1 **Zircon U/Th Model Ages in the Presence of Melt Heterogeneity**

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4 **Abstract**

5 In situ U-series zircon dating has yielded unique insights into magmatic
6 processes and the complexity of zircon crystallization. However, the approach
7 requires some knowledge of the state of isotopic disequilibrium of the melt from
8 which zircon crystallizes. Current practices for correcting initial ²³⁰Th include use of
9 an isochron array (defined by with several coexisting zircons) or two-point
10 isochrons based on a tie between each zircon with a common glass (or whole rock)
11 measurement. However, magmas are complex and measured U/Th in zircons from
12 a single extrusive can vary by up to a factor of seven, casting doubt on the
13 assumption that a single glass composition is representative of the magma from
14 which each zircon crystallized. We propose a correction scheme using the
15 measured zircon ²³⁸U/²³²Th, a U/Th partition coefficient ratio between zircon and
16 melt, and the observation that most magmas are within 15% (1σ) of the equiline.
17 Using this correction scheme, we show that uncertainties can be underestimated by
18 up to a factor of three and that published dates are potentially biased towards older
19 ages.

20 **1 Introduction**

21 Detailed insights into magmatic processes require high-temperature and -
22 spatial resolution chronometers with age resolutions of thousands to tens of
23 thousands of years. Two systems that meet these criteria are U-Pb isotope dilution-

thermal ionization (ID-TIMS; Barboni and Schoene, 2014) and in-situ U-series disequilibrium (Reid et al., 1997) zircon dating. While recent advances in precision and accuracy of ID-TIMS U-Pb dating of very young zircons have been significant (e.g., Schoene, 2014), the time-intensive nature of the method limits its widespread application and/or the size of data sets. By contrast, in-situ U-series dating, either by secondary ion mass spectrometry (Reid et al., 1997) or laser ablation inductively coupled mass spectrometry (Bernal et al., 2014), requires minimal sample preparation permitting data output at a high rate. For zircons younger than the time over which secular equilibrium is achieved (~ 400 ka; Allegre and Condomines, 1976), in situ disequilibrium dating has provided unparalleled insights into magmatic timescales and the complexities of zircon crystallization. Indeed, the first application of this approach (Reid et al., 1997) showed that volcanic zircons typically crystallize well prior to eruption when the phase becomes saturated in the magma (Watson and Harrison, 1983; Boehnke et al., 2013), potentially over half a million years prior to the time of eruption (Wotzlaw et al., 2014). Other applications of this method include dating very young volcanism (Schmitt et al., 2013; Wright et al., 2015) and determining the provenance and nature of archeological materials and sites (Coffey et al., 2014; Schmitt et al., 2014).

Disequilibrium dating using ^{230}Th exploits both the relatively short half-life (~ 75.5 ka; Cheng et al., 2013) and the strong fractionation of U from Th during zircon growth. Upon crystallization, ^{230}Th ingrows from the decay of ^{238}U , slowly erasing the initial ^{230}Th deficit until secular equilibrium is attained. Since typically only one phase (i.e., zircon) is analyzed for in-situ U-Th dating methods, as opposed

to the associated whole rock, one of the major challenges in calculating accurate ages from the measurements of ^{230}Th , ^{232}Th and, ^{238}U in zircon is determining the initial $^{230}\text{Th}/^{232}\text{Th}$ [$(^{230}\text{Th}/^{232}\text{Th})_0$]. In the case of in situ zircon U-series disequilibrium dating, use of an isochron array is not possible in general due to the lack of other phases with differing U/Th for which it can be clearly established that they are crystallizing concurrently and have sufficiently high U and Th concentrations to permit in-situ analyses. This limitation also holds for U-Pb zircon dating, but the highly radiogenic nature of most signals permits non-radiogenic daughter subtractions using an assumed value (e.g., lab blank for TIMS or modern Pb for SIMS; Schoene, 2014; Ireland and Williams, 2003). This method is only viable if the half-lives of the daughter isotopes are much longer than the timescales of interest. In a similar way, U-series zircon disequilibrium dating uses two analogous methods for correcting $(^{230}\text{Th}/^{232}\text{Th})_0$. The first is use of an 'isochron' (as defined in Schmitt, 2011), a linear regression through multiple zircon data in which the slope is proportional to age. The key difference in disequilibrium dating to a traditional isochron is that zircon crystallization or another fractionating mechanism must be changing the melt U/Th significantly in order to create a spread in the zircon U/Th (U/Th always refers to $^{238}\text{U}/^{232}\text{Th}$) results (Fig. 1 A and B show an idealized case). In contrast, a traditional isochron uses multiple phases with different partition coefficients to create a spread in the parent/daughter. For the 'isochron' approach to yield a useful date, the zircons must crystallize relatively rapidly, thus the 'isochron' is limited in application to cases where zircons crystallized in discrete batches (e.g., Fig. 2a in Schmitt, 2011).

The second $(^{230}\text{Th}/^{232}\text{Th})_0$ correction scheme is to measure a sample of glass (or whole rock) and assume that it was in equilibrium with each zircon (i.e., each date is calculated from a two-point zircon-glass isochron; Reid et al., 1997). This approach has two key requirements: 1) that the magma is chemically homogeneous and 2) the magma is in equilibrium between the production and loss of ^{230}Th (i.e., on the equiline). The second assumption has to be made because otherwise the melt value has to be age corrected for each zircon isochron, however this is not possible as the age for the correction is not known a priori. Therefore, using melts that are not in secular equilibrium biases age determinations. For further detail we refer the reader to Schmitt (2011).

However, melts by their very nature change composition throughout the magmatic process (e.g., Bachmann and Bergantz, 2004; Schmitt, 2011). Previous workers have argued that these changes are minor (Reid et al., 1997; Schmitt, 2011) due to the generally high U/Th of zircon in relation to the melt (i.e., that variations in $(^{230}\text{Th}/^{232}\text{Th})_0$ lead only to minor corrections). The basis of this assumption is the claim that higher U/Th zircons have a correspondingly higher fraction of ^{230}Th from radiogenic ingrowth compared to low U/Th zircons (Reid et al., 1997).

However, as zircon has an essentially fixed ratio of U and Th partition coefficients ($K_{\text{zir}/\text{melt}}^{\text{U/Th}} \sim 6$; Schmitt, 2011), a high U/Th zircon must have crystallized from a high U/Th melt and vice versa. A high U/Th magma will also have a higher $^{230}\text{Th}/^{232}\text{Th}$ than a low U/Th magma because $^{230}\text{Th}/^{232}\text{Th}$ directly tracks U/Th, even on short (10's of thousands of years) timescales. This system stands in contrast to those involving longer half-lives such as Rb/Sr, where $^{87}\text{Sr}/^{86}\text{Sr}$ does not change

significantly over magmatic timescales. Therefore, variations in $(U/Th)_{zir}$ could potentially bias age determinations (see Fig. 1 C and D for illustration) that assume that a single melt composition accurately characterizes a global $(^{230}Th/^{232}Th)_0$ due to the rapid decay of ^{230}Th . Indeed such evolution in $(U/Th)_{melt}$ has been demonstrated for the Long Valley rhyolite (Heumann et al., 2002).

In order to assess the significance of magma heterogeneity on age calculation, we compiled a database of zircon U/Th. Our compilation (references cited in Fig. 2 caption) shows variations in $(U/Th)_{zir}$ between 1 and 7 (Fig. 2). This range of U/Th shows that the melt from which zircons crystallized was chemically heterogeneous and changing on timescales comparable to that of zircon crystallization. We explore this source of uncertainty through an alternate correction scheme where the melt is constrained to be in the proximal vicinity of the equiline through an actualistic model. We confirm the broad observations derived from U-series zircon disequilibrium dating (e.g., pre-eruptive zircon growth) but show that specific age and uncertainty determinations for zircons in geochemically complex magma chambers can be significantly misestimated.

2 Method

Zircon data from the Belfond Dome, Lesser Antilles (Schmitt et al., 2010), nicely illustrate the complexities introduced by a spread in $(U/Th)_{zir}$. Specifically, we use zircon data for samples SL-25 and SL-51 that are not in secular equilibrium (Schmitt et al., 2010). These zircons show both a large spread in U/Th and apparent age, providing a clear demonstration of our new correction scheme for zircon U/Th

model ages. We also use the results for depth-profile analyses performed on zircons SL-25-35 and SL-25-38 (Schmitt et al., 2010).

2.1 Partition Coefficients of U and Th

Meaningful modeling of data with heterogeneous $(U/Th)_{\text{magma}}$ requires accurate knowledge of U and Th zircon/melt partition coefficients. Selection of this parameter requires care as Luo and Ayers (2009) convincingly demonstrated the limitations of present experimental methods in determination of zircon/melt partition coefficients due to kinetic effects during crystallization (e.g., Watson, 1996). We believe that the most accurate D_U/D_{Th} is that estimated from natural samples. We used zircon and glass data from the Salton Buttes rhyolites, California (Wright et al., 2015) due to their young eruption ages and limited spread in U/Th (suggesting limited magma evolution). We supplement the data by Wright et al. (2015) by also considering the partition coefficients presented by Stelten et al. (2015). Using an unweighted average of six datasets ($MSWD \approx 0.63$; $n = 6$), we calculate $K_{\text{zir}/\text{melt}}^{U/Th} = 7 \pm 0.40$ (1σ) by dividing the $(U/Th)_{\text{zircon}}$ by $(U/Th)_{\text{glass}}$ which is similar to the value of ~ 6 suggested by Schmitt (2011). Any inaccuracies in $K_{\text{zir}/\text{melt}}^{U/Th}$ will present a systematic uncertainty and do not affect the calculated spread in $(U/Th)_{\text{magma}}$ or the relative difference in ages as we use the same partition coefficients for all our calculations.

2.2 Variations in $(^{230}\text{Th}/^{232}\text{Th})_{\text{magma}}$

If every magmatic system evolved strictly along the equiline, then we could simply calculate each age by assuming the melt from which the zircon crystallized was in isotopic equilibrium. As we have noted from examination of numerous

datasets, this appears not to be true in most cases. Thus for our model, we need to estimate the typical variation of the melt with respect to the equiline during zircon crystallization. We compiled a database of whole rock and glass ($^{230}\text{Th}/^{232}\text{Th}$) and ($^{238}\text{U}/^{232}\text{Th}$) measurements to examine the natural spread in these parameters. We did not age correct our values and it is therefore possible that some values would plot further from the equiline than shown. However, as most of the rocks in our compilation are sufficiently young we do not perceive this as a significant bias. The data shows that melts can be off the equiline by up to 50% (Fig. 3) but we calculate a standard deviation for their variance from the equiline of 15%. Glass analyses plot in a more restricted range because whole rock analyses likely include accessory phases that can significantly fractionate U from Th. For our purposes, whole rock analyses are more representative of the melt but we include glass analyses in our calculation for completeness. Assuming that this is globally representative, we use this value as an input parameter in our modeling.

2.3 Model

For each zircon, we calculate a $(\text{U}/\text{Th})_{\text{magma}}$ based on knowledge of $K_{\text{zir}/\text{melt}}^{\text{U}/\text{Th}}$ (see 2.1). From the $(\text{U}/\text{Th})_{\text{magma}}$ we calculate a $(^{230}\text{Th}/^{232}\text{Th})_{\text{magma}}$ using the assumption that the melt is within 15% (at 1σ) of the equiline (i.e., $^{230}\text{Th}/^{238}\text{U}_{\text{magma}} = 1 \pm 0.15$) and then calculate a two-point isochron date. This procedure is repeated for each zircon.

Propagating uncertainties through our new model is accomplished by a parametric bootstrap resampling method (Efron, 1979). That is, we perform each calculation 1000 times and sample the corresponding data from their uncertainties

(e.g., for the $(^{230}\text{Th}/^{232}\text{Th})_{\text{magma}}$ we use a normal distribution with a mean on the equiline and a relative standard deviation of 15%).

Our model is implemented in Python version 3.4.2 and uses numpy (Van Der Walt et al., 2011) for the array structure and mathematical functions.

3 Results

Given the broad spread of U/Th recorded by SL-25 and SL-51 zircons, there is a correspondingly broad range of calculated $(\text{U}/\text{Th})_{\text{magma}}$ (Fig. 4). These variations appear random for the individual zircons (open symbols, Fig. 4) but smooth for the depth profile analyses (closed symbols, Fig. 4).

Our modeling shows that the additional uncertainty due to the lack of knowledge regarding the U/Th of the melt typically increases the errors from 5-10% to 30% for young zircons. Further, young dates are generally biased to older ages (Fig. 5) while older dates could be biased young. At this time, due to the high uncertainty on the melt composition, these biases are not significant at the 2σ level. However, despite the large uncertainties, the age changes could be geologically significant. For example, the Belfond dome data (Schmitt et al., 2010) imply a gap in zircon crystallization between ~ 20 ka and the eruption at ~ 14 ka. Using our correction, the evidence for episodic crystallization is reduced as the ~ 20 ka dates shift down to ~ 14 ka, albeit with much larger uncertainties.

4 Discussion

4.1 Time variation or heterogeneity?

Since it is clear that zircon crystallization is capable of rapidly altering melt U/Th, it is possible that the variance in this parameter in other systems is due to

time variation rather than heterogeneity. Indeed, Charlier and Zellmer (2000) observe temporal variations in magma U/Th in zircons from the Taupo Volcanic Zone, New Zealand. However, since the Belfond Dome lava has multiple coexisting $(U/Th)_{\text{magma}}$ (Fig. 3), changes in $(U/Th)_{\text{magma}}$ would need to occur often and at rates higher than the age resolution of U-series disequilibrium dating. This finding implies that $(U/Th)_{\text{magma}}$ is not controlled by a single dominant process (e.g., accessory phase crystallization), but appears to vary often and due to other processes. We further note that the variations in $(U/Th)_{\text{magma}}$ among individual zircons is larger than that from the two depth-profiling analyses. This is the expected results as the depth-profiling results show that melt U/Th changes slowly, if at all, and is different between zircons. This suggests that the melt is compositionally heterogeneous and that zircons record only their local environment.

Both of these interpretations are consistent with the findings of Bourdon et al. (1994) that major and accessory phases can significantly fractionate U/Th. For example, sphene and amphibole record lower U/Th than coexisting feldspar and glass, respectively (Bourdon et al., 1994). Therefore, magmatic evolution or reheating a cold mush (Cooper and Kent, 2014) could result in both time varying and heterogeneous $(U/Th)_{\text{magma}}$.

4.2 Changing D_U/D_{Th} ?

Given the complexities of experimentally determining zircon partition coefficients and the general lack of agreement among various studies (see review in Hanchar and van Westrenen, 2007), it is worth considering if the variations we

emphasize could be solely due to differences in partition behavior. We find this an unlikely explanation because factors such as temperature and pressure are likely to change both partition coefficients in similar ways (i.e., their ratio is unaffected; Luo and Ayers, 2009). Indeed, at constant pressure and entropy, changes in individual partition coefficients are linear in $1/T$ such that their dependence would systematically cancel and thus not affect $K_{zir/melt}^{U/Th}$. Additionally U and Th are broadly similar in their geochemical behavior and melt compatibility, fractional crystallization for example does not significantly change U/Th.

One factor that could significantly influence D_U but leave D_{Th} unaffected is a change in the oxidation state from U^{4+} to U^{6+} (Burnham and Berry, 2012). While such an effect has been reported in the literature (Bacon et al., 2007), this is likely to be a minor effect for at least two reasons. First, U^{6+} is more compatible in aqueous fluids than melts and is likely to be removed from the melt (Langmuir, 1978) if fluid is present, and second, U^{6+} does not become the dominant valence state until highly oxidized conditions rarely reached in crustal magmas (Halse, 2014). Furthermore, differing D_U/D_{Th} among zircons still requires heterogeneity or temporal change in the magma chamber which casts the same doubts on the use of a single glass composition for model age calculations.

Another consideration is that U and Th compatibility strongly depends on the melt chemistry and is known to vary significantly with Al/Na (Xing et al., 2013). While the majority of the change happens equally to both D_U and D_{Th} therefore leaving D_U/D_{Th} relatively unchanged there could be effects if there were large changes in melt composition. At present there is not enough information to assess

the significance of this effect within a single magma system. It is unlikely to be significant in most situations as both the data from Wright et al. (2015) and Stelten et al. (2015) yielded similar D_U/D_{Th} .

4.3 Viability and comparison of model zircon U-Th disequilibrium ages

In general, analyses of glass and whole rock samples do not lie on the equiline (Fig. 3). Thus $(^{230}Th/^{232}Th)_{magma}$, even if homogeneous, must evolve over time. Our modeling shows that for magma chambers in which zircons record a spread U/Th, current approaches to calculating model ages using a single glass or whole rock composition may significantly underestimate age uncertainty and can potentially misestimate age (Fig. 5). With our correction scheme, the biggest contributor to the uncertainty comes from our lack of knowledge of melt composition. Future refinement of this value through the analysis of more glass in each sample or focusing attention to zircons with adhering glass or melt inclusions could significantly improve the uncertainties. Although we should note that one has to establish that the adhering glass represents the melt from which the zircon crystallized. Indeed using melt inclusions to correct each zircon age is the ideal case.

Without these refinements, our findings complicate intercomparison of age distributions between samples. For example, Schmitt et al. (2010) compared zircon U/Th age distributions between different samples of the same geologic unit and argued that they record the same history. This comparison was performed through comparing the probability density functions (PDF) through a Kolmogorov-Smirnov test (K-S test) derived from the ages and analytical uncertainties (Schmitt et al.,

2010). As our modeling shows that larger uncertainties are warranted, due to the incorporation of the uncertainty in the melt composition, any peaks in the PDF will broaden and reduce the resolving power (i.e., specificity) of the K-S test. In other words, our modeling leads to an increase in the false positive rate (i.e., the rate at which one erroneously concludes two samples share a zircon crystallization history and by extension a magmatic history).

We emphasize that our findings do not cast doubt on the validity of U-series zircon disequilibrium dating as the observation of pre-eruptive zircon growth has been independently validated by U-Pb zircon dating (e.g., Barboni and Schoene, 2014; Wotzlaw et al., 2014). Indeed we are not questioning the basis of U-series disequilibrium dating, only the specific age and uncertainty determinations for zircons in geochemically complex magma chambers.

4.4 Origin of Magma Heterogeneity

Our results support previous conclusions that magma chambers are heterogeneous at the scale of a volcanic hand sample (Bachmann and Bergantz, 2004). In principle, in addition to accessory phase crystallization, two processes arise to explain a continuum of $(U/Th)_{\text{zircon}}$ – magma mixing (Burgisser and Bergantz, 2011; Turner and Campbell, 1986) and re-melting of a cold mush (Bachmann and Bergantz, 2004). Indeed it is widely recognized that volcanic eruptions can be triggered by injections of fresh magma (e.g., Murphy et al., 1998; Pallister et al., 1992) which results in a compositional gradient across the magma chamber. These fresh injections would also raise the temperature, possibly removing the magma from the zircon stability field (Watson and Harrison, 1983;

Boehnke et al., 2013) causing zircons to dissolve and reform as the system cools. These zircons would then record the heterogeneities present in the system as it cools.

4.5 Implications for Other Phases

U/Th disequilibrium dating is viable in any phase that fractionates U from Th but is most useful in minerals which are closed to diffusive loss of U and Th at magmatic temperatures (Cherniak and Watson, 2003). U/Th measurements have been undertaken on co-existing feldspars, apatite, and sphene (Bourdon et al., 1994), chevkinite (Vazquez et al., 2014) and allanite (Vazquez and Reid, 2004). Our model is not specific to zircon and could be applied to understanding these different phases by using appropriate D_U/D_{Th} . However, if the phase does not strongly fractionate U/Th then the correction becomes more important to the final age calculation. It is also more complicated if one were to use a phase that prefers Th over U (e.g., monazite) as the $(^{230}Th/^{232}Th)_0$ is more important when one is measuring the decay towards the equiline rather than the ingrowth of ^{230}Th . This is mostly due to the fact that melts have $^{230}Th/^{232}Th < \sim 3$ and therefore a regression will be very sensitive to the $(^{230}Th/^{232}Th)_0$. Caution is advised with minerals that do not strongly prefer U over Th, if one does not have direct measurements of the melt composition or is unable to use an isochron.

5 Conclusion

We show that assuming a single melt composition when calculating disequilibrium zircon ages in magmas with a spread in $(U/Th)_{zircon}$ can result in significant underestimates of age uncertainties and may yield erroneous dates. We

propose a correction scheme based on knowledge that magmas are typically within 15% (1σ) of the equiline when most zircons crystallize. This approach shows that published ages may have uncertainties that are underestimated by up to a factor of three. Due to the uncertainties in the melt composition, the specificity of tests comparing age distributions is reduced and thus caution is suggested when making such comparisons. Going forward, significant community effort is urged to further constrain $(U/Th)_{\text{magma}}$ variations and improvements in the precision of zircon U-series disequilibrium dating will better allow the validity of the proposed correction scheme to be evaluated.

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<https://github.com/patrickboehnke/ThUZirconCalculator>

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Figure Captions

Figure 1: This figure shows a cartoon of what happens when zircons crystallize at the same time and change the melt U/Th significantly. In panel A, the zircons crystallize and progressively deplete the melt in U relative to Th. Panel B shows what happens after a period of time passes and that due to the changing melt U/Th the zircons can be used to construct an isochron. Panel C shows a different example where a zircon crystallizes from a melt (black circle) and the melt composition subsequently changes (blue circle). Panel D shows what happens to the situation shown in C after some time elapses, the measured melt value (blue circle) is not representative of the melt from which the zircon crystallized and so the age inferred from an isochron is incorrect.

Figure 2: This figure shows the range of U/Th values measured in zircons for a variety of volcanic systems (Bernal et al., 2014; Reid et al., 1997; Vazquez et al., 2014).

Figure 3: This is a compilation of various whole rock and glass data (Bourdon et al., 1994; Charlier and Wilson, 2010; Charlier et al., 2003; Reagan et al., 2003; Reid et al., 1997; Turner et al., 1996; Vazquez and Lidzbarski, 2012; Wright et al., 2015; Zou et al., 2010) showing that magmas are generally not on the equiline, suggesting rapid changes in $(U/Th)_{\text{Magma}}$.

Figure 4: This figure shows the $(U/Th)_{\text{magma}}$ as an activity ratio versus the published ages for each zircon. Note the random appearance of the $(U/Th)_{\text{magma}}$ as a function of time, suggesting either chemical heterogeneity or rapid changes. Further, the depth-profile analyses appear to show systematic trends and large differences between zircons at the same time. Uncertainties are smaller than the symbols.

Figure 5: This figure shows an age comparison between our model results and the published model ages as a function of the published ages for each zircon. Zircons are from the Belfond Dome samples SL-25 and SL-51 (Schmitt et al., 2010). A one to one line is shown as a guide for the eye. B contains a zoomed in portion between 0 and 50 ka. All uncertainties shown are at 1σ .

480 Figure 1:
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Figure 3:

Figure 4:

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