300, and 400-600 ppm). These Sr groups in apatite correspond to the sample lithologies, reinforcing the relationship between Sr-in-apatite and the host rock chemistry. Low-Sr apatites are from the medium- to coarse-grained hornblende granodiorite (HGD), mid-Sr apatites are from the MME, and high-Sr apatites are from the fine- to medium-grained porphyritic granodiorite (FGD). Interestingly, REE patterns do not show a clear 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. 4c and d). The difference in Sr, however, seems to be reflected in age differences when individual groups are plotted on the Tera-Wasserburg concordia plot. The host rock apatite date without Sr distinctions (i.e. HGD + FGD) is 414 ± 5 Ma (n = 181, MSWD = 1.2). After the separation, the concordia intercept date for the low-Sr apatite is 420 ± 6 Ma (n = 75, MSWD = 0.88) and for the high-Sr is 408 ± 7 Ma (n = 106, MSWD = 1.3) (Fig. 15e and f). The low-Sr isochron age being older than the Concordia Age of zircon is unlikely, considering apatite has a lower T_C than zircon, and a typical timescale for apatite crystallisation would not allow a spread of several million years. Note that the date for the mid-Sr



Fig. 11. Various zircon REE patterns. Zircons from both the host rock and MME show N- and V-shaped REE patterns. V-shape patterns generally have higher LREE, smaller Ce/Ce*, and descending trend from Nd to Sm. An interesting observation in the REE pattern (b) is that many of these zircons, which are severely altered—and thus were expected to be removed in the previous Ba/Hf trimming step—have an N-shape-like REE pattern.

apatite (=MME apatite) is 408 ± 4 Ma (n = 82, MSWD = 0.99), which aligns with the date for high-Sr apatite. The physical relationship between the MME, as mafic melt blobs, and the host rock provides a clue to constrain the age of two melts; they were contemporary. Regarding this relationship, the older low-Sr apatite date is less likely to represent a true age.

While the Sr grouping seems closely related to the age grouping, the underlying mechanism remains intriguing and requires further investigation. Incorporating an older calcium-rich material with higher (207 Pb/ 206 Pb)_i into certain apatite groups as a different source of common-Pb could cause the isochron rotation. This scenario might also apply to the different Sr groups of titanite, which is further discussed in the following section.

Titanite

Similar to Ca and P in apatite, Ca and Ti are major constituents in titanite and should be monitored for anomalies. Significant deficiencies in Ca or Ti titanite spots likely indicate inclusions, altered crystals, or epoxy-filled holes. The raw dataset included three spots with only hundreds to thousands of ppm in Ca or Ti. These outliers were excluded from Fig. 6.

If a spot shows a peak in Sr in titanite, this may indicate alteration of the crystal lattice, similar to apatite, reflecting the mobility of Sr during hydrothermal activity. Additionally, Sr anomalies may indicate different origins of the titanite grains, as Sr in titanite is known for effectively discriminating magma type (Bruand et al., 2020). Fig. 16 shows titanite in the host rock and MME with Sr/Zr anomalies. These outliers suggest an excess of Sr compared to Zr, indicating alteration. The Sr/Th can also be used as Th is a fluidimmobile element, a melt enrichment indicator, and also a competing element with Sr in the decahedral site of titanite. Five spots with Sr/Zr or Sr/Th anomalies were excluded (Fig. 16c and d).

The next step can filter additional date spots that experienced an abrupt cation exchange. In a titanite crystal lattice, Sr²⁺ replaces Ca²⁺, whereas Zr⁴⁺ replaces Ti⁴⁺ (Kohn, 2017). Pit profiles during laser analysis show this trade-off relationship between Sr and Ca, and Zr and Ti: the higher the Sr (or Zr) concentration, the lower the Ca (or Ti) concentration (Fig. 17). The concentrations of Sr and Zr against Ca and Ti thus indicate a coupled substitution in the crystal structure, while a preferential incorporation of Sr may imply an open system, potentially accompanied by Pb loss. Spots with these anomalies in Sr/Ca (x10000) vs Zr/Ti (x10000) can be excluded if the anomalies form a significantly different trend from the main (igneous) one. The Sr/Ca and Zr/Ti plots with reference titanites BLR and OLT reveal five anomalies that deviate from the main trend (Fig. 16). Note that reference titanites display a narrow range of the proxie values (e.g. ~2 to 4 for the BLR and ~5.5 for the OLT Sr/Ca; Fig. 16). However, filtering based on this proxy does not yield a significantly improved age in the host rock (from 403 ± 3 to 404 ± 3 Ma). The MME age shift is from 389 ± 6 to 393 ± 4 Ma.

Titanite trace element data filtering enables the removal of outliers and potentially erroneous data points (Fig. 17). These 'outliers' might be easily recognisable without trace element data if they form large anomalies on the concordia plot. However, Fig. 16b and d shows that these outliers are often cryptic in the age plot. In addition, trace element anomaly peak profile is often



Fig. 12. KDE diagrams. (a–b) Un-filtered Concordia 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 show 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. (g–h) The results of final discordance filtering. Dates are increased in both the host rock and MME, reducing MSWD, implying that the outliers due to Pb loss were successfully removed.

transitional, suggesting diffusion (e.g. the lower laser pit profile in Fig. 17). Thus, we recommend inspecting data points based on trace element systematics, as these elements can help identify laser mistargeting, flawed crystal, or even concealed anomalies. The titanite concordia intercept date, after filtering for the host rock, aligns with the age of zircons (403 Ma for titanite and 406 Ma



Fig. 13. Tera-Wasserburg concordia plots during the data trimming process of the host rock (left) and MME (right). Colour legends indicate Ba/Hf (a and b; reddish colour gradient), Nd/Sm (c and d; greenish colour gradient), and degree of discordance (e and f; reddish colour gradient) levels. Note each filtering criteria progressively removed discordant data points. (g and h) The final step of filtering based on the threshold of 10% discordance. Red-marked data points and laser spots (BSE) show examples of age outliers compared to the major age population. It is often difficult to prevent analysing these erroneous points relying only on BSE and/or CL images. Also, note that MSWD is still higher than 1 in the MME, indicating dispersion persists.

for zircon; Figs 16 and 18). The concordia plots show improved MSWD for both the host rock (from 4.7 to 3.4) and the MME (from 3.4 to 1.8).

Similar to the approach used with apatite, the Stacey & Kramers (1975) two-stage common-Pb model was applied to anchor the $(^{207}Pb/^{206}Pb)_i$ to 0.8634. Common-Pb anchored dates and unanchored isochron dates for titanites overlap within error ranges (Fig. 16g and h): the common-Pb anchored date of the host rock is 405 ± 2 Ma (n = 110, MSWD = 3.5), while that for the MME is

 397 ± 4 Ma (n = 28, MSWD = 2.4). However, the concordia intercept date of the MME titanite (393 ± 4 Ma) is clearly younger than that for the host titanite (Fig. 18). The concordia intercept date for the MME is also younger than ages derived from zircon and apatite (Fig. 18), suggesting that the true age might be obscured by unknown factors. The age gap between different phases may indicate varied cooling ages, corresponding to the temperature gradient from ~900 °C (T_C of zircon) to ~650 °C (T_C of titanite; Cherniak, 2010; Fisher et al., 2020).



Fig. 14. Apatite data filtering scheme using trace elements and corresponding age plots. (a) The proxies Th/U and Zr/Y (×10000) can detect outliers in apatite, which potentially suffered from hydrothermal alteration. (b) The Tera-Wasserburg concordia plot for (a). (c–d) The elimination of outliers based on the Th/U and Zr/Y filtering scheme and the corresponding age plot. (e–f) Outlier distribution in Zr and LREE. Outliers mostly correspond to Zr and LREE anomalies, though some are in the main population.

Different Sr concentration levels of titanite samples reflect age differences between each Sr group, yet they differ from the pattern seen in apatite. The concordia intercept dates for the high-and low-Sr titanite are indistinguishable, both yielding 402 ± 4 and 402 ± 3 , respectively, while the mid-Sr titanite (=MME titanite) shows the younger date at 393 ± 4 Ma. Given that the apatite dates might be compromised by the input of calcium-rich material, the Sr grouping in titanite can be similarly explained, as Sr exhibits chemical behaviour akin to Ca. Likewise, the younger MME titanite date is associated with the lower common-Pb composition with a (207 Pb/ 206 Pb)_i of 0.64, akin to apatite's low values (~0.5; Fig. 15). Also, note that the MME titanite spots tend to spread towards the right side near the concordia line, possibly indicating Pb loss (Fig. 16g).

To test the combined effect of common-Pb and Pb loss, we calculated model ages to reproduce the age-shifting effect. Refer to Bonamici et al. (2015) for an outline of the general procedure of the model calculation. The initial $^{235}U/^{238}U$ ratio was set at 0.0101, back-calculated based on a modern $^{235}U/^{238}U = 1/137.82$

and the zircon age of 405 Ma. The (²⁰⁷Pb/²⁰⁶Pb)_i range of the common-Pb mixing endmember was set 0.5–0.86, with the mixing ratio ranges in 0–31%, and the Pb-loss fraction up to 10%. The parameterised model ages successfully explained the range of spot spreading as the combined effect of common-Pb mixing and Pb loss (Fig. 16g). Although a model age and its parameters do not represent the true values, they offer a quantified estimation implying that the combined effect of common-Pb mixing and Pb loss can skew dating results. In the host rock titanite, a similar 'Pb-loss tail' is observed, but the shift in date and common-Pb intercept were apparently not significant likely due to a greater number of sample spots.

Implications for the age of the Mt Stirling magmatism

The observation that V-shape zircons (Fig. 11d), which suggest hydrothermal overprint, yield different U–Pb results than the N-shape zircons indicates that the U–Pb system was not closed in these zircons (29% and 34% filtered out from the respective host



Fig. 15. Tera-Wasserburg concordia plots for the strontium-based additional filtering scheme. Red colours refer to the anchored dates. (a and b) Trace element-based filtered apatite for the host and MME without Sr grouping. (c and d) Dates for the MME apatite (=mid-Sr apatite). (e and f) Dates for the high-Sr apatite and low-Sr apatite. Note the high-Sr apatite date aligns with the date of zircon Concordia Age, while the date from the low-Sr apatite is spuriously old.

and MME). This compromised grains, however, were not evident from CL/BSE imaging. When large quantities of zircons are used for mean age calculation, the error on the calculated date can be artificially reduced (despite high MSWD), leading to potentially incorrect geological interpretations. For example, before filtering, the host rock and MME mean ages differed significantly, suggesting that the MME might have been injected into a seemingly still crystalline mush ~15 million years after emplacement of the granite. After filtering, however, the ages align much more closely, indicating that both rock types likely have a contemporaneous origin, which is geologically more plausible.

A remaining issue, beyond the trace element filtering, is the broad age range of the individual N-shape zircon (c. 50 Myr in both the host rock and MME; 440–390 Ma), which exceeds analytical reproducibility (2 SE < c. 15 Ma). Analysis of standard zircons (Table S3) supports that this age spread is real and not an artefact of analytical error. Such a prolonged range of zircon

ages has been reported in previous studies (e.g. Schaltegger & Davies, 2017; Weinberg et al., 2020). These zircons might simply indicate a prolonged formation period within the source of the melts. The lower crustal hot zone (LCHZ), as described by Annen et al. (2006), Jackson et al. (2018), and Lim et al. (2024), provides a feasible model to simulate the scenario. Located at a depth of 20–40 km, the LCHZ maintains high temperature through repeated replenishment of mafic magma pulses, enabling it to produce and store crystals for extended periods. The melts that evolved and eventually evacuated from the LCHZ would contain crystals with broad range of ages. The Ti-in-zircon thermometer (Hayden et al., 2008) indicates that most zircons formed within a temperature range of 600–900 °C (inset diagram in Fig. 9b), consistent with the condition in I-type magma (Collins et al., 2020b) and the LCHZ.

The temperature range might delineate the upper and lower limit temperatures, with the T_C of Pb in zircon (~900 $^\circ C)$ as



Fig. 16. Titanite filtering and age determination. (a) The unfiltered Sr/Th vs Sr/Zr plot and (b) the corresponding Tera-Wasserburg concordia plot. (c) The Sr/Th vs Sr/Zr plot after the filtering and (c) the corresponding age plot. Note that most of the scattering data are eliminated. (e) The 10000 Zr/Ti vs 10000 Sr/Ca filtering plot to identify outliers and (f) the corresponding age plot. (g–h) Filtered and anchored dates for the MME and host rock titanites. The dashed red common-Pb mixing line indicate the model with the parameters of 405 Ma and (207 Pb/ 206 Pb)_i = 0.86, intercepted by the red asterisk mark indicating 0% common-Pb mixing. The dashed red arrows indicate lead losses, and the black arrow depicts another modelled isochron towards (207 Pb/ 206 Pb)_i = 0.50.



Fig. 17. Time-resolved titanite spot analyses for four elements (Sr, Ca, Zr, and Ti) from the h5t sample as an example. Red circles indicate the laser spot (on BSE image) and corresponding data (on the Sr/Ca vs Zr/Ti plot). Note the trade-off relationship between Ca and Sr, and Ti and Zr indicating replacement between each other. If the anomaly (inclusion) is conspicuous, it can be easily excluded from the time frame for downhole correction (upper figure). However, if the range and contrast of anomaly is unclear, it can be challenging to adjust the time frame even if the proxy values are significantly outside the expected range and the texture appears to be intact.

the upper limit and the granodioritic melt solidus (~600 °C) as the 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 minor age (tail ages) bandwidths. This suggests that zircons from the host rock and MME were likely formed over a prolonged time span of up to 50 million years, across a temperature range of 600–900 °C. The temperature variability may have been dictated by mafic magma replenishment cycles (Annen et al., 2006; Jackson et al., 2018)—naturally not

within the plutonic body they now reside in but its deep crustal source.

Previously reported K–Ar dates for the Mt Stirling pluton are 385 ± 14 Ma for biotite and 379 ± 13 Ma for hornblende (Richards & Singleton, 1981), approximately 15–20 Ma younger than the weighted mean zircon dates in this study (Fig. 18). These hornblende–mica dates, however, may correspond to some younger fractions of zircon dates, particularly the hydrothermal zircon dates reported here. Given the low-T formation in hornblende and



Fig. 18. Date compilation of the Mt Stirling Granodiorite. Note that zircon dates are Concordia Ages expressed by both actual points (grey) and box-and-whisker plots, and apatite and titanite dates are concordia intercept dates. Titanite, zircon, and apatite dates align well, except titanite from the MME (mid-Sr) and low-Sr apatite from the host. The anchored titanite MME age overlaps the host titanite date. The variability in Sr suggests potentially different age components in the apatite group, and probably higher Sr apatites are more reliable in age determination regarding other mineral dates.

biotite (300–500 °C hydrothermal transition from homblende to biotite; Brimhall et al., 1985), coupled with their lower closure temperatures (T_c of homblende=530 °C and T_c of biotite=310 °C; Harrison, 1982; Harrison et al., 1985), these ages probably indicate hydrothermal overprinting during or after the later stages of emplacement.

It is important to note that most of the reported LFB granite ages are K–Ar ages from amphibole or biotite or whole rock Rb–Sr ages. Ages of other Victorian granitoids in the LFB range from c. 365 to c. 412 Ma based on whole rock Rb–Sr isochron ages (Gray, 1990), and 348 Ma (min) to 392 Ma (max) (370 Ma in average) from K–Ar (biotite, muscovite, and hornblende ages; Richards & Singleton, 1981). Similar relationships between younger K–Ar ages and older zircon U–Pb age relationships have been reported from the Wilsons Promontory Batholith, another LFB granite (391 \pm 14 and 379 \pm 15 Ma with K–Ar ages; Richards & Singleton, 1981, and 395 \pm 4 Ma with U–Pb zircon; Elburg, 1996). This suggests that K–Ar ages should all be treated with extreme caution, as well as geodynamic interpretations based on these ages for the LFB.

To evaluate effect of filtering, all zircon, apatite, and titanite age data were merged on a Tera-Wasserburg concordia plot (Fig. 19). The filtered host rock mineral age converges to 403 ± 2 Ma (n=294; MSWD=2.7) and the MME to 400 ± 3 Ma (n = 123; MSWD = 2.7) (Fig. 19a and b). However, common-Pb mixing trends clearly separate between the host rock apatite $((^{207}Pb/^{206}Pb)_i = 0.48)$ and the host rock titanite $((^{207}Pb/^{206}Pb)_i = 0.77)$. In light, these dates with the low common-Pb could be compromised, or at least they did not share the same environment during crystallisation, as indicated by the common-Pb+Pb-loss model. A common initial isotope composition is a prerequisite for any isochron approach, which is seemingly not the case for these two phases. Nonetheless, apatite and titanite would have formed contemporaneous, as suggested by their similar individual concordia intercept points, and also their identical dates derived from the MME minerals. The excluded data after the filtering display significantly more dispersion and are generally younger than the filtered data, indicating the potential effect of Pb loss (Fig. 19c and d).

To understand the mineral crystallisation history in the Mt Stirling pluton and to obtain an absolute age for the intrusion, a holistic approach considering zircon, titanite, and apatite age data is advised. When considering these mineral ages, note here that the zircon age is a Concordia Age, which is a cluster of single grain ages, whereas the titanite or apatite age is concordia intercept age that is reported as single age. 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 (e.g. apatite data compared to titanite data; Figs 8, 15, and 16), which on its own should not be treated as the only measure for the reliability of ages.

In an age compilation for Mt Stirling (Fig. 18), uncertainties were propagated with the long-term excess variance of 2% 2 SE for 206 Pb/ 238 U (the level 8 systematic uncertainty propagation in Horstwood et al., 2016). The concordia intercepted date for titanite (403 ± 5 Ma) is identical to that of apatite (408 ± 8 Ma) and aligns with the zircon Concordia Age (406 ± 4 Ma). Regarding the individual zircon grain age range, and highest U–Pb T_C in zircon (~900 °C), followed by titanite (500–800 °C; Fisher et al., 2020) and apatite (~350 to 650 °C or higher; Fisher et al., 2020) (Fig. 18), it appears that the intrusion cooled quickly from >900 to ~600 °C. The age of 406 Ma may represent the true crystallisation age in this lower crustal magma reservoir. Given that I-type granite has temperature ranges around 780–800 °C (Lee & Bachmann, 2014; Collins et al., 2020b), it is expected that zircon and titanite were crystallised quickly.

The presence of compromised grains in all phases, resulting in different dates, suggests that a simple, fast dating approach is no longer advisable. Their respective closure temperatures work only at magmatic condition, but hydrothermal processes below this threshold could indeed affect these chronometers. Notably, the 'protracted' age range towards 380 Ma corresponds to mica and hornblende K–Ar ages that have been previously reported as the 'true' age of the Mt Buller suite (Richards & Singleton, 1981), potentially indicating a 15-million-year hydrothermal alteration event that partially affected the grain populations studied here. Revising the absolute age of the Mt Buller suite would place the pluton towards the older range of ages for granites in the LFB (Richards & Singleton, 1981; Collins et al., 2020a).

SUMMARY AND CONCLUDING REMARKS

A large zircon age range (c. 100 Ma) in a host rock and its MME were found in the Mt Stirling Granodiorite. A step-by-step age data filtering scheme is applied to enhance zircon age data reliability:



Fig. 19. The holistic consideration of zircon, apatite, and titanite age data. (a) Filtered ages from the host rock zircon, apatite, and titanite. These data are all filtered to the last stage. Note that the calculated age 403 Ma may not represent a date of a single geologic event but a mean date from overlapping timescales of serial mineral formation, as indicated by distinct common-Pb mixing trends from apatite and titanite. (b) The filtered MME zircon, apatite, and titanite compilation, showing relatively unimodal dates. (c) Remaining age data after the filtering, from the host rock and (d) from the MME.

(1) removal of 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) exclusion of hydrothermally altered zircon by proxy Ba/Hf > 1, (5) deletion of potential hydrothermal zircons with V-shape REE patterns (Table 1), and (6) application of a 10% discordance threshold. Indeed, unfiltered age data of the host rock (399 ± 2 Ma; MSWD=9.3) and MME $(387 \pm 10 \text{ Ma; MSWD} = 26)$ show not only a wide range in ages but also large errors and MSWDs. The unfiltered MME age is also c. 10 Ma younger than the host. The filtered weighted mean age, however, is 406 ± 1 Ma (MSWD = 0.7, ~66% of spots filtered out) for the host rock and 410 ± 6 Ma (MSWD=1.7, ${\sim}80\%$ of spots filtered out) for the MME. The filtering results in smaller errors and MSWDs and indicates 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 c. 50 Ma in individual grain, which exceeds analytical reproducibility $(2 \text{ SE} = \sim 10 \text{ Ma}).$

Similar tests were carried out using apatite and titanite. For apatite, (1) major element concentration Ca and P, and (2) Zr/Y and Th/U are monitored to exclude outliers as potential microinclusions or hydrothermally altered parts. In addition, (3) Sr

should be monitored if they form distinct age groups (Table 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, (3) Sr/Ca and Zr/Ti for excluding unwanted abrupt ion exchanges, and different Sr level groups (Table 1). Applying these filters, the passed age data show smaller errors and MSWD, or enable the separation of age groups. The filtered dates from the host apatite and titanite are nearly identical to those of zircons. Common-Pb anchored apatite dates with the Stacey & Kramers (1975) model do not align with the common-Pb mixing array. Apatite data are conspicuously grouped by Sr concentration (high-, mid-, and low-Sr). The high-Sr (408 \pm 7 Ma) and the mid-Sr (408 \pm 4 Ma) dates are identical, and the low-Sr (420 \pm 6 Ma) apatites show a spuriously older date. The high- and mid-Sr apatite dates nearly correspond to that obtained from zircon (406 \pm 1 Ma). The implication is that opened system and external material input associated with different common-Pb source mixing and Pb loss can compromise Sr concentrations of calcium-rich phases such as apatite and titanite.

From a regional Lachland Fold Belt perspective, we have revised the intrusion age of the Mt Stirling pluton, based on K–Ar, by 25 Mrs towards 406 Ma based on the next combined U–Pb systematics. Considering that ages of many intrusions associated with this

Table 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 & Chappell, 1999; Chu et al., 2009)	-
4	Cryptic fluid alteration	1000*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 (distinct groups)	10000*Sr/Ca, 10000*Zr/Ti (distinct outliers compared to reference materials)

belt are based on K–Ar or Rb–Sr dates, a detailed re-evaluation of the region is advised.

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SUPPLEMENTARY DATA

Supplementary data are available at Journal of Petrology online.

CONFLICT OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY

The data in this article are available in the article and in its online supplementary material.

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