Prograde zircon growth in migmatites

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Abstract

Empirical studies of zircon in migmatites document features compatible with growth during heating at suprasolidus conditions. However, numerical modelling of zircon behaviour suggests that suprasolidus zircon is expected to grow only during cooling and melt crystallization. Here, phase equilibrium modelling coupled with mineral-melt Zr partitioning is used in an attempt to reconcile the observations from migmatites with the predictions of previous numerical models of zircon behaviour in anatectic systems. In general, an equilibrium-based model that includes Zr partitioning does not allow prograde suprasolidus zircon growth. However, melting of metapelites at temperatures just above the wet solidus may allow limited zircon growth because of the low solubility of zircon in melt coupled with a source of Zr from minor garnet and ilmenite breakdown. Preservation of this zircon requires entrapment in growing peritectic minerals during subsequent heating and further melting. Heating above muscovite exhaustion in metapelites is unlikely to grow zircon because of the progressive increase in zircon solubility as well as an increasing compatibility of Zr in the residual mineral assemblage. The modelled compatibility of Zr in the residue of a metabasite decreases during heating, but an increase in zircon solubility in melt counteracts this; prograde suprasolidus zircon growth in metabasites is unlikely. Infiltration of Zr-rich melt into a migmatite during open-system anatexis provides an additional potential mechanism for prograde suprasolidus zircon growth during high-temperature metamorphism.

KEYWORDS

anatexis, crystallization, migmatite, peritectic, zircon

1 INTRODUCTION

Zircon behaviour in suprasolidus metamorphic systems is a contentious subject. Numerical modelling predicts zircon growth only during cooling and melt crystallization (Kelsey et al., 2008; Kohn et al., 2015), whereas empirical studies infer zircon growth during prograde metamorphism in melt-bearing systems (e.g. Chen &

Zheng, 2017; Hermann & Rubatto, 2003). Understanding the discrepancy between model predictions and inferences from empirical studies is crucial for obtaining a better understanding of the mechanisms that grow, consume and recrystallize zircon during high-temperature metamorphism, and is critical for assigning geological significance to the dates and trace element concentrations obtained from them.

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Incongruent partial melting reactions generate melt and solids (i.e. peritectic minerals). The reactants are usually hydrous minerals (biotite, muscovite and hornblende) that break down to produce (mostly) anhydrous minerals (garnet, cordierite and orthopyroxene) and melt (Brown, 2013; Johnson et al., 2021; Weinberg & Hasalová, 2015). Field evidence of such reactions is common and includes a spatial relationship between peritectic ferromagnesian minerals (e.g. garnet) and leucocratic portions (dominated by feldspar and quartz) of migmatites inferred to represent the crystallized products of melt (Brown, 2013; Powell & Downes, 1990; Sawyer et al., 2011; White et al., 2004). A potential product of incongruent melting reactions is zircon in high-pressure and high-temperature metamorphic rocks (Chen et al., 2017; Chen & Zheng, 2017; Tichomirowa et al., 2018; Wang et al., 2021). However, we still have an incomplete understanding of how zirconium-an essential structural constituent of zircon-is partitioned among the various reactants and products during incongruent partial melting (e.g. Bea et al., 2006).

In this contribution, I use forward phase equilibrium modelling coupled with trace element partitioning to assess the budget of the essential structural constituents of zircon during suprasolidus metamorphism. I propose scenarios where the residual mineral assemblage and melt compositions are potentially amenable to prograde suprasolidus zircon growth and discuss which mechanisms could permit zircon growth during heating. This provides a more robust framework for interpreting the geological significance of dates retrieved from metamorphic zircon in migmatites.

2 | PARTIAL MELTING, MIGMATITES AND ZIRCON

Crustal anatexis can proceed through fluid-absent incongruent partial melting reactions, such as mica or hornblende breakdown, or through fluid-present congruent or incongruent reactions (Brown, 2013; Johnson et al., 2021; Weinberg & Hasalová, 2015). Peritectic minerals are the solid product(s) of an incongruent partial melting reaction (Johnson et al., 2021; Sawyer, 2008; Weinberg & Hasalová, 2015) and are important monitors of the prograde suprasolidus evolution of migmatites (e.g. Bartoli & Cesare, 2020).

In metasedimentary migmatites, most partial melting reactions below UHT conditions (>900°C: Kelsey & Hand, 2015) involve the breakdown of muscovite and biotite. Partial melting begins at the wet solidus if a free fluid (H_2O) is present (e.g. White et al., 2007). Above the wet solidus, heating consumes muscovite and generates anatectic melt and peritectic minerals (e.g. K-feldspar



FIGURE 1 Select simplified hydrate-breakdown partial melting reactions. Wet granite solidus from Huang and Wyllie (1973). KFMASH reactions for muscovite and biotite-breakdown melting are from Spear et al. (1999). The hornblende-out reaction is simplified from Wyllie and Wolf (1993).

and kyanite/sillimanite). At higher temperatures, biotitebreakdown melting generates garnet (at higher pressures) or cordierite (at lower pressures). For less aluminous immature clastic compositions (e.g. protoliths), orthopyroxene can also be generated at high temperatures (Johnson et al., 2008). Metabasite migmatites usuallv experience hornblende-breakdown melting (e.g. Rushmer, 1991; Wolf & Wyllie, 1994). This generates clinopyroxene as well as garnet at high pressures and orthopyroxene at lower pressures. During eclogite facies metamorphism, rutile can also be produced.

Zircon is ubiquitous in migmatites and usually contains inherited components unrelated to growth and metamorphic during anatexis, components (c.f. Rubatto, 2017) that are a direct product of growth in the presence of melt. The essential structural constituents of zircon are SiO₂ and Zr; considering that many migmatites are quartz saturated, I focus on the behaviour of Zr for the remainder of this contribution. Understanding the mechanisms that grow or consume zircon during partial melting and melt crystallization requires evaluating the changes in Zr-bearing phases (minerals and melt) in the system during metamorphism and the solubility of zircon in silicate melt. Because partial melting reactions are continuous in migmatites, the modes and compositions of different phases constantly change along a P-T path. These changes influence the Zr budget shared by residual minerals and silicate melt. Residual minerals in an

anatectic system include the reactants and the peritectic products of partial melting reactions. For the remainder of this contribution, I treat zircon separately from the other residual minerals. This simplified approach is necessary to evaluate the Zr budget of the system and the exchange of Zr between the changing reservoirs during protracted metamorphism.

3 | METHODS

Two approaches are used to explore the Zr budgets of partial melting reactions. First, I use a qualitative approach to investigate the average Zr concentrations of the reactants and products of the key fluid-absent partial melting reactions in migmatites. A second approach is a quantitative model using phase equilibrium modelling coupled to mineral-melt trace element partitioning to calculate Zr budgets of metasedimentary and metabasite migmatites. These two approaches are then used to evaluate if zircon can grow during heating and partial melting or if growth is expected during cooling and melt crystallization.

For the qualitative approach, I investigate three common fluid-absent partial melting reactions. These are shown on a simplified petrogenetic grid in Figure 1. Unbalanced and simplified incongruent melting reactions are presented below, although most reactions in metamorphic rocks are expected to be continuous (White et al., 2007). Nevertheless, these simplified reactions provide a first-order approximation of the reactants and products of the most important incongruent melting reactions in migmatites.

The first reaction is muscovite-breakdown melting and is applicable to many metasedimentary rocks. It is simplified to the following KASH reaction (Le Breton & Thompson, 1988; Spear, 1993):

 $\begin{array}{l} muscovite + quartz \rightarrow K - feldspar + kyanite/sillimanite \\ + liquid \end{array}$

(1)

At higher temperatures, most metasedimentary migmatites then experience biotite-breakdown melting. A simplified reaction in the KFMASH system is (after Le Breton & Thompson, 1988; Spear, 1993):

biotite + kyanite/sillimanite + quartz \rightarrow garnet (2) +cordierite + K - feldspar + liquid

Finally, a reaction that is applicable to metabasite anatexis is hornblende-breakdown melting through the

simplified reaction (Moyen & Stevens, 2006; Thompson, 2001):

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hornblende + quartz \rightarrow plagioclase + clinopyroxene (3) +orthopyroxene + garnet + liquid

To qualitatively evaluate which reactants and products are the main repositories of Zr in suprasolidus metamorphic systems (cf. Fraser et al., 1997), I combine the concentrations of Zr in minerals (from Bea et al., 2006) with the expected concentration of Zr in zircon saturated melt (based on the zircon solubility expression of Boehnke et al., 2013) at P-T conditions where these reactions occur and that represent a reasonable apparent thermal gradient of $\sim 1000^{\circ}$ C/GPa; these conditions are applicable to many migmatite terranes (e.g. Brown & Johnson, 2018). For muscovite-breakdown melting, this is assumed to be at 750°C and 8 kbar that is the approximate location of the KASH muscovite-breakdown univariant reaction. For biotite-breakdown melting, this is assumed to be 820°C at 8 kbar, which is just below terminal biotite stability for an average metapelite (Yakymchuk & Brown, 2014a). And for hornblendebreakdown melting, this is assumed to be 850°C at 8 kbar where orthopyroxene becomes stable for an average midocean ridge basalt (MORB) composition (Palin et al., 2016). The composition of the melt at these conditions is calculated using the relevant pseudosections and trace element models (see below for details); in general, the concentrations of Zr in melt saturated with respect to zircon are expected to be in the hundreds of µg/g (Boehnke et al., 2013; Watson & Harrison, 1983).

Reactions 1–3 are simplified and do not consider the continuous nature of partial melting reactions in natural systems (e.g. Johnson et al., 2021; White et al., 2007; Yakymchuk, 2017). Continuous reactions can be explored with phase equilibrium modelling in more complex chemical systems that are a closer approximation of the behaviour of natural rocks (e.g. White et al., 2011). Therefore, I evaluate Zr budgets and implications for zircon behaviour using phase equilibrium modelling of an average amphibolite-facies metapelite (from Ague, 1991) and an average MORB (from Sun & McDonough, 1989). These two compositions bracket the most investigated rock types in studies of migmatites and anatexis.

Phase assemblages predicted from equilibrium modelling can be combined with mass balance calculations of Zr to explore the growth and consumption of zircon during high-temperature metamorphism. Kohn et al. (2015) applied this approach using average concentrations of Zr in the various reactant and product minerals and a temperature-dependent expression for Zr concentrations

in garnet and hornblende. I build on their approach by considering changing Zr concentrations in all phases in the system based on equilibrium trace element partitioning (e.g. Hanson, 1980); this approach is commonly applied to igneous systems, but it can also be applied to suprasolidus metamorphic systems (Bea et al., 2021; Janoušek et al., 2016 ; Johnson et al., 2017; Johnson et al., 2021; Kendrick & Yakymchuk, 2020). Therefore, the modelled concentrations of Zr in all residual minerals (except zircon) vary with pressure and temperature.

Here, I combine mass balance and trace element partitioning expressions (e.g. Hanson, 1980) with the results of phase equilibrium modelling of an average metapelite and MORB to quantify the Zr budget of anatectic systems and explore the consequences for zircon growth. Phase equilibrium modelling is conducted using THERMOCALC v.3.40 (Powell & Holland, 1988) with the internally consistent dataset (ds62) of Holland and Powell (2011). Phase assemblages, proportions, and compositions are extracted from the THERMOCALC output for the metapelite and MORB across a grid with 25°C and 0.5 kbar spacing. Data are contoured with linear extrapolation between points using the MATLAB[®] software package. Minor artefacts in the contouring (e.g. jogs) are caused by narrow lowvariance fields in the phase diagrams that are smaller than the extracted data grid, but these artefacts do not affect the first-order results or interpretations. Molar phase proportions are converted to weight fractions for use with partitioning expressions based on one-element normalized modes in the THERMOCALC output. The content of H₂O for each composition was constrained such that the melt is just saturated with H₂O at the wet solidus at 8 kbar. This is a reasonable starting point that assumes no free H₂O in the system at the initiation of melting (e.g. White et al., 2007). A higher content of H₂O will result in more melt production at a given temperature and lower H₂O content will result in less.

For the metapelite, modelling is conducted in the MnO-Na₂O-CaO-K₂O-FeO-MgO-Al₂O₃-SiO₂-H₂O-TiO₂ -Fe₂O₃ (MnNCKFMASHTO) chemical system and appropriate solid-solution models (White, Powell, Holland, et al., 2014; White, Powell, & Johnson, 2014), including feldspar (Holland & Powell, 2003), spinel-magnetite (White et al., 2002) and ilmenite-hematite (White et al., 2000). For the MORB, modelling is conducted in the NCKFMASHTO chemical system using the activitycomposition models from Green et al. (2016), which include orthopyroxene, ilmenite, biotite, muscovite and garnet from White, Powell, Holland et al. (2014), White, Powell, and Johnson (2014); feldspar from Holland and Powell (2003); spinel from White et al. (2002); epidote from Holland and Powell (2011); and amphibole (hornblende) and clinopyroxene (augite) from Green et al. (2016).

Zirconium concentrations in melt and minerals are calculated using mass balance and mineral/melt distribution coefficients (Hanson, 1980). An explanation of this approach applied to migmatites is found in Johnson et al. (2021), and the detailed methodology applied in this study is found in the supporting information. Mineralmelt distribution coefficients for Zr are from Bédard (2006) that are parametrized for metabasite melting. The limitation of this approach applied to metapelites is discussed later. Specific distribution coefficients are found in the supporting information. I assume closed-system behaviour for simplicity, although open-system processes can affect the concentration of trace elements in natural systems (e.g. Huang et al., 2020; Kendrick & Yakymchuk, 2020; Schwindinger et al., 2020) and these processes are discussed later. Zircon solubility is modelled using the expression of Boehnke et al. (2013) and a stoichiometric concentration of Zr in zircon (497,664 µg/ g; Kelsev et al., 2008). When the calculated equilibrium concentration of Zr is higher than the saturation concentration of Boehnke et al. (2013) at a P-T point, the excess amount of Zr is used to calculate the zircon mode in the system (see supporting information).

RESULTS 4

4.1 | Univariant reactions and Zr budgets

A comparison of the average concentrations of Zr in reactants and products of the key partial melting reactions for metapelites and metabasites is shown in Figure 2. For muscovite-breakdown melting, K-feldspar and liquid have 1-2 orders of magnitude more Zr than the reactants (muscovite and quartz; Figure 2). However, kyanite or sillimanite are products with negligible amounts of Zr. In general, most products of muscovite-breakdown melting are expected to contain higher concentrations of Zr than the reactants (Figure 2).

Biotite-breakdown melting at low pressures is expected to generate cordierite, which will contain very low concentrations of Zr (Figure 2). This reaction also produces K-feldspar and liquid, which are both expected to contain much higher concentrations of Zr than the reactants (Figure 2). Biotite-breakdown melting at high pressures will generate garnet (Figure 2), which contains an order of magnitude higher concentration of Zr than reactant biotite (Figure 2). Most products of biotitebreakdown melting contain higher concentrations of Zr than the reactants.

Hornblende-breakdown melting is common in metabasites and less aluminous clastic metasedimentary **FIGURE 2** Average concentrations and standard deviations of Zr in silicate minerals from Bea et al. (2006) plotted as reactants of products of important hydrate-breakdown melting reactions. Metapelite-related data are from the 'migmatite' compilation of Bea et al. (2006), and the metabasite reaction uses the 'mafic granulite' values. Also plotted are calculated concentrations of Zr in melt that is just saturated with respect to zircon using the solubility expression of Boehnke et al. (2013) and the melt compositions from the modelling. Mineral abbreviations are from Holland and Powell (2011). [Colour figure can be viewed at wileyonlinelibrary.com]



rocks. This reaction generates garnet at high pressures and orthopyroxene at low pressures (Figure 2). Clinopyroxene is a common product of both high- and lowpressure melting. Hornblende can contain relatively high concentrations of Zr compared with the products (orthopyroxene and garnet) of the melting reaction. Liquid and clinopyroxene are expected to contain higher concentrations of Zr than the reactants (hornblende + quartz).

In summary, the products of the common hydratebreakdown melting reactions generally contain higher concentrations of Zr than the reactants. Consequently, the amount of Zr available to grow zircon will be less as the reactions progress during heating. However, these reactions are simplified and do not consider the proportions of the reactants and products nor the continuous nature of natural partial melting reactions. Assessing these requires a more quantitative model of Zr partitioning in the metamorphic system and is explored next.

4.2 | Phase equilibrium modelling

The budgets of Zr between phases in an equilibrated system depend on the distribution coefficients between minerals and melt as well as the proportions of the various phases in the system. The modelled stability fields of various phase assemblages are shown for the metapelite in Figure 3a and the MORB in Figure 3c. Suprasolidus phase assemblages in the metapelite can be divided into four P-T windows: muscovite-present, muscovite-absent and biotite-present, biotite-absent, and cordierite-present

(Figure 3b). The phase assemblages for the MORB can be generally divided into titanite-present, titanite-absent, garnet-present and orthopyroxene-present mineral assemblage fields (Figure 3d). Liquid proportions increase with temperature for both rock types (Figure 4a, d). For the metapelite, relatively Zr-rich peritectic minerals are garnet and ilmenite (Figure 2). Garnet and ilmenite are stable across most of the modelled P-T range (Figure 3a). Garnet proportions increase with temperature above the solidus and decrease at UHT conditions (>900°C; Figure 4b). Ilmenite proportions increase up temperature even at UHT conditions (Figure 4c). For the MORB, the main Zrrich peritectic minerals generated during hornblendebreakdown melting include garnet and clinopyroxene at moderate to high pressures. Clinopyroxene (augite) is stable across the modelled P-T range except at low pressures and temperatures just above the solidus (Figure 3c). The proportion of clinopyroxene increases with temperature (Figure 4e), and garnet is only present at high pressures (Figure 3c). The predicted mode of orthopyroxene increases with temperature at low pressures and high temperatures (Figure 4f). Titanite is another relatively Zr-rich mineral in the system and is predicted to be part of the residual assemblage up to \sim 720–800°C (Figure 3c,d).

The equilibrium concentration of Zr in zirconsaturated anatectic melt changes with variations in temperature and melt composition (e.g. Boehnke et al., 2013; Watson & Harrison, 1983). Boehnke et al. (2013) used the M parameter (a proxy for melt depolymerization) to derive a numerical expression for zircon solubility. In general, Zr saturation (with respect to zircon) requires





FIGURE 3 (a) Pressure-temperature pseudosection for an average metapelite (modified from Yakymchuk et al., 2017). (b) Simplified pressure-temperature diagram showing the stability of key minerals for melting of a metapelite (simplified from Yakymchuk, 2021). (c) Pressure-temperature pseudosection for an average MORB compositions (modified from Palin et al., 2016 and Yakymchuk et al., 2017). (d) Simplified pressure-temperature diagram showing the stability of key minerals for melting of an average mid-ocean ridge basalt (modified from Yakymchuk, 2021). MORB, mid-ocean ridge basalt. [Colour figure can be viewed at wileyonlinelibrary.com]

higher concentrations at higher M values. The M value of the melt for the metapelite decreases with increasing temperature, except at very low pressure (Figure 5a). For the metabasite, the M value does not substantially change until orthopyroxene joins the assemblage high temperature (e.g. 850°C at 8 kbar), after which it increases (Figure 5c). However, zircon solubility is also strongly influenced by temperature. The calculated zircon saturation concentration—using the formulation of Boehnke et al. (2013)—increases for both the metapelite and MORB with increasing temperature. For the metapelite, the concentration of Zr in zircon-saturated melt varies from ~100 µg/g at the wet solidus to >500 µg/g at UHT conditions (Figure 5b). For the MORB, which has higher melt M values than the metapelite at a given *P*–*T* condition (Figure 5a,c), the zircon saturation concentrations of Zr range from ~70 µg/g at the wet solidus to >800 µg/g at UHT conditions (Figure 5d). The saturation concentration of Zr in anatectic melt increases during prograde metamorphism.



FIGURE 4 Weight proportions of melt and important peritectic minerals for Zr budgets. For the metapelite, this includes (a) liquid, (b) garnet and (c) ilmenite. For the MORB composition, this includes (d) melt, (e) clinopyroxene and (f) orthopyroxene. MORB, mid-ocean ridge basalt. [Colour figure can be viewed at wileyonlinelibrary.com]

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FIGURE 5 Properties of silicate melt relevant to zircon behaviour. (a) *M* value (e.g. Watson & Harrison, 1983) for a metapelite. (b) Calculated concentration of Zr in melt that is just saturated with respect to zircon for the metapelite (using the zircon solubility expression of Boehnke et al. 2013). (c) *M* value for the mid-ocean ridge basalt composition. (d) Zr saturation for melt for the mid-ocean ridge basalt composition. MORB, mid-ocean ridge basalt. [Colour figure can be viewed at wileyonlinelibrary.com]

A monitor of the equilibrium behaviour of Zr between melt and all the residual minerals in the system is the bulk distribution coefficient of Zr, which is a function of the mineral-melt distribution coefficients and the weight fraction of minerals in the residue. For the metapelite, the bulk distribution coefficient of Zr (D_{Zr} ; see supporting information) slightly increases from the wet solidus to the muscovite-out phase boundary and increases from ~0.15 at 750°C to ~0.5 at 950°C at 8 kbar (Figure 6a). D_{Zr} increases at higher temperatures (Figure 6a). This suggests that the residual assemblage—increasingly dominated by the peritectic minerals generated during incongruent melting—becomes more compatible for Zr as heating and partial melting progress.

The MORB shows a different pattern. The bulk distribution coefficient for Zr decreases with increasing temperature (Figure 6b). For example, at 8 kbar, it decreases from ~0.45 at the wet solidus to <0.25 at 1000°C (Figure 6b). This indicates that Zr becomes more incompatible in the residual mineral assemblage with an increase in temperature.

The calculated budget of Zr between residual minerals (except zircon) and melt is shown in Figure 7 for the metapelite for two scenarios: isobaric heating at 6 kbar and 10 kbar. During heating, the relatively Zrpoor minerals (quartz, muscovite, plagioclase and biotite) are consumed and relatively Zr-rich minerals (e.g. garnet and ilmenite) are generated as peritectic products of



FIGURE 6 Bulk distribution coefficients for Zr between the residual mineral assemblage (excluding zircon) and silicate melt. (a) Metapelite: Zr becomes slightly less compatible in the residue with increasing temperature from the wet solidus to the muscoviteout field boundary and then becomes more compatible up temperature. (b) Mid-ocean ridge basalt: Zr becomes less compatible in the residue with increasing temperature. MORB, mid-ocean ridge basalt. [Colour figure can be viewed at wileyonlinelibrary.com]

partial melting reactions (Figure 7a,b). The amount of Zr hosted by melt increases with temperature (Figure 7c,d), and the majority of the Zr budget in the residue is contained in garnet and ilmenite (Figure 7e,f).

The Zr budget for the MORB along the same two isobaric heating paths is shown in Figure 8. During heating, relatively Zr-rich hornblende is consumed to generate relatively Zr-poor peritectic clinopyroxene and orthopyroxene at moderate pressures (Figure 8a), and produce clinopyroxene and relatively Zr-rich garnet at higher pressures (Figure 8b). Similar to the metapelite, the proportion of Zr in the melt for the MORB is expected to increase with temperature (Figure 8c,d). In contrast to the metapelite, the main reactant during partial melting (hornblende) of the MORB contains the majority of the Zr budget in the residue even at very high temperatures (Figure 8e,f). Ilmenite and rutile are also modest repositories of Zr in the MORB residue at high temperatures (Figure 8e,f).

In summary, the compatibility of Zr in the evolving residual assemblage changes during prograde metamorphism. For the metapelite, the residual assemblage becomes slightly less compatible for Zr prior to muscovite exhaustion, which could liberate Zr into the melt. This may be amenable for suprasolidus zircon growth during heating because of the increasing preference for Zr to partition from the residual mineral assemblage to the melt. After muscovite exhaustion, the residue becomes more compatible for Zr because of the increased proportion of the relatively Zr-rich peritectic products of continuous incongruent melting reactions during heating. This is not amenable for zircon growth during heating as the stable peritectic minerals become increasingly larger repositories for Zr. For the MORB, the residual assemblage becomes less compatible for Zr during heating. The Zr budget of the residue is dominated by hornblende, which is a reactant in partial melting reactions. The progressive breakdown of relatively Zr-rich reactant hornblende-and growth of relatively Zr-poor peritectic products-may represent a source of Zr for zircon growth during prograde metamorphism above the solidus. However, this may be counteracted by the temperature-dependent solubility of Zr in silicate melt during heating, which incorporates more Zr during heating.

5 | DISCUSSION

5.1 | Limitations of modelling

Several limitations of the phase equilibrium and trace element modelling applied here can influence interpretations in natural rocks. These include modelling in a zircon-absent system (i.e. exploring the evolving residual assemblage without considering zircon as a repository of Zr), using distribution coefficients to model Zr distributions between residue and melt, assuming closed-system



FIGURE 7 Phase assemblages and zirconium budgets during isobaric heating for the metapelite. Weight fractions of phases in the system during isobaric heating at (a) 6 kbar and at (b) 10 kbar. Zirconium budget (by mass) of the system (excluding zircon) during isobaric heating at (c) 6 kbar and at (d) 10 kbar. Most zirconium is hosted by the melt at high temperatures. Zirconium budget of the residue (excluding zircon) for isobaric heating at (e) 6 kbar and (f) 10 kbar. The majority of Zr in the residue is hosted by garnet and ilmenite. Mineral abbreviations are from Holland and Powell (2011). [Colour figure can be viewed at wileyonlinelibrary.com]

behaviour, and presuming whole-rock equilibrium in trace elements (cf. Kelsey & Powell, 2011).

The modelling presented here assumes that zircon is a passive mineral that does not directly control the Zr budget of the system but responds to changes in the Zr budget shared between the other minerals and melt. In natural systems, zircon is expected to be the dominant host of Zr in migmatites (e.g. Bea et al., 2006). Integrating zircon proportions into mineral-melt partitioning models requires the assumption that zircon partitions Zr as a trace element; this is not a valid assumption because Zr is an essential structural constituent in zircon (not a trace element) and substitution would not follow Henry's law. Consequently, the models show how Zr is expected to partition between the other minerals and melt in the system, and this represents a foundation for understanding how changing repositories of Zr can influence zircon growth and breakdown. This is an end-member scenario. A more realistic model would integrate zircon (and Zr)

into formal thermodynamic models that include the mechanisms of Zr substitution into these minerals and melt, as well as using appropriate activity-composition models (e.g. Kelsey & Powell, 2011). However, this approach is limited by the uncertainties in existing activity-composition models and the scarcity of experimental data for other Zr-bearing minerals that underpin the thermodynamic properties of Zr end-members. Therefore, the results of this study provide a first-order framework of how Zr budgets vary during partial melting between the other minerals and melt, and the behaviour of zircon can be inferred.

Mineral-melt distribution coefficients of Zr can vary with rock type and P-T conditions. Although Zr partitioning was parametrized for melting of metabasites (e.g. Bédard, 2006), there is currently no equivalent for metapelitic rocks. In general, the distribution coefficients of Zr are not expected to vary drastically for the same mineral even in a variety of rock types. For example, Zr



FIGURE 8 Phase assemblages and Zr budgets during isobaric heating for the mid-ocean ridge basalt. Weight fractions of phases in the system during isobaric heating at (a) 6 kbar and at (b) 10 kbar. Zirconium budget (by mass) of the system (excluding zircon) during isobaric heating at (c) 6 kbar and at (d) 10 kbar. Most zirconium is hosted by the hornblende and melt at high temperatures. Zirconium budget of the residue (excluding zircon) for isobaric heating at (e) 6 kbar and (f) 10 kbar. The majority of Zr in the residue is hosted by hornblende. Mineral abbreviations are from Holland and Powell (2011). [Colour figure can be viewed at wileyonlinelibrary.com]

is slightly incompatible in garnet in peridotite (Kd \sim 0.6; Kato et al., 1988), basalt (Kd \sim 0.4–0.7; Jenner et al., 1993), tonalite (Kd \sim 0.36; Jenner et al., 1993), and rhyolite (Kd \sim 0.4; Sisson & Bacon, 1992). Furthermore, similar partitioning of Zr between garnet and melt is supported by similar concentrations of Zr in garnet in various rock types (Bea et al., 2006). Although the variability of Zr mineral-melt distribution coefficients in garnet and other minerals is a limitation of this modelling, it is not expected to change the general results or interpretations.

Many migmatites are expected to experience melt loss (or melt gain) during their suprasolidus histories, and open-system behaviour can affect phase assemblages, modes compositions and during anatexis (e.g. Schwindinger et al., 2020; White et al., 2007: Yakymchuk & Brown, 2014a). Melt loss can influence the behaviour of the accessory minerals because of the depletion (or enrichment) of the system in their essential structural constituents. For example, extraction of melt with a

lower concentration of a trace element (e.g. Zr) than that of the bulk system will increase the concentration of this trace element in the residue (e.g. Rapp et al., 1987); this will extend the stability of the accessory mineral for which this element is an essential structural constituent higher temperatures (e.g. Yakymchuk to & Brown, 2014b). Extraction of relatively enriched melt will have the opposite effect and decrease the stability of this accessory mineral. For the models presented here, melt within \sim 50°C of the wet solidus has low concentrations of Zr (Figure 5b). Extraction of this melt could increase the effective bulk Zr composition of the system (e.g. Yakymchuk & Brown, 2014b) and increase zircon stability to higher temperatures. Kinetic hindrance to zircon dissolution (e.g. Harrison & Watson, 1983) could also lead to extraction of melt that is undersaturated in Zr, which would lead to slightly increased stability of zircon to higher temperatures. However, this is not expected to drive zircon growth but only extend the stability of existing zircon to higher temperatures.

Injection of externally derived melt and equilibration with the system could increase or decrease the stability of zircon depending on the concentration of Zr in the system. For example, if melt is extracted from the same protolith, but deeper in the crust, this melt can ascend upwards through the anatectic zone and interact with shallower rocks. For the same protolith, the concentration of Zr in the injected melt could be higher considering that zircon solubility increases with temperature (and depth along a reasonable geothermal gradient). The injection of this relatively Zr-rich melt-coupled with the decreases in temperature during ascent-could lead to melt that becomes oversaturated with respect to zircon during ascent and allow suprasolidus zircon growth during prograde, peak and retrograde parts of a P-T evolution. A similar model was proposed for monazite where the ascent of light rare earth element (LREE)-rich melt becomes oversaturated with respect to monazite and results in the growth of new monazite rims over resorbed cores (e.g. Yakymchuk & Brown, 2019). An analogous mechanism could result in suprasolidus zircon growth if the ascending melt becomes oversaturated with respect to zircon during ascent through the anatectic zone. However, injection of melt with lower concentrations of Zr would have the opposite effect and could trigger zircon dissolution. Melt with relatively low concentrations of Zr could be generated because of kinetic hindrances to zircon dissolution in the source (Ayres et al., 1997; Harrison & Watson, 1983), sequestration of Zr in the residue (Schwindinger et al., 2020) or derivation from a Zrpoor source. Nevertheless, open-system processes could potentially allow zircon growth at any point along the suprasolidus P-T evolution of migmatites. One caveat of open-system behaviour is that the trace element composition of externally derived melt from which the zircon crystallizes may not reflect the rock where the zircon is ultimately found. This complicates interpretations of trace element concentrations in zircon that are the product of open-system behaviour in the anatectic zone.

A final limitation of the modelling is the assumption of equilibration of major and trace elements between all phases in the system. Other contributions explore the limitations and uncertainties when applying an equilibrium approach to the major phases (e.g. Palin et al., 2016; Spear & Pattison, 2017). Here, I focus on Zr, which is a trace element in most phases in migmatites. A main hindrance to whole-rock equilibration of Zr is that it has a relatively slow diffusivity in the major minerals such as garnet and pyroxene (e.g. Griffin et al., 1989). Relatively slow diffusivity of Zr in silicate minerals is also indicated by empirical studies that document the preservation of Zr zoning in garnet (George et al., 2018; Raimondo et al., 2017; Rubatto et al., 2020). Furthermore, Zr

diffusivity in silicate melt may be slower than that of the major elements (Mungall et al., 1999), which may also hinder residue-melt equilibration of Zr. In natural rocks at suprasolidus conditions, this may result in locally undersaturated and oversaturated (with respect to zircon) volumes of melt in a migmatite that cannot be sufficiently modelled with an equilibrium approach or may require the consideration of domanial equilibration (e.g. Lanari & Engi, 2017). These local domains may be amenable to zircon crystallization from melt if a different Zr-rich mineral repository breaks down.

Terminology: Peritectic, anatectic 5.2 or metamorphic zircon?

There are many terms in the literature for zircon associated with high-temperature metamorphism and anatexis that can lead to confusion and ambiguous interpretations. Misuse of these terms can obfuscate what part of a P-T evolution (and associated tectonic process) is related to a date retrieved from zircon. Here I attempt to define these terms and describe the specific context in which they are best used for zircon in migmatites before discussing the evidence for and potential mechanisms of prograde zircon growth.

The term *metamorphic zircon* is a general term for the new growth of zircon where there is a physical boundary between this zircon and any relict cores (cf. Rubatto, 2017) or where the entire zircon grew during metamorphic (not igneous) processes. However, there will always be some overlap of igneous and metamorphic processes in migmatites especially because of open-system processes in the anatectic zone. The term metamorphic zircon does not specify where along a P-T path the zircon grew or by what mechanism it grew; therefore, this term is particularly useful when this information is unknown or is not relevant to the specific goal of the study.

The term anatectic zircon has been used as a synonym for metamorphic zircon, but only when zircon is related to melting. In some cases, anatectic zircon was used to describe zircon that grew during cooling and melt crystallization (Chen & Zheng, 2017), and in others, it describes zircon that was interpreted to have grown during heating (e.g. Liu et al., 2012). Anatexis is the process or action of transforming a substance into a liquid plus residual solids usually, but not exclusively, by adding heat (Johnson et al., 2021). In principle, zircon can crystallize from melt during heating and prograde metamorphism or cooling during retrograde metamorphism if Zr saturation (with respect to zircon) of the melt is reached or maintained. A problem with the term anatectic zircon is that partial melting (anatexis) occurs during heating (not cooling),

and applying this term to zircon that grew during cooling and melt crystallization is misleading. Although this term should only be used to describe zircon that grows during heating above the solidus, it does not specify the specific mechanism of zircon growth and is useful when this is unclear. I recommend that the term *anatectic zircon* be used only for zircon that can be demonstrated to be generated during prograde partial melting and not during melt crystallization. A caveat is that many migmatites are open systems at suprasolidus conditions (e.g. Schwindinger & Weinberg, 2017); zircon that crystallized from melt produced in situ may be difficult to distinguish from zircon that crystallized from injected melt.

A final term that has been applied to zircon generated during heating and partial melting is peritectic zircon. Peritectic zircon requires that it is the product of incongruent melting reactions just like major minerals (Johnson et al., 2021). However, the reactions that produce such zircon are not reported (e.g. Chen & Zheng, 2017; He et al., 2022). Ostwald ripening (Kawakami et al., 2013; Kohn & Kelly, 2018; Nemchin et al., 2001; Vavra et al., 1999) is an alternative mechanism of suprasolidus zircon growth that does not require incongruent melting. Direct crystallization of minerals (e.g. liquidus phases) from melt in migmatites also plays a key role in the petrogenesis of migmatites (e.g. Sawyer, 2008) and can equally be applied to zircon growth from Zr-oversaturated melt (during heating or cooling). Oversaturation could result from the crystallization of Zr-poor minerals from melt (especially during cooling) or the injection of Zr-rich melt sourced from elsewhere. These alternative mechanisms should be ruled out before interpreting a zircon as peritectic in origin. Trace element concentrations have been used to differentiate peritectic zircon from anatectic zircon (He et al., 2022), but the difference in dates and trace element characteristics can be a product of protracted crystallization in a system with changing mineral assemblages (Johnson et al., 2021). Even in the case where zircon with inclusions of nanogranites is hosted by peritectic garnet (e.g. Cesare et al., 2009), zircon growth may have been the result of a peritectic reaction or direct crystallization from melt. Therefore, the term peritectic zircon should not be used unless the specific reaction (and source of Zr) responsible for zircon growth can be elucidated. Fraser et al. (1997) demonstrated how the breakdown of Zr-rich garnet can yield zircon through net-transfer reactions in granulite-facies gneisses from East Antarctica. Degeling et al. (2001) provided a detailed mass balance calculation to show that garnet breakdown triggered concomitant zircon and cordierite growth in metasedimentary rocks from the Sveconorwegian Province. Although the reactions proposed in these studies did not include anatectic

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melt, the same approach should be applied to meltproducing reactions before concluding that zircon is peritectic and not a product of crystallization directly from melt or generated from Ostwald ripening. Zirconium isotope analyses show some promise for understanding zircon nucleation and growth in igneous and anatectic systems (Méheut et al., 2021) and may help understand the reactions that generate peritectic zircon in suprasolidus metamorphic rocks.

5.3 | Evidence of prograde zircon growth in anatectic systems

Previous numerical modelling studies predict that zircon is not expected to grow during heating and only during cooling in suprasolidus metamorphic systems (Kelsey et al., 2008; Kohn et al., 2015; Wang et al., 2014; Yakymchuk & Brown, 2014b). However, empirical studies of some migmatites demonstrate that zircon has trace element signatures and inclusion assemblages compatible growth during heating and melting (see with Rubatto, 2017). Evidence used to support prograde suprasolidus zircon growth includes trace element compositions of zircon domains, Ti-in-zircon temperatures, zircon dates and inclusions assemblages. The strengths and limitations of these approaches for inferring the conditions and mechanisms of zircon growth are discussed below. However, I emphasize that the careful integration of data from these various techniques can provide robust and useful information on the mechanisms of zircon growth in migmatites.

Trace element compositions of zircon can be used to infer growth in the presence of P-T-sensitive metamorphic minerals (e.g. Gordon et al., 2013; Hermann & Rubatto, 2003; Rubatto, 2002; Rubatto et al., 2001; Taylor et al., 2016, 2017), which can then be related to portions of a P-T evolution. For example, ratios of Gd/Yb are commonly used to infer if zircon was in equilibrium with garnet given that garnet strongly concentrates the heavy rare earth elements (Hermann & Rubatto, 2003; Taylor et al., 2015). This is a powerful tool and a core tenet of zircon petrochronology (Kohn & Kelly, 2018; Rubatto, 2017). Applying these ratios to understand where along a P-T evolution zircon crystallized relies on understanding suprasolidus garnet behaviour, which will vary for different bulk compositions (e.g. Johnson et al., 2017), whether melting is open or closed system (e.g. Yakymchuk & Brown, 2014a), and if garnet fractionation of trace elements occurs (e.g. Kendrick & Yakymchuk, 2020). With this in mind, garnet can be present during heating and cooling in suprasolidus systems (Figure 4b). Therefore, evidence of zircon growth in

equilibrium with garnet is not diagnostic of prograde or retrograde metamorphism but tracking proxies for garnet modes (e.g. Gd/Yb ratios) with dates, or Ti-in-zircon temperatures, or both can strengthen such interpretations.

Ratios of Gd/Yb in zircon in equilibrium with the residual mineral assemblage are expected to vary with pressure and temperature (Johnson et al., 2021). This ratio in zircon is mostly controlled by garnet modes; increases in garnet mode result in progressively higher Gd/Yb ratios in zircon, and decreasing proportions of garnet result in lower Gd/Yb ratios (see Figure 25 of Johnson et al., 2021). Garnet mode generally increases with temperature, but garnet can also be consumed during heating and cordierite growth at low pressures in metapelites (e.g. Pereira & Bea, 1994). Garnet modes may reach a maximum at peak metamorphic conditions, but melt loss can result in a residual assemblage that has no appreciable change in garnet mode during cooling because of an elevated solidus temperature (White & Powell, 2002). Consequently, elevated Gd/Yb ratios in zircon-commonly interpreted to record growth in the presence of garnet—can be encountered during heating, the metamorphic peak, or cooling. For P-T loops where garnet is present during prograde and retrograde segments, the Gd/Yb ratios alone may not be diagnostic of heating or cooling. An understanding of the continuous reactions that grow and consume garnet for individual samples is necessary to relate zircon Gd/Yb ratios to a particular portion of a *P*–*T* path. Unresolved microdomainal controls on heavy rare earth element (HREE) behaviour may also complicate geological interpretations (e.g. Tual et al., 2022).

Other trace element ratios in zircon have also been used to infer the conditions of metamorphic zircon growth, such as Th/U (e.g. He et al., 2022; Vavra et al., 1999). However, Th/U ratios can also be problematic because the low ratios commonly inferred to represent metamorphic zircon growth (e.g. Hoskin & Schaltegger, 2003) can occur during heating and cooling (Yakymchuk et al., 2018). Trace element systematics are also challenging to interpret if migmatites experience open-system behaviour-a very common scenario in anatectic systems (e.g. Weinberg et al., 2021)-with the injection of externally derived melt that may have a source with a different composition or residual mineral assemblage than the sampled rock. Although trace element concentrations are not diagnostic of zircon growth during heating or cooling and complicated by opensystem processes in suprasolidus rocks, they can be used with other information to develop a holistic understanding of the conditions of zircon growth and the geological significance of dates retrieved from metamorphic zircon.

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Titanium-in-zircon thermometry is also used to infer where along a suprasolidus P-T evolution zircon crystallized (e.g. Chen & Zheng, 2017). A temperature estimate alone cannot differentiate if the zircon was generated during heating or cooling. In addition, this thermometer relies on three key assumptions: first that the activity of titania (a_{TiO2}) with respect to rutile is known (e.g. Ferry & Watson, 2007); second, there are no chemical potential gradients in Ti throughout the system during zircon growth (i.e. equilibrium); and third, that Ti substitutes into zircon as a trace element whose concentration is linearly proportional to its activity (i.e. follows Henry's law). Most migmatites do not contain rutile that can be shown to be in equilibrium with zircon during growth, although there are exceptions (e.g. Gervais & Crowley, 2017; Storm & Spear, 2009). Most studies that utilize Ti-in-zircon thermometry assume a fixed activity of titania in the system during zircon growth, and this variable is poorly constrained in most natural samples (Fu et al., 2008; Kelsey & Hand, 2015; Schiller & Finger, 2019). The activity of titania is usually buffered by the oxide mineral assemblage (e.g. Ashley & Law, 2015), but it can also vary with the silicate mineral assemblage (Essene, 2009; Kirkland et al., 2021; Yakymchuk et al., 2017, 2019), and these assemblages will change along a P-T evolution (Guevara & Caddick, 2016) leading to variable titania activities during protracted metamorphism. The presence of complex microstructures in migmatites (e.g. symplectites and selvedges) suggests the preservation of chemical potential gradients of H₂O, K₂O and Na₂O in migmatites (White et al., 2008). If chemical potential gradients of these relatively mobile species can be preserved, then it is probable that local gradients of less mobile TiO₂ were also present during metamorphism. Consequently, there may not be a fixed titania activity because of progressive changes in the mineral assemblage as well as the development of chemical potential gradients in TiO2. This makes the application of Ti-in-zircon thermometry hard to justify in rutile-absent migmatites. Titanium substitution into zircon may also not follow Henry's law (Hofmann et al., 2009), complicating thermometry applications because Ti may not behave like a trace element in zircon. Therefore, Ti-in-zircon thermometry should be used with caution considering the poorly constrained variations in titania activity in space (e.g. in various microstructures) and time (e.g. during a protracted P-T evolution) as well as uncertainties around Ti substitution mechanisms into zircon.

U–Pb geochronology is used to retrieve the isotopic ratios (and dates) from zircon that can be related to a metamorphic evolution and link zircon domains to specific segments of P-T path (e.g. Hermann &

Rubatto, 2003). Dates retrieved from zircon U-Pb geochronology become increasingly precise with the development of new and refined analytical approaches (Schoene, 2014). Except for rocks that experience prolonged UHT metamorphism (Kelsey & Hand, 2015; Kohn & Kelly, 2018), concordant U-Pb dates retrieved from zircon in metamorphic rocks are generally considered robust. Although nanoscale clumping of Pb in hightemperature zircon can affect the dates retrieved from analyses with high spatial resolution, this is not expected to be a major factor for routine analytical approaches (Whitehouse et al., 2014), but it will become an issue as the spatial resolution of in situ microbeam techniques improves. Current debate focusses on whether ranges of U-Pb dates obtained from high-temperature metamorphic rocks record continuous growth over a protracted P-T evolution or record discrete events that were then affected by Pb mobility resulting in an array of dates (e.g. Kohn & Kelly, 2018). These scenarios can be difficult to discern from each other as the analytical uncertainty of individual analyses may overlap concordia even if Pb mobility was a contributing factor. A discrete age scenario can be supported by also investigating the populations of trace element concentrations or stable isotope ratios of different microdomains in zircon (Hermann & Rubatto, 2003; Rubatto et al., 2009). However, a complication in linking dates and trace element concentrations from zircon in some migmatites is that the dates, zoning and trace element characteristics can be decoupled from each other (Flowers et al., 2010; Kunz et al., 2018; Pitra et al., 2022). This potential decoupling of U-Pb dates from trace element characteristics suggests that even split-stream analysis of U-Pb dates and trace element concentrations of zircon could vield incorrect interpretations.

The most robust indicator of zircon growth from silicate melt is the presence of melt (glass) inclusions or polycrystalline aggregates of former melt (nanogranites). Although rare, zircon can preserve polymineralic inclusions interpreted as the crystallized remnants of melt trapped at the zircon-melt interface during zircon growth (e.g. Bartoli et al., 2016; Bartoli & Cesare, 2020; Pertsev et al., 2021). Nanogranite inclusions in zircon have been documented in metapelites (Cesare et al., 2009; Harley & Nandakumar, 2014; Kawakami et al., 2013; Liu et al., 2020) and in intermediate to basic migmatites (e.g. Chen et al., 2015; DesOrmeau et al., 2018). In principle, melt can be trapped in growing zircon during heating and partial melting or cooling and melt crystallization. Cesare et al. (2009) documented melt inclusions at the interface between an inherited zircon core and an overgrowth in zircon; this grain is hosted by peritectic garnet that itself has nanogranite inclusions. This provides

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unambiguous evidence that zircon grew during prograde partial melting and not during melt crystallization. Other studies have documented nanogranites in zircon that was inferred to have grown from anatectic melt (e.g. Chen et al., 2015), but this zircon could have grown during cooling and melt crystallization or during heating and melt generation. For example, Harley and Nandakumar (2014) interpret polycrystalline inclusions in zircon to record melt trapped during cooling and melt crystallization after peak temperature. Although interpretations of where along a P-T path suprasolidus zircon grew can vary, nanogranites preserved in zircon provide unambiguous evidence of growth in the presence of melt and inclusions of these zircon in peritectic minerals, such as garnet (Cesare et al., 2009), demonstrate that zircon can grow during heating and partial melting. Reconciling the results of equilibrium models of zircon behaviour in migmatites (e.g. Kelsey et al., 2008) with observations and inferences from empirical studies is a crucial step for understanding the underlying mechanisms that allow zircon to grow in anatectic systems.

5.4 | Mechanisms of prograde suprasolidus zircon

New zircon can grow during heating at suprasolidus conditions by either the redistribution of Zr from existing zircon or when a new source of Zr becomes available for zircon growth. The modelling presented in this study explores the second mechanism, but the redistribution of Zr sourced from zircon can be accomplished by Ostwald ripening. This is a process whereby small particles (e.g. minerals) in a melt-bearing system will preferentially dissolve and reprecipitate onto larger particles to minimize surface energy (e.g. Jurewicz & Watson, 1985). Although its efficacy is debated for major metamorphic minerals such as garnet (Carlson, 1999; Miyazaki, 1991), it has been proposed for the accessory minerals (Kawakami et al., 2013; Miyazaki et al., 2019; Nemchin et al., 2001; Vavra et al., 1999). Ostwald ripening does not increase the mode of zircon in an anatectic system, but it redistributes the essential structural constituents to allow new zircon growth via grain coarsening. Ostwald ripening is expected to be most effective when the melt is saturated in the essential structural constituents of zircon, of which Zr has the lowest diffusivity (e.g. Mungall et al., 1999) and its diffusion in silicate melt is probably a limiting step in new zircon growth via Ostwald ripening (e.g. Kohn & Kelly, 2018). The kinetic aspects of zircon dissolution also need to be considered in natural systems (e.g. Harrison & Watson, 1983; Watson, 1996). Nonetheless, Ostwald ripening may represent a process that can

lead to suprasolidus growth of zircon during the prograde portion of a P-T evolution.

The modelling presented here explores the evolving compatibility of Zr in the residual assemblage as melting proceeds to investigate non-zircon sources of Zr during anatexis. The conditions most amenable to zircon growth in anatectic systems occur when the solubility of zircon in silicate melt is low-this is most likely at low temperatures—and when Zr is relatively incompatible in the products of the metamorphic reactions. Higher temperatures generally yield larger melt fractions in migmatites, and this melt requires more Zr to reach zircon saturation (Boehnke et al., 2013; Borisov & Aranovich, 2019; Gervasoni et al., 2016; Watson & Harrison, 1983). Therefore, lower temperatures are more likely to result in a scenario where zircon can grow (through Ostwald ripening or the release of a new source of Zr) because there is a better chance that the melt is saturated or oversaturated in Zr with respect to zircon. The compatibility of Zr in the residual assemblage varies across P-T space for the metapelite and the MORB (Figure 6), and this has consequences for zircon growth in anatectic systems.

For the metapelite, the investigated P-T range applicable for most crustal metamorphism-can be divided into two general fields, including *P*–*T* conditions below muscovite exhaustion (~660-750°C depending on pressure; Figure 3b) and P-T conditions above it. Muscovite-stable mineral assemblages become less compatible for Zr during heating above the wet solidus (Figure 6a) because garnet and ilmenite modes decrease (Figure 7a,b). For 6 kbar, this occurs from the wet solids $(\sim 680^{\circ}\text{C})$ to $\sim 700^{\circ}\text{C}$ (Figure 7a), whereas the consumption of garnet and ilmenite occurs over a wider range of temperature for isobaric heating at 10 kbar from the wet solidus ($\sim 680^{\circ}$ C) to 750°C (Figure 7b). This is because of the continuous melting reactions between the wet solidus and the K-feldspar-in field boundary; these continuous reactions are similar to the discontinuous KFMASH and KFMASHTO reactions (from White, Powell, Holland et al., 2014):

$$\begin{array}{l} \mbox{garnet} + \mbox{muscovite} + \mbox{quartz} + \mbox{H}_2 O \rightarrow \mbox{kyanite}/\mbox{sillimanite} \end{tabular} (4) \\ + \mbox{biotite} + \mbox{liquid} \end{array}$$

garnet + muscovite + ilmenite

+magnetite \rightarrow kyanite/sillimanite + biotite + liquid (5)

For both of these univariant reactions, the reactants contain relatively Zr-rich minerals (garnet and ilmenite)

and the products contain Zr-poor minerals (kyanite/sillimanite and biotite). For the continuous reactions in MnNCKFMASHTO—more realistic for natural systems—modelled in this study, the consumption of



FIGURE 9 Legend on next page.

garnet, muscovite and ilmenite produces melt, plagioclase, biotite, and kyanite or sillimanite (Figure 7a,b). When coupled with the relatively low solubility of zircon at these low temperatures (Figure 5b), this creates a scenario where the melt may become saturated or even oversaturated in Zr (with respect to zircon) with heating and can result in the growth of new zircon from melt (Figure 9a). This could nucleate new zircon but more likely allow growth of rims over inherited zircon cores, which is expected to be more energetically efficient (e.g. Nemchin et al., 2001).

The amount of Zr in the major minerals is usually small compared to the amount hosted by zircon (e.g. Bea et al., 2006; Spandler et al., 2003), and the availability of zircon along grain boundaries versus the proportion shielded as inclusions in other minerals is also debated (Bea, 1996; Watson et al., 1989). As an end-member scenario, consider that all zircon is locked away or is unreactive, and the concentration of Zr in melt is a product of trace element partitioning of Zr between the zirconabsent phase assemblage. This will mean that the effective bulk Zr concentration is small. Further consider a metapelite with a whole-rock concentration of 200 µg/g Zr and assume that 90% of this Zr resides in zircon and that it is unreactive; this leaves an effective system concentration of 20 μ g/g Zr that is hosted between the residual mineral assemblage (e.g. garnet, ilmenite, biotite and plagioclase; Figure 7e) and anatectic melt. This model presents a simplified scenario that does not consider zircon in mineral-melt partitioning, but it is a reasonable approximation for understanding the non-zircon budget of Zr and how this is distributed in an equilibrium system between the residual minerals and the melt. The stability of zircon for this scenario—a system with 20 µg/g Zr shared between the residual minerals and melt-is shown in Figure 10a. The contour represents the P-T

FIGURE 9 Schematic diagram showing the potential sources and sinks for Zr during heating and partial melting. Peritectic minerals are shown in the interior of the melt pocket. Modal proportions are schematic. (a) Low-temperature partial melting of a metapelite may result in oversaturated melt (with respect to zircon), and liberation of Zr from garnet and ilmenite breakdown could lead to zircon growth in melt during heating. (b) Hightemperature melting of a metapelite results in undersaturated melt and the generation of the Zr-rich peritectic minerals garnet and ilmenite. New zircon growth is not expected during heating. (c) Partial melting of a metabasite. The peritectic mineral assemblage is relatively Zr poor, but the main sink for Zr is the undersaturated melt. Prograde suprasolidus zircon growth is not expected. Mineral abbreviations are from Holland and Powell (2011). [Colour figure can be viewed at wileyonlinelibrary.com]

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conditions where the concentration of Zr in the melt is equivalent to that needed to saturate the melt with respect to zircon. In other words, this is the terminal stability of zircon. At temperatures above this line, zircon is expected to be absent. At temperatures below this line, zircon is stable, but its mode will change during heating.

The mode of zircon in the system at temperatures below terminal zircon stability is shown in Figure 10b. In general, the zircon mode slightly increases during heating from the wet solidus, but it rapidly decreases when the temperature approaches terminal zircon stability (Figure 10b). The calculated weight fractions of zircon in this system for isobaric heating at 10 kbar and 6 kbar are shown in Figure 10c,d. Note that the modelled weight fractions are very small and represent less than a tenth of the total amount of zircon (new zircon plus unreactive inherited zircon) in the system considering the starting concentration of 200 µg/g Zr. For 10 kbar, heating from the wet solidus (682°C) to 700°C is expected to grow zircon (Figure 10c). Zircon is consumed from 700 to 712°C, and no new zircon is expected to survive above 712°C, which is the terminal stability of zircon. For 6 kbar, heating from the wet solidus (679°C) to 692°C is expected to grow zircon (Figure 10d). Heating above 692°C at 6 kbar will progressively consume this newly formed zircon and it will be completely consumed by 735°C, which is the terminal zircon stability at this pressure (Figure 10d).

In addition to limited new growth of zircon, the melt is zircon-saturated below terminal zircon stability. This has two implications for suprasolidus prograde zircon growth. First, consider a scenario where the breakdown of a major mineral (e.g. muscovite; Figure 9a) releases included zircon into the melt at temperatures below terminal zircon stability. This zircon is expected to survive up to terminal zircon stability because the melt is already saturated. This zircon (subsolidus or inherited) may also represent the substrate for growth of limited new zircon, which will probably occur as metamorphic rims that envelop inherited zircon. The presence of metamorphic rims on inherited zircon is a common observation in migmatites (e.g. Rubatto, 2017). Second, melt saturated with respect to zircon is amenable to the redistribution of Zr that could allow zircon growth through a process such as Ostwald ripening (e.g. Nemchin et al., 2001). Ostwald ripening will not increase the mode of zircon in the system but could allow for the dissolution of small inherited zircon and crystallization of metamorphic zircon rims on larger grains in a pocket of melt. At the temperatures below terminal zircon stability in our example (~700-735°C; Figure 10a), Ostwald ripening may be effective for dissolving small (<10 µm) zircon grains and forming larger grains over geologically reasonable timescales (Kohn & Kelly, 2018).



FIGURE 10 Growth of prograde suprasolidus zircon in a metapelite. (a) P-T diagram showing the terminal stability of zircon for a system with 20 µg/g shared between the residual minerals (excluding zircon) and melt. The terminal stability contour is equivalent to when the concentration of Zr in the melt (from trace element partitioning) is equivalent to the concentration required for zircon saturation using the zircon solubility expression of Boehnke et al. (2013). (b) Calculated modes of zircon for P-T conditions just above the wet solidus. (c) Mode of zircon for an isobaric heating path at 10 kbar. (d) Mode of zircon for an isobaric heating path at 6 kbar. [Colour figure can be viewed at wileyonlinelibrary.com]

Although limited new zircon growth (or new metamorphic rims on inherited zircon) is predicted at temperatures within 10°C of the wet solidus for metapelites (Figure 10c,d), this zircon is expected to be consumed during further heating. Preservation of this newly formed zircon requires that it become physically isolated from the melt or that there are kinetic hindrances to dissolution. Entrapment in growing peritectic minerals during further heating, such as garnet, is unlikely in this model because garnet is expected to be consumed (Figure 7a,b) during the heating window (\sim 680–700°C) in which new zircon growth is predicted (Figure 10c,d). Kinetic hindrances to dissolution may be the cause of zircon preservation, especially at these

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relatively low temperatures. This is plausible considering the observation of nanogranite-bearing zircon (inferred to be related to growth in anatectic melt) hosted by peritectic garnet in metapelitic enclaves in volcanic rocks from the Neogene Volcanic Province (Cesare et al., 2009).

Heating to higher temperatures (e.g. above terminal zircon stability in Figure 10a) in the metapelite results in an increased compatibility of Zr in the residual mineral assemblage (Figure 6a) and, when coupled with the increasing solubility of zircon in melt with temperature, is not amenable to prograde suprasolidus zircon growth. For example, consider the reactants of biotite-breakdown melting in a metapelite and the generation of anatectic

melt at a triple junction between these minerals (Figure 9b). At the reaction site, melt is generated along with peritectic garnet and ilmenite. The Zr budget is dominantly hosted by zircon, which may be in contact with the melt pocket or locked away as an inclusion in a different mineral such as biotite. As the reaction proceeds, trace amounts of Zr in the reactant assemblage (mainly biotite) will become available to the melt. The main sinks for Zr include the melt and the peritectic minerals. As temperature increases, the compatibility of Zr in the residual assemblage increases (Figure 6a) and the amount of Zr that the melt can contain without reaching zircon saturation increases (Figure 5b). Unless there is zircon in contact with melt to buffer the Zr concentration, the melt will begin undersaturated with respect to zircon and become progressively more undersaturated because of the increased solubility of zircon with temperature (Figure 5b) and because of dilution with increasing melt fraction (Figure 4a). As inclusions of zircon become exposed to the melt, they are expected to dissolve because the melt is undersaturated and the compatibility of Zr in the mineral assemblage is increasing (Figure 6a). It is unlikely that this pocket of melt will be oversaturated with respect to zircon because of these factors. Consequently, new zircon is not expected to grow during heating at temperatures well above the wet solidus in metapelites.

For the MORB, the compatibility of Zr in the residual assemblage decreases with increasing temperature (Figure 6b). Progression of the continuous hornblendebreakdown reaction will generate melt and relatively Zrpoor peritectic minerals (Figure 8). However, this is countered by the relatively high solubility of zircon in the more intermediate melt compositions compared with the metapelite (Figure 5). Therefore, hornblende-breakdown melting is expected to release Zr into zirconundersaturated anatectic melt (Figure 9c) and is not expected to result in prograde suprasolidus growth. Consider a MORB with an average whole-rock concentration of Zr (100 μ g/g; e.g., Gale et al., 2013) and assume that 90% of this is locked away in zircon (e.g. Spandler et al., 2003) that is unreactive; this leaves 10 μ g/g Zr available in the system between the other residual minerals and the melt. In this scenario, equilibrium concentrations of Zr in melt based on trace element partitioning across the modelled *P*–*T* range are $<30 \mu g/g$. However, the zircon saturation concentrations across the modelled P-T range are >70 μ g/g (Figure 5d). There are no suprasolidus *P*–*T* conditions modelled where the calculated concentration of Zr in melt is higher than zircon saturation. In other words, there is no excess Zr available to make zircon. Consequently, prograde zircon growth in the MORB is not expected.

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The trace element partitioning model for Zr explored here for metapelite and MORB yields mostly similar results to previous equilibrium-based modelling studies (Kelsey et al., 2008; Kelsey & Powell, 2011; Kohn et al., 2015; Yakymchuk et al., 2017). In general, zircon growth is expected only to occur during cooling and not heating in suprasolidus system. The main difference is that the Zr partitioning model presented in this study predicts a very narrow window for prograde suprasolidus growth at temperatures just above the wet solidus (Figure 10a), but the preservation of this zircon is problematic. Preservation of this zircon in peritectic garnet is unlikely because garnet is expected to be consumed during heating at temperatures immediately above the wet solidus. Considering the interpretation of prograde suprasolidus zircon in peritectic garnet in natural samples (e.g. Cesare et al., 2009), the whole-rock equilibrium approach to understanding zircon behaviour (e.g. Kelsey et al., 2008; this study) may not appropriately reflect natural processes.

The main limitation of this study is assuming an equilibrium approach to trace element equilibration among all phases in the system (zircon, residual minerals and melt). One aspect that could benefit from further study is the heterogeneous distribution of Zr in pockets of anatectic melt because of the relatively slow diffusivity of Zr in silicate melt (Mungall et al., 1999). A similar scenario has been proposed for monazite growth from apatite because of local saturation at the apatite-melt interface because of the variable diffusivities of Ca, LREE and P in silicate melt (Wolf & London, 1995; Yakymchuk & Acosta-Vigil, 2019). Empirical studies that investigate the microstructural locations of zircon in migmatites (e.g. Schwindinger et al., 2020), the nature of polyphase peritectic zircon and inclusions in minerals (e.g. Bartoli & Cesare, 2020), trace element mapping in major minerals (e.g. Rubatto et al., 2020), and highprecision in situ geochronology can be used to evaluate the limitations of the equilibrium approach applied here and develop new insights into the mechanisms that control zircon behaviour in natural anatectic systems.

6 | **CONCLUSIONS**

Zircon behaviour in migmatites during prograde metamorphism is modelled using phase equilibrium modelling coupled with mineral-melt partitioning of Zr between the residual mineral assemblage and anatectic melt. Prograde suprasolidus zircon growth is not expected to occur in an equilibrated system except possibly at temperatures immediately above the wet solidus for metapelites. This may lead to prograde suprasolidus

metamorphic zircon rims on existing (inherited or subsolidus) cores through Ostwald ripening or direct crystallization from oversaturated melt. Preservation of this zircon during heating in a metapelite is unlikely considering the increasing melt fraction, increasing zircon solubility with temperature and the increased compatibility of Zr in the residual mineral assemblage. For the model metapelite, heating and melting above muscovite exhaustion (i.e. through biotite-breakdown melting) generates residual assemblages more compatible for Zr and, coupled with increasing zircon solubility at higher temperatures, is not amenable to prograde suprasolidus zircon growth. For a MORB composition, the residual assemblage becomes less compatible for Zr during prograde metamorphism, but this is counteracted by the increasing solubility of zircon in melt and prograde suprasolidus zircon growth is not expected. Future studies should conduct in situ analysis of zircon and document the inclusion assemblages and zoning patterns with high-resolution techniques to evaluate if prograde suprasolidus zircon growth is an appropriate mechanism for individual samples.

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DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

Table S1. Mineral-melt distribution coefficients for Zr used in modelling. Values are from Bédard (2006) unless specified otherwise. Mineral abbreviations from Holland and Powell (2011).

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