Zircon survival, rebirth and recycling during crustal melting, magma crystallization, and mixing based on numerical modeling

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Abstract. Improved methods of geochronological dating and in situ isotopic (O, Hf) and trace elemental distribution in zircons require new physical model that explains their behaviour during crustal melting. We present results of numerical modeling of zircon dissolution in melts of variable compositions, water contents, temperature, and thermal histories. The model is implemented in spherical coordinates with two moving boundaries (for crystal and the surrounding melt cell outer edge) using simplified mineral phase relationships, and accounting for melt proportion histories as a function of melting and crystallization of major minerals. We explore in detail the dissolution of variably sized zircons and zircon growth inside of a different rock cell size held at different temperatures and undersaturations and provide an equation for zircon survivability. Similar modeling is performed for other accessory minerals: apatite and monazite. We observe the critical role of rock cell size surrounding zircons in the survivability of zircons. Diffusive fill away from a dissolving 100 µm zircon into a large >3 mm cell takes $10^2$-$10^4$ years at 750-950 °C, but zircon cores may survive infinitely in smaller than 1mm cells. Heating followed by cooling for a similar amount of time leads to dissolution followed by nucleation and growth, but new zircon growth remains smaller than the original within the cell. The final zircon size is also investigated as a function of microzircons crystallizing on a front of major minerals leading to shrinking cell sizes and bulldozing of Zr onto the growing zircon surface. We explore in detail the
survivability and regrowth of zircon inside and outside of dikes and sills of different sizes and temperatures, and in rock compositions, on timescales of their conductive cooling and heating, respectively. For zircon-rich rocks, only the largest >200 m igneous bodies are capable of complete dissolution/reprecipitation of typically sized zircons at significant distances from the intrusion. Smaller intrusions result in partial dissolution and rim overgrowth. Zircons captured near the contact of conductively cooling sills undergo greater overgrowth than dissolution. In contrast, heat wave propagation from the sill will completely dissolve and reprecipitate zircons in Zr-poorer rocks many diameters of the sill away and often $10^3$-$10^4$ years after the sill intrusion. A single thermal spike and melting episode is capable of generating the observed complexity of isotopically-diverse and geochronologically-zoned zircons. A MATLAB program is presented for users to apply in their specific situations. [387 words]

**Keywords:** zircon, monazite, diffusion, numerical modeling, crustal melting, MATLAB

**INTRODUCTION**

Zircon, as well as other accessory minerals such as rutile, apatite, and monazite are important tools for geochronology, trace elemental, and isotopic research (for review see Kempe et al., 2000; Hanchar & Hoskin, 2003; Valley, 2003; Hermann & Rubatto, 2009). With the advent of microanalytical isotopic techniques in the past decade, geologists can now easily and inexpensively unravel geochronologic and isotopic information stored inside these minerals. Refractory accessory minerals are often inherited from earlier magmatic episodes, making them useful for tracking magma evolution and compositional history (Trail et al., 2012; Schmitt et al. 2011; Drew et al., 2013; Vazquez & Reid, 2002; Rubatto & Hermann, 2007; Miller et al., 2011; Claiborne et al., 2010; Chamberlain et al., 2014).

Zircon, in particular, is an important tool and a time capsule to reveal the O and Hf isotopic evolution, and the trace elemental melting-differentiation histories of their host melts/rocks (e.g.,
Vervoort & Patchett, 1996; Valley, 2003; Wotzlaw et al., 2012, 2014; Colón et al., 2015). In situ U-Th-Pb ion microprobe dating of zircons has resulted in the recognition of both “short” (<50 kyr) and “long” residence times (>100 kyr) in the magmatic zircon record and in crystallizing intrusions and volcanic magma bodies (Reid, 2011). However, while ion microprobe uncertainties of individual spots are adequate to recognize inherited xenocrystic cores (Fig. 1), the errors of these methods are sometimes too large (>10^4-10^5 years) to resolve crystallization histories for each zircon and make inferences about the duration of zircon growth and the state in which zircons were stored (e.g. prolonged crystallization in a mushy magma, or punctuated episodes of growth and subsolidus storage). In situ dating young zircons by U-Th disequilibrium methods provides better precision, but the best precisions are limited to young, <50 k.a. zircons (Charlier and Zellmer, 2000; Strom et al., 2011; Carley et al. 2011). The advent of the most precise methods of geochronologic dating – chemical abrasion ID-TIMS (CA-ID-TIMS) for whole or partial crystals allows the interrogation of zircon magmatic histories with 0.1% relative age precision (Schoene & Schmitz, 2007; Schaltegger et al., 2009). These precisions translate into millennia (or even century) timescales for young magmatic bodies (e.g. <±2000 years for a 0.6-4 Ma tuffs, Wotzlaw et al., 2014, 2015; Rivera et al., 2014). By dating individual zircons, we are now able to recognize and resolve processes of crystallization, hydrothermal alteration, and remelting of magma bodies within the overall timescale of magma solidification into rock. Such recognition is best for medium to large volume magma bodies that cool on longer timescales. In particular, for large-volume “hot and dry”, near-liquidus rhyolites such as the Kilgore tuff of Heise volcanic field, and Lava Creek, Mesa Falls, and Huckleberry Ridge tuff of Yellowstone (Watts et al., 2011; Bindeman et al., 2008), CA-ID-TIMS dating has now demonstrated that zircons can be dissolved and precipitated in less than 2-4 kyr (Wotzlaw et al. 2014, 2015). However, very different records result from “cold and wet”, near-solidus rhyolites and dacites such as the Fish Canyon tuff (zircon ages >150 kyr, Bachmann et al., 2002; Wotzlaw et al., 2013).

Mineral-diffusive and dissolutional processes provide a method for resolving shorter timescales than U-Th-Pb dating and are often used to predict months to decades timescales.
between magma recharge and eruption (Druitt et al., 2012; Costa et al., 2013; Cooper & Kent, 2014; Carrichi et al., 2014). Recent discoveries of ubiquitous O and Hf isotope heterogeneities in zircons with nominally identical ID-TIMS ages (Bindeman & Simakin, 2014; Colón et al., 2015; Wotzlaw et al., 2014, 2015) suggests faster, 10-1000s of years processes of (i) melting of isotopically-diverse protoliths above zircon saturation temperatures resetting U-Pb ages, followed by (ii) new zircon crystallization from the immediate environment (melt cell), and then (iii) segregation and mixing of these initial melts to make the (short-lived) magma body. The chaotic convective mixing of isotopically diverse magma batches results in diverse zircon populations in erupted rhyolites (Bea, 2010; Bindeman & Simakin, 2014).

These recent advances require a new model of zircon (and other refractory accessory minerals) survivability and recycling as a function of external and internal parameters. Much experimental work on accessory mineral solubility and diffusion has been done by E. B. Watson and T. M. Harrison and their collaborators for the past 30 years, as well as recently by many other researchers (e.g., Rubatto and Hermann, 2007; Bernini et al. 2013). E.B. Watson (1996) combined solubility and diffusion equations and presented a numerical treatment of zircon survivability that has remained an important milestone paper for the past 20 years. The present paper advances the treatment in Watson’s (1996) paper by providing an easy MATLAB-based computational platform for user-specific situations of zircon and other accessory mineral crystallization along T—X(H2O) composition-time paths. It uses new experiments and parametrizations of zircon-melt saturation; it also uses a compilation of new diffusion coefficients parametrized to the temperature and water content of melt leading to about 2x shorter lifeline of zircons. We introduce optional M-factor dependence on temperature. The model uses a realistic situation of a finite melt reservoir around zircon (cell) and provide a systematic study of the effect of the cell size on zircon dissolution/growth kinetics; zircon can get dissolved and then nucleate. Additionally, this study involves the influence of major mineral crystallization/dissolution on the finite melt cell size and on the Zr concentrations at the far end of the cell. We also use a %melt-Temperature phase diagram that can be changed by a user, appropriate for both partially melted crustal rocks and near-
liquidus rhyolites. This study eliminates a small error in equation 12 of Watson (1996)*. Finally, our approach and code are easily convertible to other accessory phases for which there are saturation and diffusion data, such as monazite and apatite.

METHODS: CONTROLLING PARAMETERS AND NUMERICAL MODEL

Description of parameters of the model and their physical meaning

Elementary Cell and mass exchange within it

Fig. 2 presents conceptual view of zircon distribution in a rock and Fig. 3 outlines our model of a spherical zircon surrounded by a melt cell with two moving boundaries. Given that zircon cell sizes are much larger than the zircon size, zircons can be approximated as spheres (e.g. Watson, 1996) and the spherical model is the closest approximation to natural melting scenarios of assessor mineral within a certain cell size (Fig. 2). However, we also set up the initial model in linear and cylindrical coordinates. Fig A1 in the Appendix compares dissolution outcomes giving expectedly faster dissolution and growth for spherical coordinates.

Zircon growth/dissolution rates are limited by slow diffusion of zirconium (Zr) in/out of the crystal-melt interface (Fig. 3). Following Harrison and Watson (1983), we assume local thermodynamic equilibrium between the crystal and the melt at the interface, \( r = s \), where \( r \) is a radial coordinate, and \( s \) is zircon surface. We note however that the outermost (~1nm) surface of accessory minerals with a very high concentration of constitutive element on their contact with the melt may have less trivial partition relations than major minerals (Rustad, 2015), but these effects are not implemented here. The boundary layer is the region adjacent to the interface characterized by concentration gradients in the melt due to dissolution or growth of the zircon. We also assume that each zircon crystal is surrounded by a melt cell of a finite radius, \( L \). The cell contains a zircon crystal in the center, surrounded by a melt layer \( s < r < R \) and a layer of major

*An error in Equation 12 of Watson (1996) is in conversion to spherical coordinates and ignoring \( V \cdot C(r, t) \) term; this error however resulted in small differences with our computations (Appendix, Fig A2), likely due to the typically small value of zircon growth rates, \( V \).
element crystals $R \leq r \leq L$. The Zr concentration at the far end of the melt reservoir ($r = R$) should be primarily controlled by the diffusion of Zr coming from the dissolving zircon in the center of the cell. This concentration may also be affected by the crystallization of the major minerals (e.g., feldspar, quartz, biotite) due to their very low concentrations of Zr and hence the build up of Zr in front of their crystallization. It is possible to adjust partition coefficients to account for more compatible Zr behaviour, for example due to microzircon crystallization in the major phases’ boundary layers (e.g., Bacon, 1989, see below). Finally, we set up the model using zircon as an example, but numerical dissolution/crystallization experiments are applicable and also presented for monazite and apatite.

Zircon sizes, number densities and distances between zircons and cell sizes

A very important parameter for any zircon dissolution and growth model is the model cell size and distance between individual crystals. Thin section identification of minor abundance (<<1 volume %) and small (<100 µm) minerals does not provide adequate particle statistics to determine spacing. Instead, Bindeman (2003) performed acid dissolution of pumices from a series of well-known large and small eruptive products and measured crystal size distribution (CSD) and quantitative particle number density per unit of magma volume for quartz and zircon. Examples given in Table 1, suggest that typically 28 to 300 individual zircon crystals occupy each cm³ of dense rock-equivalent, corresponding to an average distance between zircons of 3 to 0.6 mm prior to vesiculation, assuming equal spacing of particles. Using the example from the Youngest Toba Tuff (Fig. 2), which contain 96 zircons per cm³ melt (Table 1), the measured average distance between twelve >150 µm zircons (with radius of 75 µm), constituting half of crystallized zircon volume, is 1.86 mm; and the single biggest 230 µm zircon, constituting 10% of total zircon’s volume, is 3 mm away from its peer in the next melt cell volume. These and other measurements in Table 1 provide an assessment of appropriate individual zircon cell sizes to use in modeling. In particular, upon dissolution the biggest zircons will survive the longest and be surrounded by the
biggest cell size. The cell size determines the length of diffusion away from a dissolving zircon-melt boundary.

**Fig. 2** presents a conceptual view of cells as diffusional spheres of influence for zircons of different sizes that would approximately satisfy measured zircon CSDs and estimated distances between particles of different sizes. We distinguish two geologically relevant situations with cell sizes. For an igneous or metaigneous rock undergoing melting and crystallization, the distance between zircons of different size will be established by mutual interaction of the growing zircons upon the start of crystallization. As a result, a common collective CSD is maintained within each hand specimen-wide volume of rock (defining cells), containing $10^2$-$10^3$ of zircons (**Table 1**). For sedimentary and metasedimentary rocks that went through chemical weathering and density water sorting, zircons and other accessory minerals may occur in layers, making distance between neighbouring zircons small in mafic layers, and large in quartz-feldspathic layers. Such a geometrical configuration will influence cell sizes upon heating, melting, and diffusional accessory mineral dissolution. Dissolution will be retarded in accessory mineral-rich layers, leading to their preservation, while in adjacent quartzo-feldspathic layers, sparser accessory phases will undergo enhanced dissolution upon heating (see below). Furthermore, zircons can become occluded by other Zr-free phases. Bea and Montero (2013) numerically described conditions of zircon survival when shielded by other phases. Microscopic inclusions of zircons are present in many biotites, amphiboles, and rarely feldspars. Bacon (1989) described saturation with accessory minerals on the boundary of crystallizing feldspars, a topic that we address below by numerical modeling.

In our model, for a given size of zircon, cell size can be specified either independently, or by bulk Zr concentration in a rock, which is a function of zircon mass and ambient melt Zr concentration. In both melting and crystallization, the zircon boundary layer will maintain $C_{\text{sat}}$ concentration, and diffusion will strive to attain equilibrium across the cell. There is no flux with adjacent cells because it is assumed that the neighbouring cells with zircons of different size (**Fig. 2**) contribute Zr via diffusion uniformly in N adjacent cells around the cell of interest. When selecting zircon size, cell size, and temperature, the model allows for selection of zircon under- or
over-saturation conditions via the parameter $\Delta U$, see below. Such an initial condition may correspond to instantaneous temperature overstepping (thus different $C_{\text{sat}}$), or zircon appearance in a melt of different composition and thus $C_{\text{sat}}$ due to rapid mixing of magmas with different Zr concentrations for example.

Zirconium diffusion in melt

Dissolution of minerals in high viscosity, low diffusivity silicate melts is almost always controlled by slow diffusion through the melt of their constituent elements (Zhang et al., 1989; Zhang, 2012). In the case of zircon, apatite, and monazite, the diffusion coefficients of their constituent 3+, 4+ and 5+ elements have $D = 10^{-12} - 10^{-15}$ cm$^2$/s at relevant magmatic temperatures (700-1200 °C, Harrison & Watson, 1983; Zhang et al., 2010 and references therein), the lowest compared to major oxides (Baker, 1991; Acosta-Vigil, 2006). The diffusion coefficient of zirconium, $D$, is a function of temperature, $T$, and water content, $X_{H_2O}$ (Harrison and Watson, 1983, see Table 2 for parameters and units). Heat diffusion and diffusion of water are orders of magnitude faster than the diffusion of Zr, (Zhang et al., 2010), thus, we can assume instantaneous equilibration of the temperature and the water concentration within the cell and consider these parameters as external.

Water decreases activation energies and increases diffusion coefficients by 2-3 orders of magnitude between 950-650 °C (Watson & Harrison, 1983; Harrison & Watson, 1984; Rapp & Watson, 1986; Xu & Zhang, 2009; Zhang, 2012). This effect is likely through making diffusion clusters and increasing the amount of non-bridging oxygen or OH atoms and molecules available for charge compensation during diffusive jumps of these highly charged cations. Harrison and Watson (1983, 1984) and Zhang et al. (2010) noted that the addition of the first 1-2 wt% of water produces the most dramatic effect on the acceleration of diffusion by several orders of magnitude, but the effect of further water addition from 3-4 wt% to 6 wt% increases $D$ by less than a factor of five. We compiled published diffusion coefficients of Zr at different temperatures and water
contents as given by Zhang et al. (2010), with most data from Watson’s and Harrison’s experiments. These experimentally determined relationships are parametrized in our model as:

\[ \ln(D) = \frac{11.4X_{H_2O} + 3.13}{0.84X_{H_2O} + 1} - \frac{21.4X_{H_2O} + 47}{1.06X_{H_2O} + 1} \cdot \frac{1000}{T} \]  \hspace{1cm} (1)

This approximation does not take into account the influence of melt F and Cl content on Zr diffusion, which has strongly different activation energies for diffusion (Baker & Watson, 1988).

Zircon saturation \( C_{sat} \) and compositional M factor

A series of dissolution-crystallization experiments of zircons in melts ranging in composition, water content, and temperature were conducted by Harrison and Watson (1983), Watson and Harrison (1983), Rubatto & Hermann (2007), Hermann & Rubatto (2009) and Boehnke et al. (2013) and calibrated \( C_{sat} \) dependence on T and composition. The compositional factor that affects zircon solubility is defined as: \( M = (Na + K + 2Ca)/(Al*Si) \), where elements are given in molar proportions. Increasing alkali content and melt peralkalinity increases zirconium solubility and thus larger M-factors require higher Zr concentrations to cause zircon saturation. Boehnke et al. (2013) presented an updated calibration of the Watson and Harrison (1983) model, where \( C_{sat} \) is a function of T and M:

\[ C_{sat} = 490000 / \exp \left( \frac{10108}{T} + 1.16(M-1) - 1.48 \right). \]  \hspace{1cm} (2)

M-factors may decrease with igneous differentiation. We performed MELTS and RhyoliteMELTS (Ghiorso & Sack, 1995; Gualda et al., 2012) crystallization experiments on a series of USGS standard rock compositions to model M-factor dependency on T and composition (Fig. 4). We note that because pure feldspar endmembers have large M-factors, and quartz has M-factor = 0, melting of a silicic assemblage will lead to the progressive increase in partial melt M-factor upon dissolution of quartz, then decreasing proportions of Ab and Or in feldspars, which
move toward more An-rich composition. The function of M-factor dependency on temperature (°K) that was implemented in this work (Fig. 4b) is:

\[ M = 4.8 \times 10^{-6} T^2 - 8.4 \times 10^{-3} T + 4.84; \]  

(3)

Our results are comparable with earlier statements by Watson and Harrison (1983), Miller et al., (2003) and Boehnke et al. (2013) that multiply-saturated silicic melts have M factors within a narrow range of 1.3 -1.8. Second order polynomial approximation better reflects the expected shallowing of M-factors with decreasing temperature as the granitic eutectic (and thus constant composition) is approached, vs. a linear extrapolation of higher temperature experimental data (e.g., M= 0.5+0.0013T(°C) used by Harrison et al. 2007). It is also possible to keep the M factor constant within melting-crystallization regime within our program.

Temperature-%melt relations and crystallization of major minerals

Upon melt cooling or heating, crystallization or melting-dissolution of zircon from its defined cell will also be accompanied by crystallization or melting of major silicate phases such as feldspars, quartz, and pyroxenes (Fig. 3). The general topology of the granitic eutectic includes increases in x% (crystal content) at small variations in T. Increasing pressure and water content results in decreasing the eutectic temperature to a minimum of ~630°C at ~10 kbar (Clemens & Vielzeuf, 1987); shallow 1-2 kbars silicic systems such as Fish Canyon or Bishop Tuffs have eutectic temperatures of 710-750°C (Bachmann et al., 2002; Hildreth, 1977). Low temperature magmas such as these are almost always water saturated with at least 4 wt% and commonly up to 6 wt% water (Wallace et al., 1999). Liquidus temperatures are more strongly affected by initial water content than solidus, which are likely to be always water-saturated (Holtz, 1992). Hot and dry Yellowstone and Snake River Plain rhyolites may contain only 1-2wt% water at the liquidus (e.g. Almeev et al., 2012) and thus have high temperature at 850-950 °C (Loewen and Bindeman, 2016), but even those will reach 4-5 wt% water and thus a ~750 °C low pressure eutectic and solidus at higher degrees of crystallization. It is thus important (but not critical as our modeling shows) to set up the preferred T-%melt function for a cell that is undergoing zircon dissolution.
Anatexic melts formed by the dehydration of amphibolites and gneisses can be user-defined, based on the most realistic situations.

As none of the major minerals take up Zr, the bulk Zr partition coefficient between these minerals and melt is close to zero (~10^{-1}-10^{-4}; see http://earthref.org/KDD website for partition coefficients); pyroxene, amphiboles and garnets have slightly higher K_{Zr} = 0.1 - 0.6 range but they rarely crystallize without feldspars (K_{Zr} < 0.01) leading to bulk K_{Zr} << 0.1. The effect of the crystallization/melting of major minerals on zircon growth/dissolution are significant especially at higher crystallinity where major phase growth will affect bulk melt Zr concentration in the vicinity of zircon crystals. The compositional effect of the major phase crystallization is implemented at the independent boundary of zircon cells (Fig. 3). Crystallization leads to movement of the melt-major phase interface at a rate, W, which is determined by the temperature-%melt relation function, and the partition coefficient for Zr for major phases, K_{Zr}, defined in the program or set up by the user. Microzircon inclusions may nucleate on the front of their crystallization.

**Zircon nucleation**

Upon cooling of a melt cell volume, zircon is allowed to nucleate in an area exceeding C_{sat} concentration by oversaturation, -ΔU. The center of the cell normally contains undissolved zircon (or shortly thereafter, a trace memory of higher Zr concentration left after zircon dissolution), favoring nucleation to proceed there. Nucleation is implemented in the model by setting up a small oversaturation -ΔU of 0.5-5 ppm, defined by a user. Nucleation of zircons due to oversaturation near an advancing external cell boundary of growing major phases is not explicitly realized due to the one-dimensional, spherical coordinate set up of our model, but it is realized through microzircon nucleation and its effect on the bulk phase K_{Zr} value (Fig. 3, see below).

**Equations and Boundary conditions**

Transport of Zr in the melt cell is governed by the standard diffusion equation that in a spherical case can be written as:
\[ \frac{\partial C}{\partial t} = \frac{D(T, X_{H2O})}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right). \quad (4) \]

Here \( C \) is the concentration, measured in ppm, \( r \) is the radius counted from the centre of the zircon crystal, and \( t \) is the time (Table 2). Eq. (1) is solved only inside the melt part of the cell \( s < r < R \), because diffusion of Zr in the major crystal phases is very slow in comparison with the diffusion in the melt.

Boundary conditions at crystal-melt interface \((r = s)\) reveal local thermodynamic equilibrium and mass conservation of zirconium.

\[ r = s : -D \frac{\partial C}{\partial r} \bigg|_{r=s} = J = V [C_m - C_z]; \quad C_m = C_{sat}(T). \quad (5) \]

Here \( V \) is the growth rate of zircon, \( C_m \) is the concentration of Zr in the melt, and \( C_z = 490,000 \) ppm is Zr concentration in zircon. The saturation concentration \( C_{sat} \) of Zr mainly depends on temperature and melt composition which are governed by equations in Watson and Harrison (1983) and Boehnke et al. (2013), integrated into the model. On the outer melt boundary \((r = R, \text{ Fig. 3})\) mass partitioning of Zr between major minerals and the melt is specified:

\[ r = R : -D \frac{\partial C}{\partial r} \bigg|_{r=R} = J = W [C_m - C_X]; \quad C_X = KC_m. \quad (6) \]

Here \( W \) is the velocity of the outer boundary, \( C_X \) is the concentration of zirconium in major minerals, and \( K \) is its Zr distribution coefficient, \( C_{Zr}^{\text{major}} / C_{Zr}^{\text{melt}} \). Discussion of particular values of parameters in eq. (1-3) will be presented below.

In order to solve eq. (1) with boundary conditions (2, 3) we first make a coordinate transformation to a moving domain:

\[ \xi = \frac{r - s}{R - s}; \quad \xi(r = s) = 0; \quad \xi(r = R) = 1. \quad (7) \]
This transformation allows eq. (1) to be solved in a fixed coordinate frame. After application of eq. (4), eq. (1) becomes:

\[
\frac{\partial C}{\partial t} + \frac{V(\xi - 1) - W(\xi)}{R - s} \frac{\partial C}{\partial \xi} = \frac{D(T, X_{H_{2}O})}{(R - s)^2} \frac{\partial}{\partial \xi} \left( r(\xi) \frac{\partial C}{\partial \xi} \right).
\]  

(8)

Boundary conditions do not change their functional form except for the calculation of the fluxes:

\[
\xi = 0: -\frac{D}{R - s} \frac{\partial C}{\partial \xi} |_{\xi=0} = V[C_m - C_{\xi}]; \quad C_m = C_{\text{init}}(T)
\]

\[
\xi = 1: \frac{D}{R - s} \frac{\partial C}{\partial \xi} |_{\xi=1} = W[C_m - C_{X}]; \quad C_{X} = K C_{m}.
\]

(9)

The system (eqs. 5-6) is discretized using a finite volume approximation assuming a fully implicit scheme. The resulting 3-diagonal matrix linear equation is solved by the Thomas method (Conte & deBoor, 1972), which is unconditionally stable. This allows the model to make no restrictions on the time step based on the CFL (Courant–Friedrichs–Lewy) condition (Courant et al., 1928). Mesh independence of the results was achieved by comparison of solutions with finer and coarser meshes and a simultaneous decrease in the time step. The programing was realized in MATLAB and the code is available in the supplementary material.

RESULTS

Below, we first explore dependencies of different parameters on each other using numerical experiments of zircon dissolution at different temperatures and degrees of undersaturations in cells of different size, then dissolution and crystallization at different rates of heating and cooling.

Second, we consider zircon dissolution and crystallization over geologically realistic timescales and thermal histories, by integrating our model with a model of conductive cooling and heating by intrusion of magma bodies (dikes and sills) into the crust.
Dissolution at constant temperatures but different cell size and $\Delta U$

At any $T$, zircons may be kept undersaturated ($\Delta U > 0$), oversaturated ($\Delta U < 0$), or in equilibrium ($\Delta U = 0$) with their surrounding melt cells. From a geological point of view, rapid or instantaneous changes in saturation can be achieved by: i) zircons being captured into a different (under- or oversaturated, hotter or colder) melt in the course of magma mixing or rapid disaggregation of solid fallen roof material (e.g., Beard et al., 2005; Bacon & Lowenstern, 2005; Acosta-Vigil et al., 2010; Simakin & Bindeman, 2012) leading to rapid zircon contact with melts, or via ii) due to rapid (overstepping) temperature increases or decreases leading to zircon under- or over saturation. Contact metamorphism, roof melting, stoping, and rapid target rock melting upon meteorite impact (e.g., Cavosie et al., 2010) are examples of likely scenarios. Typically more sluggish temperature changes in deep to mid crustal anatexis in metamorphic rocks and migmatites, and in subduction zones may mean that temperature will control the saturation conditions of zircon and other minerals. However, fluctuation of amounts and compositions of fluids in migmatites (Rubatto et al., 2006) and in subduction zones (e.g., Hermann and Rubatto, 2009) coupled with fracture dynamics may produce punctuating regimes of zircon under- or over-saturation within its own cell upon melting. Bulk compositional control matters too: for mafic rocks with detrital zircons such as amphibolites and metagreywackes, the melting will result in zircon-undersaturated melts, while for zircon-rich layers in a gneiss melting will result in Zr oversaturation.

Effect of cell size

Fig. 5 models the amount of time required for zircon dissolution at different levels of undersaturation inside of melt cell volume of fixed size. By varying the cell size (Fig. 6) at a given Zr undersaturation and constant temperature we investigated kinetics of zircon dissolution – how long does it take for zircon of a given size to either: 1) dissolve completely within a melt cell (Fig. 5a), or alternatively, 2) dissolve to a smaller size and reach Zr saturation within it (Fig. 5b). As is illustrated in Fig. 5, the outcome depends simply on the total bulk concentration of Zr within a cell.
(zircon+melt) and \( C_{\text{sat}} \), if \( C_{\text{bulk}} > C_{\text{sat}} \), zircon will survive, alternatively it will get dissolved. Zr undersaturation, \( \Delta U \), has equivalence in temperature of 8 °C per 10 ppm Zr using the saturation formulation of Boehnke et al. (2013). Such outcomes are easy to understand by thinking of dissolution of a single NaCl crystal in undersaturated water solutions of various volumes (cell size), kept at different temperatures. However the difference of NaCl-water solution analogy with zircon-melt, is that zircon contains 490,000 ppm Zr while much lower Zr concentrations between 10 -10³ ppm Zr are required for zircon saturation in silicate melts (e.g., Harrison & Watson, 1983), thus tiny amounts of zircon dissolution will saturate the melt. Additionally, unlike the almost instantaneous saturation of the water solution with dissolving NaCl, the filling of the cell with Zr and the resulting achievement of equilibrium zircon size takes a long diffusional time. The NaCl analogy may be also thought for a major mineral, such as plagioclase-melt situation.

Models at 950 °C and M factor = 1.8 and different \( \Delta U \) (Fig. 6) demonstrate the role of cell size in determining zircon survivability. Dissolving zircon fills small cells with Zr more quickly, decreasing diffusion gradients and increasing the dissolution time. Increasing cell size to > 3-4 mm rapidly accelerates dissolution rates and reduces dissolution time. At 20 ppm undersaturation and large cell sizes, it will take 400 years to dissolve a 100 µm radius zircon, while 1600 years is required to dissolve zircon inside of a 3 mm cell size to reach \( C_{\text{bulk}} = C_{\text{sat}} \). Further dissolution time does not significantly decrease with increase in cell sizes past 3-4 mm providing a minimum time estimate for zircon dissolution at given undersaturation.

Effects of changes in \( \Delta U \) and temperature

Not surprisingly, as temperature affects both \( C_{\text{sat}} \) and diffusion coefficients (Harrison and Watson, 1984), the survivability of zircon is strongly dependent on the temperature at a given \( \Delta U \) and cell size (Fig. 6). A temperature increase of 100 °C shortens the total dissolution time of a large 100 µm zircon in a melt with \( \Delta U =20 \) ppm by a factor of 10.

An increase in undersaturation \( \Delta U \) from 20 to 100 ppm decreases the minimum dissolution time by a factor of ~4.5 for zircon of identical size (Fig. 6). For experiments at 750 °C and small
$\Delta U$ of 20 ppm, minimum zircon dissolution times in large cells are measured in 30, 50, and 100 kyr in smaller cells. For 80 ppm maximal possible undersaturation (so $C_{\text{sat}} - \Delta U=0$) dissolution times are 7-10 kyr. At an intermediate temperature of 850 °C, dissolution at $\Delta U=20$ and 100 ppm in 5 mm cells take 3.5 kyr and 0.55 kyr respectively. These dissolution experiments demonstrate that only large $\Delta U >50$ ppm undersaturation plays a significant role in accelerating zircon dissolution. Because of the rather steep increase in $C_{\text{sat}}$ with T (e.g., 8 °C per 10 ppm, Boehnke et al., 2013), undersaturation increases the concentrational gradients near the dissolving zircon boundary and tiny amounts of zircon dissolution rapidly decreases the effect of the original undersaturation.

Dissolution and Growth Rates

Fig. 7 considers dissolution rates, $V$, of different sized zircons inside of a large 5 mm cell, which is almost infinite relative to the zircon crystal size. The dissolution rate at first is nearly constant and then slowly increases after dissolution of the outer ~20% of the original zircon radius. The dissolution of the final 20% of the original radius (or remaining 1% of the zircon volume) proceeds with accelerating rate. This relationship is a simple outcome of radial diffusion in spherical coordinates, directly applicable to natural conditions. The boundary condition (eq. 5) along the dissolving zircon boundary requires an accelerating $V$ to keep up with the required supply of Zr from the smaller and smaller surface area of a shrinking crystal. The same effect is illustrated in Fig. 5a where the rates of dissolution are greater for smaller zircons. The 10 µm zircons start dissolution with about 10 times faster rates than 100 µm zircons. The rate increases twice for the dissolution for the last 2 µm (see steep profile at 1.81 yr on Fig 5a). This rather simple result has important implications for zircon survivability; small zircons will dissolve disproportionally faster at any change in T leading to undersaturation, explaining the common occurrence of concave-up zircon crystal size distributions in igneous rocks (Bindeman, 2003; Simakin & Bindeman, 2008). Modeling expectedly shows that the reverse is also true, upon nucleation, zircon growth rate is also faster for smaller crystals (Fig. 7b).
Approximation of Dissolution and Growth Rates

The above estimates (Figs. 5-7) should provide the reader with expected timescales of zircon dissolution/crystallization in realistic ranges of $T$ and $\Delta U$. In order to quantify this, we performed 100 growth and dissolution runs at different constant temperatures and degrees of undersaturation for zircons of variable size. We used cells greater than 4 mm (Fig. 6) in which there is little dependence of zircon growth or dissolution rate on cell size. The total Zr concentration in the rock in these runs ranged from 50-500 ppm.

The approximation fit using DataFit software leads to the following expressions for rates, $V$, and zircon radius, $\bar{R}$, tested in zircon radii between 30-90 µm and $T$ from 650 to 950 °C:

$$V^* \bar{R}^n (10^{15}) = X_2*exp(-0.034 + 13.4 * X_1 - 2.90 * X_1^2) \quad (10)$$

$$n = 0.991-0.0247*X_1 - 0.116*X_2 - 0.0071*X_1^2 + 0.0603*X_2^2 -0.17*X_1*X_2 \quad (11)$$

where $X_1 = (T (°C)-650)/300$ and $X_2 = \Delta U/C_{sat}$ (where $C_{sat}$ is a f($T$); (values of these variables change from 0 to 1). These equations can be used to estimate the survivability of zircons of different sizes in user-specific static situations. They are compared to equation 17 of Watson (1996) and predict 20-40 times faster dissolution of zircons (Fig A2, Appendix).

Linear temperature increase from solidus to liquidus at different rates

In the previous section our models examined the results following instantaneous achievement of zircon under or over-saturation (parameter $\pm \Delta U$). We next explore how different rates of temperature increase and decrease will affect zircon dissolution/crystallization inside of a cell volume of the same size, while keeping $\Delta U$=0. As the diffusion of Zr in the melt is the highest at the higher T, we explore the relation between the rate of temperature increase and the slow Zr diffusion reaction to “overstepping” temperature, before diffusion from the zircon boundary can adjust.
Different rates of linear T increase

Linear rock heating from solidus at 650 °C to liquidus at 950 °C was performed at different rates ranging from 0.02 °C/yr to 10 °C/yr, all resulting in complete zircon dissolution (Fig. 8). We observe that the dissolution at \( dT/dt < 1 \) °C/yr are primarily controlled by the rate of temperature increase (the rate the \( C_{sat} \) at the higher temperature is crossed). At rates higher than 5 °C/yr, it is the slow diffusional cell fill with Zr that determines (slows down) the dissolution rate. At \( dT/dt \) between 1 and 5 °C, these rates are influenced by both the rate of T increase and slow Zr diffusion. Thus, at rates higher than 5 °C/yr, dissolution and diffusion away from the dissolving boundary cannot keep up with the rapid rate of T increase due to the slow diffusion of Zr in the cell. As a result, zircon dissolution rates and minimum times to complete dissolution (which are ~50 years in this case) are comparable to dissolution at a terminal and constant 950 °C (Fig. 6). Very rapid temperature increases can be viewed as putting the original zircon in a pre-set undersaturation equivalent to \( \Delta U = 185 \) ppm (\( C_{sat} \) difference between 650 and 950 °C).

The realistic heating and cooling rates due to conductive heat fluxes from the cooling igneous bodies are modeled below and are shown on Fig. A3 in the Appendix. The heat is transferred via conduction and rarely exceeds 1 °C/yr and then only for a short period of time, next to the contact with a sill. Translated to natural scenarios, this is applicable to contact metamorphism/melting caused by the intrusion. Higher rates of conductive heating are thus rarely realized (e.g., Huppert and Sparks, 1988), but instantaneous heating is equivalent to a small piece of rock or zircon captured and submerged in a magma of different temperature and \( \Delta U \), or to rapid magma mixing, similar to what is modeled in Fig. 5. Much lower rates of heating/cooling are realized in far fields of cooling dikes and sills and in regional metamorphism/anatexis (< 0.02 °C/yr, Fig. 8, 16 below and Fig. A3). However, due to the exponential dependence of dissolution rates on T, the topology of the dissolution curves (e.g. Fig. A3) can be fitted by a concave down exponential and include a long delay at lower temperature followed by a rapid collapse of zircon size at peak temperatures. In other words, it is the highest temperature that matters; the prehistory of temperature increase matters much less.
Linear temperature increase followed by symmetrical temperature decrease

Fig. 9 presents a case of a symmetrical temperature history: heating to the liquidus leading to zircon dissolution, followed by cooling to the solidus and zircon growth. Different cell sizes are modelled with zircon completely dissolving in the largest cells and partially dissolving and achieving some minimal size in smaller cells. This simulation illustrates that once zircon fully dissolves and Zr diffusively equilibrates throughout the cell, it takes longer for zircon to recrystallize from the melt to the same original size within the same original melt cell volume. This result is not intuitive and implies a non-symmetrical nature of dissolution then growth to regain the same size after a return to the original conditions following a heating event.

Temperature evolution inside and outside of a cooling dikes and sills

As present work considers crustal melting/magma crystallization histories via surviving/crystallizing zircons, it is necessary to consider the temperature-time history of the rock inside and outside of a cooling igneous body. Sill and dike intrusions are critical in delivering heat and maintaining elevated temperature in the host rock (Annen & Sparks, 2002; Dufek & Bergantz, 2005). The position of the zircon cell volume inside or outside of a sill, with specified phase diagram (T-X diagram) permits monitoring the progress of zircon dissolution and subsequent growth, or lack of these if conditions are not met. A heat wave propagating from a sill with initial temperature, $T_d$, in country rocks with a $T_c$ will pass through each coordinate point perpendicular to the sill with decreasing peak temperature and increasing wavelength with a distance from the sill (Fig. 10; A3). Outside of the sill the highest temperature peak, equivalent to half-temperature ($T_d-T_c)/2$, is realized at the contact between the sill and the country rocks. At this boundary, zircon dissolution starts almost instantaneously after sill emplacement. Distances $x =10-10^2$ meters away from the sill will get heated at time $t \sim x^2/k$, where $k$ is the thermal conductivity $\sim 0.6*10^{-6}$ cm$^2$/s (Carlslaw & Jaeger, 1959). Partial melting of rocks at these areas creates conditions for zircon dissolution but often with a delay of $10^2-10^3$ years (Fig. 10) after the arrival of the heat wave.
T-t histories around conductively cooling dikes and sills of a certain half-width \( h \) at coordinate from the sill center \( x \), is given by the analytical solution from Crank (1975):

\[
T = \frac{(T_d - T_0)}{2} \left( \text{erf} \left( \frac{h - x}{\sqrt{kt}} \right) + \text{erf} \left( \frac{h + x}{\sqrt{kt}} \right) \right)
\]

(12)

Fig. 10 demonstrates temperature profiles around a cooling 950 °C, 100 m thick sill showing the temperature histories of zircon cells at varying distances from the sill center. The melting and latent heat sink (Stefan problem) is not taken into account here for simplicity and melting will shorten the width of the heat wave. For relatively small melting degrees, conduction will still dominate. Temperature-time histories were monitored in three points: i) inside of a sill, aimed at modeling dissolution of zircons captured from the country rock; ii) at the contact; and iii) zircon at a distance from a sill in rocks that undergo small degree partial melting. The survivability of zircons, as well as the amounts of dissolution and subsequent rim growth are different in these three positions (Fig. 11-13) and are obviously strongly dependent on the temperature and the thickness of the sill as well as the country rock temperature.

In our modeling we experimented with sills thickness varying from 10 to 900 m with \( T = 950-1300 \) °C intruded into rocks of 450 °C to 750 °C; most runs were done considering subsolidus <650 °C rocks. We have also computed the rates of cooling and heating of individual zircon cells at different positions relative to the sill (Fig. A3, Appendix). For a short period of several years internal and external contact areas, adjacent to the contact zone undergo \( \frac{dT}{dt} \) greater than 2 °C/yr. As we already explored in Fig. 8, even at high temperature this amount of time is insufficient to cause significant dissolution of any except the smallest zircons. Most zircons will thus experience dissolution-reprecipitation processes at a more prolonged duration and \( \frac{dT}{dt} < 1 \) °C/yr.

Zircon dissolution and survival inside and outside of intruded dikes and sills

Zircon dissolution, core survival, and regrowth in Zr undersaturated sills depends on the timescales of their cooling (Fig. 10). The progress of dissolution depends on the duration at each changing temperature step as the diffusion coefficient and \( C_{sat} \) are temperature-dependent. Zircons
of 40-100 µm radius provide good marker points for the dissolution of the median to the largest zircon sizes within a population. The individual rock cell size around each zircon was 0.7 to 1.7 mm, which was computed based on observed zircon sizes (Table 1) and constant whole-rock Zr concentrations, we chose 220 ppm total Zr for country rocks and 110 ppm for intruded sills. This choice assumes that Zr concentration doubles upon cooling and 50% crystallization of an originally 950 °C silicic sill when it reaches thermal equilibrium with the country rocks assuming that T-composition relationship (Fig. 4c), or generic liquid line of descent, is the same for the sill and the country rocks. This is analogous to silicic magma accumulation zones, where different batches of zircon-saturated liquids stall, crystallize, give up heat, and undergo ~ 50% differentiation (e.g. Bea, 2010).

The T-t history of each melt volume inside and outside of the sill may have four outcomes:

1) all zircons of certain size dissolve completely and never reprecipitate; 2) zircons dissolve completely but reprecipitate (e.g. Fig. 9, Fig A4) leaving no inherited cores and resetting U-Pb, O, and Hf isotopic information as well as trace element signatures; 3) zircons partially dissolve but are overgrown by a new rim with isotopic and chemical characteristics of the new melt leaving behind zircons with inherited cores; 4) zircons are minimally affected during heating due to short duration and/or small magnitude of temperature perturbation and no rim growth occurs.

Zircon dissolution/reprecipitation within a dike/sill

Fig. 11 presents modeling results for \( R = 40 \mu m \) zircon dissolution inside of 0.74 mm cell with \( \Delta U=100 \) ppm Zr undersaturation corresponding to a bulk rock Zr concentration of 120 ppm. This rock cell with zircon in the center is then placed in different positions inside of a sill of given thickness. The following observations can be made: (1) sills will only dissolve zircons in their slowly cooled interior when there is sufficient time for dissolution to occur, while the rapidly cooling contact zones of the dikes/sills will cool too rapidly for zircons to dissolve, and (2) the proportion of interior sill thickness with complete zircon core obliteration increases as the square root of sill thickness. Sills thinner than 10 m half-thickness will dissolve only the outer 1 µm on
typical zircons, sills with 50 m half-thickness will completely dissolve 30% of zircon external
radius. Sills with a >200 m half thickness will be able to dissolve 30-35 µm, or 80% of external
radius of zircons in within 4/5 of sill’s interior portion on timescales of their cooling. Inside of
thicker sills, zircons with radii $\bar{R} = 40$ and 100 µm dissolve rapidly in 16 and 19 years,
respectively, regardless of the size of the sill. This suggests that for thick sills it is the kinetics of
zircon dissolution at high temperature and at given undersaturation that controls the dissolution
time, not the sill cooling timescales. For thinner sills, the main control on zircon dissolution is the
rate at which the sill cools.

Zircon dissolution/reprecipitation in country rocks heated conductively by a dike/sill

Next, we place the same zircon cell with $\Delta U=0$ (thus in $C_{sat}$ condition at 650 °C) outside of
the sill (Fig. 12) to observe dissolution then growth process as the heat wave passes. Modeled
zircon survivability has the same simple relations of sill thickness vs. distance from the sill (Fig.
12) and rapid transitions from complete dissolution to minimal change as in the sill interior. Zircon
dissolution time, however, is always long and is controlled by the temperature history of each
dissolving zircon inside of a melt pocket (Fig. 9-10). Thin sills will produce smaller and shorter
heat spikes then thicker ones. Zircons in areas 100 m away from a 300 m thick sill will only start
dissolving ~500 years after sill intrusion, and zircons reach minimum size in 3000 years before
starting to regrow. This situation is analogous to the influence of Basistoppen Sill on Sandwich
Horizon in the Skaergaard Intrusion 100 meters away (Wotzlaw et al., 2012) dated by ID-TIMS to
have experienced a geochronologically-recognizable several thousand years delay of dissolution
after Basistoppen intrusion.

An increase in sill temperature obviously increases the zone of complete dissolution of
zircons in country rocks, and this relationship is a simple linear function of sill half thickness (Fig.
13). Thick (>200 m) sills are capable of obliterating zircons (thus erasing their U-Pb geochronologic
and isotopic information) at comparable distance to their own thickness in this realistic 0.7 mm cell.
The farthest areas will experience zircon dissolution many thousands of years after sill intrusion.
This observation predicts a spatial distribution of ages younging outside of the sill for many thousands of years, a timescale that is now resolvable by ID-TIMS. This should both set up limits for dating thermal “episodes” using zircons that can be treated as “periods” lasting thousands of years (Fig. 17, A4). Spatial distributions of ages in the field and their recognition in accordance with our simple theory may also set up a natural test for future geochronology efforts.

Sill intrusion into country rocks of different temperature

We also model sills with half thicknesses of 100 m, a constant temperature of 1200 °C, but variable initial country rock temperatures between 450 and 650 °C (Fig. 14), representing environments ranging from cold hydrothermal systems to the lower or mid-crustal wet granite solidus. We used the same 40 µm zircons within the large 1.5 mm and the small 0.7 mm cell used above. Diffusion was allowed to proceed even at the lowest temperature, assuming zircon was always surrounded by a sphere of melt at the temperature of the country rocks. As the lowest 450-550 °C temperatures are below the granitic eutectic, the interstitial melt can be imagined as an interstitial pegmatitic/hydrothermal solution, which can exist at such temperatures (Tuttle & Bowen, 1958; Lundstrom, 2009), although the rates of dissolution are negligibly small on the short timescales of heat wave migration at these low temperatures. For simplicity, we avoided bulldozing effects and major minerals were taken to contain microzircons and $K_{Zr}$=1, thus partial melting did not cause an additional undersaturation with respect to Zr.

For 1.5 mm diffusion cells, zircon dissolution proceeds far away from the sill, and the dependence of the size distance of zircon obliteration zone on country rock temperature is exponential: The 450 °C rocks have 13 m next to the sill with obliterated zircons; for 600 °C rocks this zone expands to 140 m, while the hottest 650 °C country rocks loose zircons 600 m away from the sill. The latter requires up to 25 kyr after the sill intrusion to occur. The peculiar feature of zircon dissolution in bigger 1.5 mm cell is the lack of new zircon nucleation over long (30 kyr) durations (e.g., Fig. 9). For 0.7 mm cells, the dissolution proceeds in a correspondingly smaller area of the sill, about half that of the 1.5 mm cell, also with an exponential dependence on rock
temperature (Fig. 14). We conclude that country rocks with incipient Zr undersaturation (greater cell sizes with the same zircon size in the middle) can loose zircons by heat coming from a relatively small sill.

**Effects of major mineral crystallization, bulldozing, and precipitation of microinclusions of zircon**

In this paper we implemented a boundary condition with two independently moving boundaries (Fig. 3), which permits to explore the effect of major phase crystallization on Zr concentration inside of the shrinking or expanding melt cell volume, and of kinetically-induced Zr enrichment on the outer boundary.

**Volumetric effects of major phase crystallization**

Crystallization of major phases effectively shrinks the cell-size and melt volume available for Zr diffusion toward growing crystal. Because of the cubic relationship between sphere’s volume and the radius, this influence on zircon cell size is insignificant: 50% volume crystallization of the outer radius is only 11% of the sphere’s outer radius, and thus diffusion distance. Conversely, 99% inward volume crystallization leaves 13% of the radial distance corresponding to 1% melt volume around zircon. Such relationships permit modeling of very low degrees of crustal melting around commonly-sized 10-100 µm radius zircons inside of 0.3-3 mm wide cells (Fig. 2).

The main influence of crystallization is to increase Zr concentration in the melt, thus changing Zr saturation conditions inside of the cell. At small degrees of 10-20% crystallization these compositional changes are less significant, but the large temperature change at this crystallinity has a large effect on $C_{sat}$ (Fig. 4). However major phase crystallization effects are dramatic for the greater crystal percentages at lower T (e.g. near eutectic) realized in subvolcanic, plutonic rocks and migmatites. Near the eutectic, changes in T are insignificant relative to changes in crystallinity, thus $C_{sat}$ conditions and Zr concentration in melt does not change much due to...
temperature, but may change significantly due to melting or crystallization of Zr-free or poor
major phases. Upon heating, the melt boundary of the cell retreats leaving behind Zr-free, high M-
factor melt (aka egg white, Fig. 3) that surrounds zircon with its $C_{\text{sat}}$ melt shell $s < r < R$ (Fig. 3,
aka yolk), this egg white will have zero Zr concentration in the initial melt, which will also have higher
M factor, capable of greater solubility of Zr. Such a nearly isothermal, eutectic scenario will result
in conditions of almost unlimited radial Zr diffusion into infinite space from the dissolving zircon,
leading to its accelerated disappearance. The additional effect of the major phases on zircon
survival and the diffusion conditions around them is through compositional and M-factor
variations that accelerate or decelerate zircon dissolution and growth (Fig. 4b).

Kinetic effects

The advancing/retreating outer crystal melt boundary with rate $W$ (Fig. 3) may “bulldoze”
in high concentrations of Zr that will affect the Zr diffusion profile and thus zircon growth or
dissolution histories. Upon rapid crystallization, our numerical model predicts significant increases
in Zr concentrations due to the major phase crystallization (Fig. 15). Watson and Muller (2009)
additionally considered the effects of trace element partitioning into zircon due to non-equilibrium
crystallization. As our model does not implicitly consider zircon nucleation, in order to create the
appearance of zircon microinclusions inside of major phases, one can set up the increased bulk
partition coefficient $K_{\text{Zr}} = (\text{major phase with } 0 \text{ ppm Zr plus zircon microinclusions with } 490,000
\text{ppm Zr})/(\text{concentration of Zr melt})$. The choice of $K_{\text{Zr}}$ can be governed by the $\Delta C = C_{\text{sat}} - \Delta U$
concentration of Zr in the bulldozed outer zone, to keep it from kinetically increasing to
“unreasonably high” concentrations defined by user. It is unrealistic for example to expect Zr
oversaturations to exceed tens of ppm without nucleation (e.g. Bacon, 1989).

Our experimentation documents that cooling rates of 0.1-1 °C/yr characteristic of 950 °C
dikes and sills intruded into 650 °C rocks (Fig. A3) generate significant bulldozing effects. Such
cooling rates correspond to maximum major mineral growth rates of 0.5 vol%/yr in our model.
However, numerical experimentation with a 600 m sill intruded into hotter 750 °C rocks is
characterized by much slower cooling rates on the order of 0.01-0.04 °C/yr and there are no bulldozing effects. Such cooling rates result in 0.04 vol%/yr major mineral crystallization. Zircons grow to the same size whether at $K_{Zr} = 0.01$ or 1. $K_{Zr}$ in the range of 0.1 to 0.3 are most appropriate for realistic cooling rates, and $K_{Zr} = 0.9$-1 for most extreme cases of rapid cooling, and major mineral bulldozing effects (Fig. 15).

Other accessory minerals

We have also performed analogous modeling with other accessory minerals for which solubility and diffusion have been determined: apatite (Harrison & Watson, 1984) and monazite (Rapp and Watson, 1986); results of these are presented in Fig. 16 with separate code lines in the MATLAB program in the Appendix. While dissolution of monazite and apatite into an infinite volume of melt with maximal undersaturation is more rapid in equivalent conditions to zircon (due to the slower diffusion coefficient of the later), dissolution in a cell of identical size is comparable, because it is primarily determined by the kinetics of temperature increase, rather than individual rates of diffusion of Zr, P, and REE into infinite space. Given the usually large sizes of apatites compared to zircon, dissolution in limited cells may in theory lead to equal or even better preservation of apatite than zircon. Again, it is the cell size and saturation conditions within the cell that determines the relative survivability of accessory minerals. We notice that experimentally-determined diffusion coefficients of P, Y and REE as compared to Zr exhibit large variations in activation energies (Rapp & Watson, 1986) and the choice of diffusion coefficients sometimes determines the outcome especially when propagated to a lower T range. New and better-controlled lower T (700-800 °C) diffusion experiments are required.

Other factors influencing zircon dissolution

We next briefly discuss other factors that can modify zircon dissolution rates. Although we investigated conductive regimes of heat transfer, convection in sills will have a limited influence by accelerating zircon dissolution. Convection raises up contact temperatures to higher than the
half difference \((T_d-T_c)/2\) between the magmas and country rocks in contact (Fig. 10b), proportional to the intensity of convection and the Nusselt number (Huppert & Sparks, 1988).

Convection also keeps \(T_d\) more uniform throughout the sill, but the overall duration of time of high \(dT/dt\) regime is shorter, providing little benefit to zircon dissolution. Convection in sills, and its effect on maintaining higher temperature in the interior, can be taken from numerical experiments of Bea (2010) and Simakin and Bindeman (2012). The latter data for thin convective 7-30 m sills is available and when compared to conduction of sills of equivalent size, it demonstrates factor of ~1.5 more rapid initial temperature drop inside of the sill during convection, followed by the cessation of convection and prolonged conduction in a crystal-locked state (Bea, 2010). On the outside of the sill, convective rise of the contact temperature is short-lived. Thus, convection leads to little or no benefit to zircon dissolution, but it plays an important role in mixing zircons of different dissolution histories and isotopic values together within a cooling sill or a magma body (e.g., Bindeman and Simakin, 2014).

Another factor is the relative motion of melt and zircon that sharpens diffusive gradients and may theoretically accelerate growth/dissolution. The process can be scaled through the Peclet number \(\text{Pe}=\frac{V L}{D}\) times the melt viscosity (Levich, 1962). The analytical solution of Levich (1962) for formula to be valid and cause advective acceleration of dissolution is for \(\text{Pe}\) greater than ~1. For zircon sinking in a silicic melt with a viscosity of 10\(^6\) Pa-s a typical zircon with \(\rho = 4.6 \text{ g/cm}^3\) and \(\Delta \rho = 2.3 \text{ g/cm}^3\) and radii of 40 and 100 \(\mu\)m will experience Stokes settling of 1.1 and 6.9 mm/year (10\(^{-9}\) and 5*10\(^{-8}\) cm/s), Peclet number of <1, insufficient to make any difference. Because of the slow diffusion of Zr in melt (10\(^{-12}\) cm\(^2\)/s), sinking therefore plays an insignificant role in zircon dissolution/crystallization.

**Implication for precise U-Pb geochronology**

Our models on zircon dissolution and recrystallization above suggest directions for improving geochronology, isotopic, and trace elemental studies of zircons. Chemical abrasion ID-TIMS methods (Schoene & Schmitz, 2007; Schaltegger *et al.*, 2009) targets single or partial zircon
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grains and often relies on the six to eight youngest grains as recording the last magmatic episode, while older grains (that are impossible to date with enough precision by in situ ion microprobe methods) are called antecrysts or xenocrysts. U-Th methods for the youngest rocks permit high precision in situ analyses (Charlier and Zellmer, 2000; Strom et al., 2011; Carley et al., 2012; Stelten et al. 2015).

Figs. 17 and A4 (Appendix) models bulk U-Pb age evolution in the case of complete zircon dissolution followed by growth at different distances from the sill over the conductive cooling timescale of a 500 m thick sill with either 950 °C or 1200 °C initial temperatures, on natural timescales of their cooling in 650 °C country rocks. At distances ranging from 10 to 500 m from the sill, an initial 40 µm radius zircons will completely dissolve, but new zircon will reappear after 12-16 ka as the partially molten rock cools below zircon saturation. While theoretically zircon should grow to the original zircon size of 40 µm within each cell, the last 2-3 µm outer radius will take exceedingly long time due to decelerating cooling rates, and if crystallizing minerals will take some Zr (Fig. 3), zircon will remain smaller.

We plotted zircon age since its regrowth and observe nearly linear relationship of age vs % of crystallized zircon volume (doubled-arrowed lines on Fig. 17), and compare these with in situ dates by U-Th disequilibrium methods for cores and outer rims of zircons by Stelten et al. (2015) for three young Yellowstone lavas. These lavas: Grants Pass, West Yellowstone and Pitchstone Plateau erupted sequentially between 118 and 75 ka from approximately the same area in Yellowstone caldera along its western lineament, and contain rims identical to the eruption age and cores that are offset by tens of thousand of years (Table 5 of Stelten et al. 2015). These authors interpreted these zircons as antecrysts inherited from a single caldera-wide, evolving crystal mush requiring no thermal perturbation (as their other data seems to shows). We notice in their data, earlier datasets from Vazquez and Reid (2002), and Watts et al. (2012) that most zircon volume in each lava is U-Pb rejuvenated and is of eruption age, and core age is offset from rims by a fixed amount, and both the cores and the rims get progressively younger in each successive lava. A possible alternative explanation is that each of these lava flows represent punctuated sequestration
of melts, in which their protolith (progressively more differentiated rock or mush) of each earlier lava flows are parental to the subsequent lava and magma batch with rejuvenated zircons. **Fig. 17**

tests this possibility and demonstrate that an incrementally intruded (e.g. Annen and Sparks, 2002) 500 m-thick hot sill (aka “hot plate”) is capable of not only rejuvenating the preexisting crystal mush or a solid rock in required proportions, but does so robustly above zircon saturation to at least 850°C as is required by phase equilibria (Almeev et al 2012), and high oxygen isotopic temperatures (Loewen and Bindeman, 2015). Thinner and colder sills will induce less remelting and preserve some zircon inheritance farther from their contact. The subsequent cooling and crystallization of sequestered high degree melts will proceed >50%, reach zircon saturation and generate the observed zircon core-rim relationships observed by Stelten et al. (2015).

The modeling on **Fig. 17** also demonstrates that upon complete dissolution and continuing cooling, zircon will delay its new crystallization for up to 10-30 kyr, erasing xenocrystic memory, but then reappear and grow with a nearly linear dependence of volume with time (**Fig. 17, A4**). If dated by IDTIMS methods, its average age will be an integral of this linear function after a delay. While zircon air abrasion is now almost an abandoned practice, we recommend performing it on zircons prior to ID-TIMS dating to get even better recognition of zircon crystallization interval and to determine the slope. Running large and small zircons (e.g. Charlier and Zellmer, 2000) and consideration of details of zircon CSD (e.g., Simakin and Bindeman, 2008) should also become a common practice. Given simple linear relationship observed, small crystal, bulk and an abraded core of a large crystal should enable simple reconstruction of age-volume relationship, and thermal histories of a rock.

**Diffusion profiles around dissolving grains**

We used our code to model the measured Zr concentrations in glass around a 80 μm zircon from a Yellowstone’s Summit Lake flow (**Fig. 18**, see Loewen and Bindeman, 2015 for data and petrological context). Increase in Zr concentration close to the zircon boundary demonstrates the preservation of a quenched dissolution profile around zircon. Given diffusion distances, the
heating event that caused this dissolution lasted only several months and requires preeruptive
magma temperature increase by 13°C. In order to be preserved, and eruptive quench lasting
<0.05yr is required, and the heating even can be speculated to be as preeruptive or as an eruption
trigger. This natural documentation of preserved profiles in glass around dissolving zircon creates
a tool for learning about timescales of magmatic processes that can be directly modelled using the
code presented here. Given sometimes thin (tens of microns) profiles, the use of NanoSIMS may
be required to resolve details in the ~5-10 µm range around a dissolving crystal, and in particular a
hump in Zr concentration related to temperature change (Fig 18).

CONCLUDING REMARKS

Our modeling captured the main features of zircon behavior upon crustal melting through
cycles of dissolution-nucleation and growth, and we observe a wide and quantifiable range of
controls and outcomes that can be of practical use and predictive value for user-specific situations.

1) Approximation equations 10-11 predict lifelines of zircons of different size as a function of
temperature and Zr undersaturation.

2) Elementary cell size has fundamental significance in survivability of zircon and other
accessory minerals. For a given cell size, even mild temperature fluctuations in Zr
undersaturated rocks (e.g. amphibolites) lead to zircon disappearance and no new growth
upon cooling; likewise zircon in Zr oversaturated rocks (gneisses) will experience
overgrowth upon melting.

3) Dissolution of other accessory minerals, apatite and monazite, made of slow diffusing 3+
and 5+ elements with low saturation levels have comparable lifelines upon heating that are
controlled by the cell sizes and temperature histories of the rock, in far greater extent than
relative diffusion differences between constituent elements of these minerals.

4) Consideration of temperature histories in and around cooling dikes and sills predicts
alternating areas of complete disappearances of cores and areas where cores survive and are
overgrown by rims. As zircons inherit O and Hf isotopic values from their immediate melt
cell, even a single thermal episode can generate isotopic diversity of zircon population.

5) Zircon ages get younger away from the sill as the heat wave propagates, resetting ages
sometimes with a delay of $10^3$-10$^4$ years after the sill intrusion and we observe simple near-
linear increase of zircon volume with age of crystallization resulting from conductive
cooling timescales; this should enable two-point determination of cooling duration by in
situ or ID-TIMS methods, by relying on cores and rims of zircon.

6) For zircon-rich rocks, only the largest >200 m igneous bodies are capable of complete
dissolution/reprecipitation of typically sized zircons at significant distances from the
intrusion while in Zr-poorer rocks loose zircons many diameters of the sill away. Smaller
intrusions result in partial dissolution and rim overgrowth.

7) Co-crystallization of surrounding major mineral provide accelerating effects on zircon
growth due to bulldozing effect of Zr. Large Zr oversaturation on the boundary may result
in microzircon crystallization, leading to large effective Zr partition coefficient for major
mineral.

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Jörg Hermann and two anonymous reviewers for careful and insightful internal and external
reviews and editorial comments.

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http://www.petrology.oupjournals.org/
**Figure Captions**

**Fig. 1** Cathodoluminescence images, core and rim ages, dissolution boundaries and isotopic zoning of zircons from Yellowstone (modified after Bindeman et al. 2008). Numbers and distances correspond to the image, core (~0.9 Ma) and rim (0.5 Ma) ages are SHRIMP-derived and demonstrate inheritance of older, high-$\delta^{18}$O cores into low-$\delta^{18}$O magma, upon remelting following caldera collapse of Yellowstone at 0.62 Ma.

**Fig. 2** Schematic model of measured zircon crystal size distribution and particle volume concentrations from sample YTT102 from the Youngest Toba tuff (Table 1). The cell surrounding each individual zircon delineates a volume of diffusional sphere of influence that maintains identical Zr concentration at cells boundaries at equilibrium. Computed distances between large (230 $\mu$m, 3 mm cell) and median (75 $\mu$m, 1 mm cell) zircons are shown.

**Fig. 3** Modelled set up with zircon and melt cell volume and two independently moving boundaries with velocities V and W. The spherical diffusional cell’s radius is L, saturation conditions are maintained at zircon of radius $\hat{R}$ at surface s, Zr concentration, C, at the external melt boundary L is defined through the bulk partition coefficient of a major phase (with zircon microinclusions uniformly precipitated upon crystallization due to bulldozing effects of a major Zr-free phase on contracting melt volume). The rate W of expansion or contraction of the melt volume is a function of a T-X phase diagram (Fig. 4c) and time.

**Fig. 4** M-factor dependencies and phase diagram.

a) M-factor variations as a function of SiO$_2$ for standard USGS rock compositions (from andesite to rhyolite), Yellowstone magmas and feldspar end-members. Notice that quartz-free, feldspar-rich compositions, and lower silica melts have higher M-factors.

b) M-factor dependence on temperature for liquidus compositions of melts shown in a) computed at 3wt% water and computed liquidus in MELTS program. See supplementary material for compositions and temperatures used in this effort.

c) Phase diagram (solidus-liquidus relations) used in this work after crystallization experiments of composition 102 at 2 kb (Piwinski, 1968). The best-fit line is given as
%melt fraction = 1.13656*10^{-9}*T^4-3.8926*10^{-6}*T^2+4.9848*10^{-3}*T^2-2.832*T+602.99,
where T is in °C.

Fig. 5 Dissolution kinetics of a small 10 µm zircon into melt with ∆U = 100 ppm of initial Zr
undersaturation at 950 °C in different cell volumes (cell radius –Distance)

a) 0.3mm cell: zircon dissolves completely to C_{bulk} value of 119 ppm in 1.82 yr. Notice
steepening of the diffusion profile right before complete dissolution at 1.81yr.

b) 0.16mm cell: 5 µm zircon core survives and provide enough Zr to fill the melt cell around it
with C=C_{sat} of 199 ppm.

Fig. 6 Zircon dissolution timeframes for crystals of 100 µm radius, as a function of elementary
cell volume, different temperatures, and degrees of original melt Zr undersaturation, ∆U.
Notice that cells greater than 2-3 mm are "infinite" leading to nearly permanent sharp
dissolution gradients and comparable dissolution times. At 950 °C these times are 100-400
years at 20 and 100 ppm undersaturation, at 750 °C the times are 30-50 ky, due to both slower
diffusion of Zr in melt and lower lower zircon solubility, diminishing the overall diffusive flux.

Fig. 7 a) Dissolution rates of 10 and 100 µm zircons as a function of remaining zircon radius
within 5 mm cell volume at 950 °C for 20 and 100 ppm Zr undersaturation. Notice the increase
do dissolution rate with shrinking crystal size for each case, explained by the increasing
surface/volume ratio. For a small 10 µm zircon, diffusion is essentially an open boundary
condition, while a 100 µm zircon with 20 ppm of undersaturation leads to longest dissolution
time as back diffusion from the boundary of the cell slows the dissolution rate.

b) Growth rates of an originally 5 µm radius zircon at 100 ppm oversaturation within a 5 mm
cell volume, showing a similar growth rate size dependency.

Fig. 8 Linear rock heating from solidus at 650 °C to liquidus at 950 °C at different rates (0.02°
to 10°C/yr) leading to zircon dissolution. Velocity in cm/s refers to moving dissolving zircon-
melt boundary, t/t_{diss} is time normalized to total dissolution time given in years next to each
line. Original zircon radius R =100 µm, remaining zircon radius is shown by tick marks, bulk
cell Zr concentration (zircon + melt) is 220 ppm, computed original cell size is L= 1.72 mm
and expands to 2.2 mm upon major minerals melting, original ∆U =0. At rates higher than 5
°C/yr, the cell’s Zr concentration cannot keep up with the rate of T increase so the zircon
dissolution rates and times to complete dissolution (~50 years) are comparable to dissolution at
a constant 950 °C and the equivalent undersaturation of 185 ppm (C_{sat} difference between 650
and 950 °C, as in Boehnke et al. 2013 formulation).

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Fig. 9 Zircon dissolution and rebirth with a 0.1 °C/yr temperature rise within a variable cell volume. M-factor varies as a function of T. Notice that despite a symmetrical temperature history, zircon size history is not symmetrical as zircon growth is slower after diffusive dispersal of Zr into far fields of melt cell. Zircon will eventually regain its original size but after longer time of diffusive growth at lower T.

Fig. 10 Zircon dissolution inside and outside of a 950 °C, 100 m sill emplaced into 650 °C country rocks.

a) Temperature evolution is based on Crank (1975) conductive cooling.
b) Computed Temperature-square root or time paths.
c) Three zones inside of sill and two zones outside of the sill are shown. Inside of a sill, Inherited zircons are variably dissolved then overgrown on timescales of sill cooling; in country rocks: proximally all zircons dissolved and were replaced by newly precipitated zircons, far away zircon cores survived.

Fig. 11 Zircon dissolution inside of a cooling, originally 950 °C sill of variable thickness

Fig. 12 Dissolution of \( \hat{R} = 40 \) µm zircon in contact aureoles of a conductive dike/sill of given thickness and temperature. Minimal zircon radius is shown as contour lines, \( L = \) melt cell size. Vertical tick marks show years to complete dissolution.

Fig. 13 Effect of sills of various thickness and temperatures on country rocks with zircons leading to dissolution of 40 and 100 µm radius zircons. Vertical tick marks show years to complete dissolution.

Fig. 14 Effect of country rock temperature on zircon survival with a 1200 °C sill of 200 m thickness.

Fig. 15 Buldozing effects of major phase crystallization on Zr concentration and growth rate of zircon inside of a 5 mm cell. Zircon is originally 100 µm captured in the center of a 200 m, 950 °C sill with zircon undersaturation \( \Delta U = 100 \) ppm.

a-c) Conductive cooling history of the sill, crystal proportion, and cooling rate for 1000 years.
d) Evolution of zircon radius at different bulk partition coefficients of Zr between major minerals and melt. Notice initial dissolution of zircon due to original Zr undersaturation of the melt, followed by growth inside of the cell.
e) Concentration profiles of Zr between zircon (left boundary) and major mineral (right)
moving boundaries. Notice in d and e that if major minerals do not take Zr ($K_{Zr} = 0.01$, lack of
microzircon nucleation), significant Zr enrichment occurs near the right boundary that leads to
accelerated zircon growth.

**Fig. 16** Dissolution of 100 $\mu$-m zircon, apatite, and monazite in silicate melt of different SiO$_2$
content with 3 wt% H$_2$O during 0.1 °C T rise from 650 °C to 950 °C. Cell size is 1.5 mm.

**Fig. 17** Progress of volumetric crystallization of zircon in 650°C country rocks upon passage
of a conductive thermal wave from a neighboring 250 m half-thickness, 950°C (a) and 1200°C
(b) initial temperature sills. Distances from the sill outer boundary. Rapid dissolution of zircons
is followed by nearly linear (double-arrowed line) growth of zircon volume vs time. The PP
(Pitchstone Plateau, diamonds), WY (West Yellowstone, squares) and GP (Grants Pass,
triangles) are zircon core and rim ages from the young Yellowstone lavas dated by U-Th in situ
methods (Stelten et al. 2015). Core-rim age difference is placed on our modeled curves, each
requiring host melt crystallization (Fig. 4c) by >50% after thermal rejuvenation by a sill. See
text for discussion.

**Fig. 18** Ion microprobe profile (15$\mu$m spot size) across rhyolite glass from a zircon crystal in the
Summit Lake flow of Yellowstone (sample YS08-05, Loewen and Bindeman, 2015) and modeled
curves (this work). Higher concentrations of Zr in the vicinity of the boundary suggest that zircon
was dissolving for 0.1-0.5 years before the eruption and that this dissolution profile was quenched
by the eruption, likely due to cooling and rapid water loss upon emplacement, leading to a rapid
decrease in water-dependent Zr diffusion coefficients, leading to a rapid drop in Zr diffusion rates
(by 2 orders of magnitude, Zhang et al., 2010;) which is essentially equal to an equivalent
temperature drop of 100 °C, per Eq 1 in text.

Appendix Figures A1-A4
297x210mm (114 x 114 DPI)
Fig. 4

305x213mm (72 x 72 DPI)
Dissolution of 20 μm zircon

T=950°C

ΔU=100 ppm Zr.

Zircon, \( \bar{R} = 10 \mu m \)

166x219mm (72 x 72 DPI)

http://www.petrology.oupjournals.org/
Fig. 6

265x201mm (72 x 72 DPI)
Fig 7a
315x214mm (72 x 72 DPI)
Fig. 15a-c

169x221mm (72 x 72 DPI)
Fig. 18.

$T$ increase from 824 to 837 °C

- ● SIMS data in glass
- heating, 0.5 yrs
- heating, 0.1 yrs
- 0.15 yrs heating then quench
- 0.2 yrs heating, then 0.05 yr slow cooling

$221 \text{ ppm}$

@680 μm

Distance from zircon boundary, μm

293x227mm (72 x 72 DPI)
Table 1. Characterization of sizes, abundance, particle concentration of zircons from major tuffs and lavas and distance between crystals

<table>
<thead>
<tr>
<th>Tuff Sample</th>
<th>Eruptive T Unit</th>
<th>Zr set T °C</th>
<th>% Zr</th>
<th>Zircon cm³</th>
<th>Mean Zircon cm³</th>
<th>Median Zircon cm³</th>
<th>Max Zircon cm³</th>
<th>Mean distance between zircons of given size, mm</th>
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</thead>
<tbody>
<tr>
<td>Bishop (B7)</td>
<td>Late, Long Valley Caldera, CA, 750 km², 0.76 Ma</td>
<td>714</td>
<td>735</td>
<td>9</td>
<td>78</td>
<td>9</td>
<td>12</td>
<td>13.5</td>
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<tr>
<td>LV-27 Early</td>
<td>714</td>
<td>735</td>
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<td>78</td>
<td>9</td>
<td>12</td>
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<td>LV-751 Late</td>
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<td>76</td>
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<tr>
<td>LV-748 Late</td>
<td>817</td>
<td>776</td>
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<td>73</td>
<td>140</td>
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<td>200</td>
<td>51</td>
<td>25.5</td>
<td>345</td>
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<td>Lava Creek (LCT), Yellowstone Caldera, WY, 1000 km², 0.64 Ma</td>
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<td>70</td>
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<td>84</td>
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<td>37</td>
<td>95</td>
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<tr>
<td>Huckleberry Ridge (HRT), Big Bend Caldera, WY, 2500 km², 2.04 Ma</td>
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<td>19</td>
<td>77</td>
<td>328</td>
<td>25</td>
<td>7.6</td>
<td>108</td>
<td>76</td>
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<tr>
<td>HRT-C, C Late</td>
<td>897</td>
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<td>443</td>
<td>33</td>
<td>7.4</td>
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<td>Mesa Falls (MFT), Island Park Caldera, ID, 300 km², 1.3 Ma</td>
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<td>37</td>
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<td>168</td>
<td>49</td>
<td>29.2</td>
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<tr>
<td>Monterey (MT-1)</td>
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<td>29.2</td>
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<tr>
<td>Ammonite Bluffs (ABT), Timber Mountain Caldera, NV, 1000 km², 11.43 Ma</td>
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<td>14</td>
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<td>121</td>
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<td>TM-15 Early</td>
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<td>TM-17 Late</td>
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<td>107</td>
<td>28</td>
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<td>96</td>
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Note: * is measured particle abundance per cm³ of melt.
** Computed from measured zircon CSO and assuming equal spacing to maintain cell's constant Zircon concentration.

See Bird (2003) for CSO and additional information for these samples.
<table>
<thead>
<tr>
<th>Crystal</th>
<th>Zr content</th>
<th>SiO2 ppm</th>
<th>Zr Conc</th>
<th>% Zr</th>
<th>n</th>
<th>Mean Zircon Zircon Zircon Zircon</th>
<th>Zircon</th>
<th>Zircon Zircon</th>
<th>Zircon</th>
<th>Zircon</th>
<th>Total distance between 200um 80um 20um n</th>
<th>of given size** mm</th>
<th>0.76 Ma</th>
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</table>

*See Bindeman (2003) for CSD and additional information for these samples.*
Table 2 Parameters and abbreviations used in this paper

| r | radial coordinate in zircon cell, cm |
| s | zircon surface of radius $\hat{R}$, melt/zircon boundary |
| R | melt cell radius, mm |
| L | rock (melt) cell, mm |
| $\xi$ | non-dimensional linear coordinate |
| V | growth/dissolution rate of zircon, cm/s |
| W | growth/dissolution of the major phases at the outer cell boundary |
| $C_m$ | is the concentration of zirconium in the melt, |
| $C_z$ | 490,000 ppm is Zr concentration in zircon |
| $C_x$ | concentration of Zr in a major phase |
| $C_{bulk}$ | Bulk Zr concentration in a rock or cell (zircon plus melt) |
| $K_{Zr}$ | bulk Zr partition coefficient between major phase and melt, $C_{Zr,major}/C_{Zr,melt}$ |
| $C_{sat}$ | T and M-factor dependent saturation concentration (Watson and Harrison, 1983; Boehnke et al., 2013) |
| $\Delta U$ | Zr undersaturation relative to $C_{sat}$, ppm of Zr |
| M | M-factor, $=(\text{Na+K+2Ca})/(\text{Al}\cdot\text{Si})$, where elements are given in molar proportion inside of 1 mol of silicate melt |
| $D$ | diffusion coefficient of Zr in melt, dependent on temperature $T$ and $X_{H2O}$, m$^2$/s |
| $X_{H2O}$ | water wt% fraction in melt |
| $T$ | temperature, °C or °K |
| $T_{eutectic}$ | eutectic temperature, °C |
| $T_d$ | Temperature of the dike/sill |
| $T_c$ | Temperature of the country rocks |
| X | composition, % crystal |
| k | thermal diffusivity in rocks and magmas, $0.6\cdot10^{-6}$ m$^2$/s |
| h | dike/sill thickness, m |
| x | linear coordinate from dike/sill center outward, m |