A simple and robust method for calculating temperatures of granitoid magmas

Meng Duan^{1,2} · Yaoling Niu^{2,3,4} · Pu Sun^{1,2} · Shuo Chen^{1,2} · Juanjuan Kong¹ · Jiyong Li¹ · Yu Zhang² · Yan Hu¹ · Fengli Shao¹

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Abstract

Calculating the temperatures of magmas from which granitoid rocks solidify is a key task of studying their petrogenesis, but few geothermometers are satisfactory. Zircon saturation thermometry has been the most widely used because it is conceptually simple and practically convenient, and because it is based on experimental calibrations with significant correlation of the calculated zircon saturation temperature (T_{Zr}) with zirconium (Zr) content in the granitic melt (i.e., $T_{Zr} \propto Zr_{MELT}$). However, application of this thermometry to natural rocks can be misleading, resulting in the calculated T_{Zr} having no geological significance. This thermometry requires Zr content and a compound bulk compositional parameter M of the melt as input variables. As the Zr and M information of the melt is not available, petrologists simply use bulk-rock Zr content ($Zr_{BULK-ROCK}$) and M to calculate T_{Zr} . In the experimental calibration, T_{Zr} shows no correlation with M , thus the calculated T_{Zr} is only a function of Zr_{MELT} . Because granitoid rocks represent cumulates or mixtures of melt with crystals before magma solidification and because significant amount Zr in the bulk-rock sample reside in zircon crystals of varying origin (liquidus, captured or inherited crystals) with unknown modal abundance, $Zr_{BULK-ROCK}$ cannot be equated with Zr_{MELT} that is unknown. Hence, the calculated magma temperatures T_{Zr} using $Zr_{BULK-ROCK}$ have no significance in both theory and practice. As an alternative, we propose to use the empirical equation T_{SiO_2} (°C) = $-14.16 \times SiO_2 + 1723$ for granitoid studies, not to rely on exact values for individual samples but focus on the similarities and differences between samples and sample suites for comparison. This simple and robust thermometry is based on experimentally determined phase equilibria with $T \propto 1/SiO_2$.

Keywords Zircon saturation thermometry · Magma temperature · Granitoid magmatism · SiO_2 approximation for magma temperature

Introduction

In studying the petrogenesis of magmatic rocks, determination of magma temperature is one of the basic tasks. This is relatively straightforward for basalts and basaltic rocks because of the experimentally well-established phase relationships between the liquidus phases such as olivine, clinopyroxene and plagioclase and the melt as a function of temperature (e.g., Roeder and Emslie 1970; Bender et al. 1978; Walker et al. 1979; Langmuir and Hanson 1981; Nielsen and Dungan 1983; Weaver and Langmuir 1990; Grove et al. 1992). The magma temperature is essentially linearly proportional to the MgO content of the melt, which is the MgO content of quenched basaltic glasses (or approximated with aphyric basalts or groundmass of basalts) (Niu et al. 2002). To calculate the magma temperatures of granites and granitic rocks is not straightforward despite their inverse

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✉ Meng Duan
meng.duan@qdio.ac.cn

✉ Yaoling Niu
yaoling.niu@durham.ac.uk

¹ Key Laboratory of Marine Geology and Environment, Institute of Oceanology, Chinese Academy of Sciences, 7 Nanhai Road, Qingdao, Shandong 266071, China

² Laboratory for Marine Geology, Qingdao National Laboratory for Marine Science and Technology, 1 Wenhai Road, Qingdao, Shandong 266061, China

³ School of Earth Science and Resources, China University of Geosciences, 29 Xueyuan Road, Beijing 100083, China

⁴ Department of Earth Sciences, Durham University, Durham DH1 3LE, UK

correlation with SiO₂ content of the melt (Bowen 1928; Tuttle and Bowen 1958). The difficulty is several fold: (1) with the exception of highly evolved granites and rhyolitic glasses, most granites and granitoid rocks do not represent melts but are cumulates (Niu et al. 2013; Chen et al. 2015, 2016; Lee and Morton 2015; Barnes et al. 2019) or melt-solid mixtures because of incomplete melt-solid separation during melt extraction (containing restite minerals/lithic fragments, Clemens and Stevens 2012) and magma (i.e., crystal mush) evolution owing to high melt viscosity; (2) mineral pairs with temperature-sensitive exchange reactions in granitic rocks, if any (e.g., two-feldspar thermometry, Brown and Parsons 1981; Kroll et al. 1993; Benisek et al. 2004, 2010; Anderson et al. 2008), record temperatures of sub-solidus equilibrium, rather than liquidus temperatures (i.e., melt temperatures of mineral crystallization).

This difficulty has been largely overcome by the zircon saturation thermometry thanks to the meticulous experimental calibration by Watson and co-workers (Watson 1979; Watson and Harrison 1983, 1984; Boehnke et al. 2013). This thermometry has been widely used and is considered to “provide a simple and robust means of estimating magma temperatures” (Miller et al. 2003). We agree that the concept of the zircon saturation thermometry is sound, and the experimental calibration is robust by Watson and co-workers. However, as we show here, application of this thermometry to natural rocks using bulk-rock (instead of melt) compositions is misleading and suggest that caution must be exercised before indiscriminate use of this thermometry.

As an alternative, we propose to use “bulk-rock” SiO₂ content as a proxy for estimating granitoid crystallization temperatures, whose individual values should not be considered as “exact”, but their comparisons between samples and between sample suites are geologically significant for granitoid petrogenesis.

Zircon saturation thermometry

Watson and Harrison (1983) show that the saturation behavior of zircon in granitic magmas (during melting and crystallization) depends on both melt composition and temperature, which, on the basis of experimental calibration, is expressed by:

$$\ln(D_{Zr}) = [-3.80 - 0.85(M - 1)] + 12900/T_{Zr} \quad (1)$$

where D_{Zr} is the concentration ratio of Zr in the stoichiometric zircon to that in the melt (Zr_{MELT}), T_{Zr} is the absolute temperature in Kelvin, and M is the compositional parameter of the equilibrated melt [$M = (Na + K + 2Ca)/(Al \times Si)$]. This expression has recently been revisited and reaffirmed (Boehnke et al. 2013). Rearranging this equation enables

direct calculation of the temperature of the granitic melts (Miller et al. 2003):

$$T_{Zr} = 12900 / [\ln(D_{Zr}) + 0.85M + 2.95] \quad (2)$$

Because Zr in zircon is stoichiometrically constant (~497,000 ppm), D_{Zr} is solely a function of Zr_{MELT} , and T_{Zr} is thus a function of Zr content and M value of the melt. This means that if magmas parental to granitic rocks under study are known to be saturated with zircon and if bulk-rock compositions can be approximated as representing the melt, then the magma temperatures can be calculated using Eq. (2), as widely used over the last decades since 1983.

The assumption of zircon saturation is readily proven because of the widespread occurrence of zircon crystals with crystallization ages (at least at the rims and edges of zircon crystals) in all granite and granitoid samples. However, the assumption that the bulk-rock compositions represent melt compositions cannot be true in almost all cases (see above). If granitoids are proven not to represent melt compositions, then Eq. (2) fails simply because neither D_{Zr} nor M is meaningful. Hence, the zircon saturation thermometry, despite its thermodynamic and experimental footing, cannot be used in practice to calculate the temperatures of magmas parental to granitoid rocks. The problem is serious and is multi-fold.

Although widely used, the bulk-rock Zr content ($Zr_{BULK-ROCK}$) is not Zr_{MELT} , but the sum of Zr in zircon crystals and Zr in the rest of the rock. One could assume the latter as representing the melt if the rock is highly evolved, but its Zr content cannot be determined from the bulk-rock without knowing modal proportions of zircons. In this case, because $Zr_{BULK-ROCK} > Zr_{MELT}$, the calculated T_{Zr} overestimates the crystallization temperatures of magmas (Miller et al. 2003). On the other hand, for granitoids with dioritic compositions that accumulate/solidify early from the parental magmas of relatively high temperature and low viscosity, $Zr_{BULK-ROCK} < Zr_{MELT}$ because Zr still resides largely in the residual/evolving melt at this early stage of crystallization. In this case, the calculated T_{Zr} underestimates the crystallization temperatures of magmas.

In granitoids, inherited and xenocrystic zircons are common, and their contribution to $Zr_{BULK-ROCK}$ is difficult to assess. Hanchar and Watson (2003) put forward a method by using back-scattered electrons (BSE) or cathodoluminescence (CL) images to estimate the volume of inherited zircon, which still has large uncertainty. In this case, the calculated T_{Zr} depends on $Zr_{BULK-ROCK}$ that is highly influenced by the volume of inherited and xenocrystic zircons in granitoid samples.

As discussed above, rock samples from granitoid plutons rarely represent pure melt, but cumulates comprising crystals and residual melts. This makes the calculated bulk-rock M parameter irrelevant to the expected M of the melt, which

can further deviate T_{Zr} from the true melt temperatures. However, as the experimentally calibrated T_{Zr} shows no correlation with M and all other compositional parameters (discussed in more detail below), M is not, but $Zr_{BULK-ROCK}$ is, the primary source of the error for the calculated T_{Zr} .

The above analysis states explicitly that the zircon saturation thermometry cannot be used to calculate the temperatures of magmas that solidifies to form granitoid plutons using bulk-rock compositions. That is, the calculated T_{Zr} values have large unknown errors and thus have no significance. Figure 1 illustrates these problems. For a melt parental to granitic rocks with $Zr=400$ ppm (moderately enriched Zr content in the granitoid rocks from natural samples), $M=1.3$ and $T_{Zr} \approx 880$ °C, magma cooling causes zircon crystallization and Zr depletion in the residual melt. When the melt cools to ~ 790 °C, there will be ~ 0.05 wt% zircon crystallized and ~ 150 ppm Zr left in the mixture of residual melt and other liquidus phases which are not efficiently segregated from the melt. The ~ 790 °C would be mistaken as $T_{Zr}=880$ °C calculated using Eq. (2) because inefficient zircon separation makes the bulk-rock still have the original ~ 400 ppm Zr. The calculated T_{Zr} would be even higher if there are inherited/captured zircons in the bulk-rock compositions, which is common in granitoid rocks.

On the other hand, for a melt parental to intermediate cumulate dioritic rocks with $Zr=400$ ppm, a higher M of 1.6

Fig. 1 Zr versus T_{Zr} plot, visualizing that calculated T_{Zr} values are a function of Zr content and M value. Zr content in the melt phase decreases as the result of cooling and zircon crystallization. Using the bulk-rock Zr content as the substitute of melt Zr content would introduce large errors in the estimated magma temperatures

and $T_{Zr} \approx 840$ °C, early cumulation of dioritic rocks effectively separated from the parental melt with low $Zr_{BULK-ROCK}$ content (~ 50 ppm estimated with 0.01 wt% zircon in the bulk-rock cumulate) would give T_{Zr} of ~ 650 °C, in huge contrast with the real T_{Zr} of ~ 840 °C (Fig. 1). The above simulations may not be perfect but demonstrate significant deviations of the calculated T_{Zr} values using $Zr_{BULK-ROCK}$ from the true magma temperature values for different types of granitoid rocks (felsic granitic plutons consisting of crystals and residual melts vs. intermediate dioritic rocks of early cumulate origin with less melt trapped or retained). The examples in Fig. 1 can be further demonstrated by comparing such calculated T_{Zr} values and the T values estimated by using “bulk-rock” SiO_2 content of granitoid rocks better reflecting their true crystallization temperatures (see below). Similarly, without knowing major element composition of the melt, but using bulk-rock major element analyses, we can easily have errors on the compound parameter M . In addition, uncertainties in the M values between 1.3 and 1.6 due to bulk-rock composition (e.g., containing restite crystals) treated as melt composition would lead to a further ~ 40 K deviation in the calculated T_{Zr} values although M shows no understood contribution in the zircon saturation thermometry (see below).

Comparison of data on natural samples with experimental results

In this section, we use bulk-rock major and trace element data of syn-collisional I-type granitoid samples saturated in zircon from the Qilian, Kunlun and Qinling Orogens in central and western China (Chen et al. 2015, 2016; Zhang et al. 2015; Duan et al. 2016; Li et al. 2016, 2017; Kong

Fig. 2 Total alkalis silica (TAS) diagram showing the compositions of plutonic samples from Qilian, Kunlun and Qinling Orogens (Chen et al. 2015, 2016; Zhang et al. 2015; Duan et al. 2016; Li et al. 2016, 2017; Kong et al. 2017, 2019, 2020; Shao et al. 2017)

Fig. 3 Plots of the bulk-rock Zr contents (a) and $D_{Zr, \text{zircon/melt}}$ (b) against the calculated T_{Zr} values of granitoids (same samples as in Fig. 2) using the zircon saturation thermometry (Watson and Harrison 1983). For comparison, the experiment data used for zircon thermom-

etry calibration (Watson and Harrison 1983) are also plotted. The insets plot all the experimental data. Note that only nine experimental data points are in the compositional range of natural granitoid samples

et al. 2017, 2019, 2020; Shao et al. 2017). In addition, we have collected granitoid data compiled through the Earth-Chem portal (<http://portal.earthchem.org/>). This was done to further illustrate that caution is required when using zircon thermometry Eq. (2) to calculate “magma temperatures” for natural granitoid samples.

The syn-collisional granitoids from the Qilian, Kunlun and Qinling Orogens in central and western China show

large compositional variations in the TAS diagram (Fig. 2), reflecting their crystallization from variably evolved magmas with varying temperatures (Chen et al. 2016). Figure 3 shows $Zr_{\text{BULK-ROCK}}$ and the calculated D_{Zr} plotted against the calculated T_{Zr} Eq. (2) of granitoid samples, compared with the experimental data (Watson and Harrison 1983). The apparent consistency between the two is not proof of the validity of the calculated T_{Zr} for granitoid samples because they are

Fig. 4 Plot of $M [(Na + K + 2Ca)/(Al \times Si)]$ and independent major element parameters against the calculated T_{Zr} values of granitoids using zircon thermometry (Watson and Harrison 1983)

intrinsically linked by Eq. (2), but does show the significance of experimental calibration of Eq. (2) with $T_{Zr} \propto Zr_{BULK-ROCK}$ and $T_{Zr} \propto 1/D_{Zr}$. We point out that while there exist many experimental data for the calibration, only nine of these data sets were found to be appropriate for natural samples in terms of melt compositions and temperature range.

To evaluate the compositional effects on magma temperatures or the calculated T_{Zr} using Eq. (2), we plot compositional parameter M Eqs. (1) and (2) and its constituent parameters against the calculated T_{Zr} (Fig. 4) and $Zr_{BULK-ROCK}$ (Fig. 5) for both natural rock data and experimental data used for calibrating the equations. One could claim the existence of some sort of correlation between experimental temperatures and experimental charge compositions (although it is not at all obvious), there is certainly no correlation of any sort between the calculated temperatures

and compositional parameters for natural bulk-rock compositions. This phenomenon itself is unexpected because $T \propto MgO$ and $T \propto 1/SiO_2$ are well understood through experimental petrology (Bowen 1928; Tuttle and Bowen 1958; Gerke and Kilinc 1993; Grove et al. 1997). As seen in Fig. 3 insets and above discussion, most experimental charge temperatures are very high, and the temperature data pertinent to granitoid magmatism are rather sparse (only 9 data points). According to Eq. (1), $M \propto Zr_{MELT}$ is expected, which seems to be the case for the experimental data with scatter, but is not true for bulk-rock data Zr and bulk-rock compositions (i.e., the compound parameter M and the constituent parameters; Fig. 5). Hence, while the experimental calibration of zircon saturation thermometry is robust, its application to natural granitoid rocks using bulk-rock instead of melt Zr content is erroneous.

Fig. 5 Co-variations between M $[(Na + K + 2Ca)/(Al \times Si)]$ and independent major element parameters and bulk-rock Zr contents of granitoid samples, compared with experimental data

Comparison of T_{Zr} and T_{SiO_2} calculated from major element compositions

MgO contents of basaltic melts have been demonstrated experimentally to be proportional to the magma temperature (see above and review: $T = 1026 \times e^{[0.01894 \times \text{MgO (wt\%)}]}$ given by Niu et al. 2002). This simple MgO- T relationship is derived from various experiment data and involves no extra parameters other than MgO content in basaltic melts (quenched glasses or groundmass; Niu et al. 2002). To explore the relationships between major element abundances (e.g., SiO_2 and MgO) and temperatures in andesitic and felsic magmas, we compiled the experimental data (including the temperatures and major element compositions of the melts) studying the crystallization evolution of andesitic and felsic magmas (Helz 1976; Carroll and Wyllie 1989; Sisson and Grove 1993; Moore and Carmichael 1998; Alonso-Rerez et al. 2008; Nandedkar et al. 2014, 2016; Ulmer et al. 2018). Only experiments with liquidus minerals of amphibole, plagioclase, quartz and micas which are common mineral phases

in granitoid rocks are used; experimental data with liquidus minerals of olivine, clinopyroxene and orthopyroxene are excluded. The data are shown in Figs. 6a, b.

Figure 6 shows that with decreasing temperature, SiO_2 increases and MgO decreases in the melt, consistent with cooling induced fractional crystallization of the more mafic minerals from the melts (e.g., amphibole). The large scatter in the temperature at a given SiO_2 or MgO results from different experimental conditions (e.g., composition of starting materials, pressure and H_2O content). Nevertheless, temperature-dependent trends for both SiO_2 and MgO are obvious, especially when these data are averaged with compositional intervals (Figs. 6c, d). In Fig. 6c, SiO_2 and temperatures are averaged in 3.0 wt% SiO_2 intervals, and in Fig. 6d, MgO and temperatures are averaged in 0.5 wt% MgO intervals, giving significant trends that can be expressed by

$$T_{\text{SiO}_2} (\text{°C}) = -14.16 \times \text{SiO}_2 (\text{wt\%}) + 1723 \quad (3)$$

$$T_{\text{MgO}} (\text{°C}) = 887.6 \times [\text{MgO (wt\%)}]^{0.0989} \quad (4)$$

Fig. 6 Plots of silicate melt temperatures measured during experiments against SiO_2 and MgO contents of the compiled experimental data (Helz 1976; Carroll and Wyllie 1989; Sisson and Grove 1993; Moore and Carmichael 1998; Alonso-Rerez et al. 2008; Nandedkar et al. 2014, 2016; Ulmer et al. 2018). The temperatures show a negative correlation with SiO_2 (a) and a positive correlation with MgO

(b) as expected from experimental petrology. The large scatter of the temperature values at a given SiO_2 or MgO results from different experimental conditions. These experimental data are further averaged within the intervals of 3 wt% SiO_2 and 0.5 wt% MgO and give simple but reasonable SiO_2 - T (c) and MgO- T (d) relationships

These two equations are by no means perfect without considering other compositional effects but can effectively capture the predominance of SiO_2 and MgO in describing magma temperatures for felsic and intermediate magmas constrained by experimental phase equilibria.

Figure 7 compares T_{Zr} calculated using Eq. (2) and T_{SiO_2} and T_{MgO} calculated using Eqs. (3) and (4) respectively for the syn-collisional granitoid rocks in central and western China. The good positive trend between $\text{Zr}_{\text{BULK-ROCK}}$ and the calculated T_{Zr} (with correlation coefficient $R > 0.8$) simply comes from self-correlation seen in Eq. (2) with the scatter coming from the bulk-rock compositional parameter M . It is obvious from Fig. 6 that despite the scatter (Figs. 6a, b) and large uncertainties (Figs. 6c, d), SiO_2 and MgO in the melts can effectively describe the temperatures of granitoid magmatism. Hence, it is logical to use Eqs. (3) and (4) to estimate “magma temperatures” for natural granitoid samples. Figure 7 shows these estimates, which, as expected, share no resemblance to T_{Zr} nor show any correlation with Zr contents. We should note, as discussed above, that no granitoid samples represent true melts (Niu et al. 2013; Lee and Morton 2015), but cumulates from melts or mixtures of melt with crystals (including inherited restite ones) before magma solidification. Hence, the calculated T_{SiO_2} and especially T_{MgO} derived from experimental melts Eqs. (3) and (4) from Fig. 6 in Fig. 7 are not truly magma temperatures, because cumulate minerals (e.g., amphibole) have lower SiO_2 and much higher MgO content than the true melts. This is proven to be the case in Fig. 8, which shows systematically higher T_{MgO} than T_{SiO_2} in the syn-collisional granitoid rocks in central and western China. However, in contrast to bulk-rock Zr content which varies significantly during magma differentiation and is highly influenced by the crystallized, inherited and captured zircons, the major element composition (especially SiO_2) of granitoid rocks is sufficiently similar to the composition of the melt. Therefore, Eq. (3) can be used to approximate the magma temperatures.

Fig. 8 Comparison between the calculated T_{MgO} and T_{SiO_2} , which shows systematically higher T_{MgO} than T_{SiO_2}

Figure 9 compares T_{SiO_2} calculated using Eq. (3) and T_{Zr} calculated using Eq. (2) for the natural granitoid samples. Obviously, there is a large discrepancy between the calculated T_{SiO_2} and T_{Zr} , with T_{SiO_2} being generally higher than T_{Zr} for samples with less evolved compositions (e.g., those with $\text{SiO}_2 < \sim 67$ wt%) and $T_{\text{SiO}_2} < T_{\text{Zr}}$ for more evolved samples (e.g., those with $\text{SiO}_2 > \sim 67$ wt%) (also see below). In addition, despite the scattering, T_{SiO_2} of granitoid samples have significant correlations with the major element compositions (except for Na_2O) as expected in terms of experimental phase equilibria and liquid lines of descent. In contrast, there are no correlations between T_{Zr} and the major element contents. To testify the validity of the above observations, we use downloaded data of worldwide granites from the EarthChem Portal (<http://portal.earthchem.org/>) on 19 August, 2019, using the following parameters: (1) key words (granites); (2) sample type (plutonic rocks); (3)

Fig. 7 Plot of the calculated T_{SiO_2} vs. T_{Zr} (a) and T_{MgO} vs. T_{Zr} (b) against whole-rock Zr contents of granitoid samples

chemistry (whole-rock major elements and Zr content). Furthermore, samples with $\text{SiO}_2 < 53$ wt%, $\text{MgO} > 6$ wt% and abnormally high Zr content (> 1000 ppm) were left unconsidered. About 400 granite data sets that meet the conditions are used to plot bulk-rock major element compositions as a function of T_{SiO_2} Eq. (3) and T_{Zr} Eq. (2); Fig. 10. These granite data show similar systematics as the granitoid rocks in central and western China (Fig. 9). The T_{SiO_2} show significant correlations with major element compositions, which are, as expected, consistent with understood liquid lines of decent though these global samples mostly share no genetic relationship. In contrast, the T_{Zr} shows no correlation with major element compositions, indicating its irrelevance to granitoid magma evolution. Hence, it is logical to use bulk-rock based T_{SiO_2} , instead of T_{Zr} to estimate the temperature of granitic magmas. Nevertheless, we do not encourage to

use individual T_{SiO_2} values as being “exact” but emphasize their petrological significance when comparing between samples and between sample suites in studying the granitoid petrogenesis.

In order to further compare the T_{SiO_2} and T_{Zr} values calculated from natural granitoid samples and from data sets collected from the EarthChem portal, we use $\Delta T (= T_{\text{SiO}_2} - T_{\text{Zr}})$ to show the deviation between the calculated T_{SiO_2} and T_{Zr} and as a function of SiO_2 and bulk-rock Zr content, respectively (Fig. 11). From Fig. 11a, ΔT show tight negative correlation with SiO_2 , ranging from $\sim +400$ °C for intermediate dioritic rocks with low SiO_2 to -300 °C for felsic granitic rocks with high SiO_2 . Figure 11a illustrates significant deviation of the calculated T_{Zr} values from the likely magma temperatures approximated by T_{SiO_2} (see above), with the T_{Zr} values lower than the expected magma temperature ($\Delta T > 0$)

Fig. 9 Correlations of the major elements and whole-rock Zr contents with calculated T_{SiO_2} vs. T_{Zr} of the granitoid samples. Total Fe expressed as Fe_2O_3^* (wt%). Same samples and data as in Fig. 2

Fig. 10 Plots of the major elements and whole-rock Zr contents against the calculated T_{SiO_2} vs. T_{Zr} of granitoid samples compiled from the EarthChem Portal (<http://portal.earthchem.org>). Total Fe

expressed as $Fe_2O_3^*$ (wt%). The T_{Zr} values calculated using zircon saturation thermometry (Watson and Harrison 1983) do not show any correlations with major element compositions

for intermediate dioritic rocks (low SiO_2) and higher than the expected magma temperatures ($\Delta T < 0$) for felsic granitic rocks (high SiO_2). The above observation is in fact consistent with the simulation in Fig. 1. For intermediate dioritic rocks which usually show cumulate texture and represent early fractionation products from the melts, most Zr resides

in the residual melts. In this case, $Zr_{BULK \text{ DIORITIC ROCKS}}$ is much lower than the true Zr_{MELT} , and T_{Zr} calculated using this low $Zr_{BULK \text{ DIORITIC ROCKS}}$ gives lower values than the actual magma temperatures ($\Delta T > 0$). On the other hand, the more felsic granitic rocks reflecting high viscosity magma are mixtures of melt and crystals with high abundances

Fig. 11 The differences of calculated temperatures using the two different methods of $\Delta T (=T_{SiO_2} - T_{Zr})$ with SiO_2 (a) and bulk rock Zr content (b). ΔT shows an apparent negative relationship with SiO_2 ; the intermediate rocks with < 67 wt% SiO_2 having positive ΔT and more felsic rocks with > 67 wt% SiO_2 having negative ΔT (a). There-

fore, the deviation between the calculated T_{Zr} and the realistic magma temperature approximated by T_{SiO_2} is mainly caused by the deviation between $Zr_{BULK-ROCK}$ and the true Zr_{MELT} as illustrated by the negative correlation between $Zr_{BULK-ROCK}$ and ΔT (b)

of zircons of varying origin (liquidus, captured or inherited crystals). Therefore, the $Zr_{\text{BULK GRANITIC ROCKS}}$ are much higher than Zr_{MELT} and the calculated T_{Zr} using high $Zr_{\text{BULK GRANITIC ROCKS}}$ gives higher values than the true magma temperatures ($\Delta T < 0$). This is further illustrated by the negative correlation between the bulk rock Zr content and ΔT (Fig. 11b). Samples with low Zr content showing positive ΔT and underestimated T_{Zr} whereas samples with high Zr content showing negative ΔT and overestimated T_{Zr} (Fig. 11b).

In fact, the failure in using bulk-rock Zr content to estimate the magma temperature of granitoids is evident in theory. This is because in contrast with SiO_2 that is essential constituents of silicate minerals and rocks, Zr is petrologically not required for granitoid magmatism. It is important to note that we do not devalue the significance of Zr because it determines the presence and abundance of zircons in granitic rocks and zircons contain valuable information such as the age of granitoid crystallization and also the ages of granitoid magma sources and source histories preserved in captured and inherited zircons. However, we should also note the fact that Zr (as a trace/minor element) and zircon (as an accessory mineral) do not participate in and thus cannot control the granitoid phase equilibria. Hence, it is logical and readily understood that Zr content in a rock cannot provide information on phase equilibria, including the magma temperature. This simple analysis plus the illustrations above explain that there is no thermodynamic and/or petrological reason why the granitoid magma temperatures as approximated by T_{SiO_2} should correlate with bulk-rock Zr contents (Figs. 9k, l). Hence, the calculated T_{Zr} values give no information on magma temperatures but are derivatives of $Zr_{\text{BULK-ROCK}}$. Therefore, we conclude that caution is needed before indiscriminate and continued use of the zircon saturation thermometry.

Conclusions

Zircon-saturation thermometry has been a convenient tool widely used to calculate magma temperatures in granitoid studies over the last decades. It uses Zr_{MELT} as an input because experimental calibration shows $T_{Zr} \propto Zr_{\text{MELT}}$. However, what is available in rock samples is $Zr_{\text{BULK-ROCK}}$, not Zr_{MELT} . Because for felsic granitic rocks representing mixtures of melts and crystals, Zr_{MELT} (unknown) = $Zr_{\text{BULK-ROCK}} - Zr_{\text{ZIRCON}}$ (49.7 wt% Zr with unknown abundance) – $Zr_{\text{OTHER CUMULATE MINERALS}}$, and for early cumulate dioritic rocks, $Zr_{\text{BULK-ROCK}}$ is lower than Zr_{MELT} , T_{Zr} values calculated using $Zr_{\text{BULK-ROCK}}$ thus have no petrological significance.

Zr as a trace element in rocks and magmas and zircon as an accessory mineral do not participate in and cannot

control the granitoid phase equilibria. Therefore, there is no petrological footing that $Zr_{\text{BULK-ROCK}}$ should correlate with granitoid magma temperatures. We suggest using SiO_2 content as a proxy to estimate granitoid magma temperatures, T_{SiO_2} , because SiO_2 is an essential constituent of granitoid rocks and magmas, and because $\text{SiO}_2 \propto 1/T$ is constrained by experimental phase equilibria.

Because granitoids do not represent melt compositions, but the compositions of mixtures of cumulate crystals and inefficiently extracted melt, we do not encourage to accept the calculated T_{SiO_2} as true magma temperatures for individual samples, but we advocate the petrological and geological significance of varying T_{SiO_2} values between samples and between sample groups for comparison in the study of granitoid petrogenesis.

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References

- Alonso-Perez R, Müntener O, Ulmer P (2008) Igneous garnet and amphibole fractionation in the roots of island arcs: experimental constraints on andesitic liquids. *Contrib Mineral Petr* 157:541–558
- Anderson JL, Barth AP, Wooden JL, Mazdab F (2008) Thermometers and thermobarometers in granitic systems. In: Putirka KD, Tepley III FJ (eds) *Minerals, Inclusion and Volcanic Processes*. *Rev Mineral Geochem. Mineral Soc Am Chantilly* 69:121–142
- Barnes CG, Werts K, Memeti V, Ardill K (2019) Most Granitoid Rocks are Cumulates: Deductions from Hornblende Compositions and Zircon Saturation. *J Petrol* 60:2227–2240
- Bender JF, Hodges FN, Bence AE (1978) Petrogenesis of basalts from the project FAMOUS area: experimental study from 0 to 15 kars. *Earth Planet Sc Lett* 41:277–302
- Benisek A, Dachs E, Kroll H (2010) A ternary feldspar-mixing model based on calorimetric data: development and application. *Contrib Mineral Petr* 160:327–337
- Benisek A, Kroll H, Cemič L (2004) New developments in two-feldspar thermometry. *Am Mineral* 89:1496–1504
- Boehnke P, Watson EB, Trail D, Harrison TM, Schmitt AK (2013) Zircon saturation re-revisited. *Chem Geol* 351:324–334
- Bowen NL (1928) *The Evolution of the Igneous Rocks*. Princeton University Press

- Brown WL, Parsons I (1981) Towards a more practical two-feldspar geothermometer. *Contrib Mineral Petr* 76:369–377
- Carroll MR, Wyllie PJ (1989) Experimental Phase Relations in the System Tonalite-Peridotite-H₂O at 15 kb; Implications for Assimilation and Differentiation Processes near the Crust-Mantle Boundary. *J Petrol* 30:1351–1382
- Chen S, Niu YL, Li JY, Sun WL, Zhang Y, Hu Y, Shao FL (2016) Syn-collisional adakitic granodiorites formed by fractional crystallization: Insights from their enclosed mafic magmatic enclaves (MMEs) in the Qumushan pluton, North Qilian Orogen at northern margin of the Tibetan Plateau. *Lithos* 248–251:456–468
- Chen S, Niu YL, Sun WL, Zhang Y, Li JY, Guo PY, Sun P (2015) On the origin of mafic magmatic enclaves (MMEs) in syn-collisional granitoids: evidence from the Baojishan pluton in the North Qilian Orogen, China. *Miner Petrol* 109:577–596
- Clemens JD, Stevens G (2012) What controls chemical variation in granitic magmas? *Lithos* 134–135:317–329
- Duan M, Niu YL, Kong JJ, Sun P, Hu Y, Zhang Y, Chen S, Li JY (2016) Zircon U-Pb geochronology, Sr-Nd-Hf isotopic compositions and geological significance of the Late Triassic Baijiazhuang and Lvjing granitic plutons in West Qinling Orogen. *Lithos* 260:443–456
- Gerke TL, Kilinc AI (1993) Enrichment of SiO₂ in rhyolites by fractional crystallization: an experimental study of peraluminous granitic rocks from the St. Francois Mountains, Missouri, USA. *Lithos* 29:273–283
- Grove TL, Donnelly-Nolan JM, Housh T (1997) Magmatic processes that generated the rhyolite of Glass Mountain, Medicine Lake volcano. N California *Contrib Mineral Petr* 127:205–223
- Grove TL, Kinzler RJ, Bryan WB (1992) Fractionation of mid-ocean ridge basalt (MORB). In: Morgan JP, Blackman DK, Sinton JM (eds) *Mantle flow and melt generation at mid-ocean ridges*. AGU American Geophysical Union, Washington, DC 71:281–310
- Hanchar JM, Watson EB (2003) Zircon Saturation Thermometry. In: Hanchar JM, Hoskin PWO (eds) *Zircons*. *Rev Mineral Geochem. Mineral Soc Am Chantilly* 53:89–112
- Helz RT (1976) Phase relations of basalts in their melting ranges at P H₂O = 5 kb. Part II Melt Compositions *J Petrol* 17:139–193
- Kong JJ, Niu YL, Hu Y, Zhang Y, Shao FL (2020) Petrogenesis of the Triassic granitoids from the East Kunlun Orogenic Belt, NW China: Implications for continental crust growth from syncollisional to post-collisional setting. *Lithos* 364/365:105513
- Kong JJ, Niu YL, Duan M, Xiao YY, Zhang Y, Guo PY, Sun P, Gong HM (2019) The syncollisional granitoid magmatism and crust growth during the West Qinling Orogeny, China: Insights from the Jiaochangba pluton. *Geol J* 54:4014–4033
- Kong JJ, Niu YL, Duan M, Zhang Y, Hu Y, Li JY, Chen S (2017) Petrogenesis of Luchaba and Wuchaba granitoids in western Qinling: geochronological and geochemical evidence. *Miner Petrol* 111:887–908
- Kroll H, Evangelakakis C, Voll G (1993) Two-feldspar geothermometry: a review and revision for slowly cooled rocks. *Contrib Mineral Petr* 114:510–518
- Langmuir CH, Hanson GN (1981) Calculating mineral-melt equilibria with stoichiometry, mass balance, and single component distribution coefficients. In: Newton RC, Navrotsky A, Wood BJ (eds) *Thermodynamics of Minerals and Melts*. Springer-Verlag New York 1981. Springer, New York 1:247–271
- Lee CTA, Morton DM (2015) High silica granites: Terminal porosity and crystal settling in shallow magma chambers. *Earth Planet Sc Lett* 409:23–31
- Li JY, Niu YL, Chen S, Sun WL, Zhang Y, Liu Y, Ma YX, Hu ZX, Zhang GR (2017) Petrogenesis of granitoids in eastern section of the Central Qilian Block: Evidence from geochemistry and zircon U-Pb geochronology. *Miner Petrol* 111:23–41
- Li JY, Niu YL, Hu Y, Chen S, Zhang Y, Duan M, Sun P (2016) Origin of the late Early Cretaceous granodiorite and associated dioritic dikes in the Hongqilafu pluton, northwestern Tibetan Plateau: A case for crust-mantle interaction. *Lithos* 260:300–314
- Miller CF, McDowell SM, Mapes RW (2003) Hot and cold granites? Implications of zircon saturation temperature and preservation of inheritance. *Geology* 31:529–532
- Moore G, Carmichael ISE (1998) The hydrous phase equilibria (to 3 kbar) of an andesite and basaltic andesite from western Mexico: constraints on water content and conditions of phenocryst growth. *Contrib Mineral Petr* 130:304–319
- Nandedkar RH, Ulmer P, Müntener O (2014) Fractional crystallization of primitive, hydrous arc magmas: an experimental study at 0.7 GPa. *Contrib Mineral Petr* 167:1015
- Nandedkar RH, Hürlimann N, Ulmer P, Müntener O (2016) Amphibole-melt trace element partitioning of fractionating calc-alkaline magmas in the lower crust: an experimental study. *Contrib Mineral Petr* 171:71
- Nielsen RL, Dungan MA (1983) Low pressure mineral-melt equilibria in natural anhydrous mafic systems. *Contrib Mineral Petr* 84:310–326
- Niu YL, Gilmore T, Mackie S, Greig A, Bach W (2002) Mineral chemistry, whole-rock compositions, and petrogenesis of Leg 176 gabbros: data and discussion. *Proc. ODP. Sci Results* 176:1–60
- Niu YL, Zhao Z, Zhu DC, Mo XX (2013) Continental collision zones are primary sites for net continental crust growth - A testable hypothesis. *Earth-Sci Rev* 127:96–110
- Roeder PL, Emslie RF (1970) Olivine-Liquid Equilibrium *Contrib Mineral Petr* 29:275–289
- Shao FL, Niu YL, Liu Y, Chen S, Kong JJ, Duan M (2017) Petrogenesis of Triassic granitoids in the East Kunlun Orogenic Belt, northern Tibetan Plateau and their tectonic implications. *Lithos* 282–283:33–44
- Sisson T, Grove T (1993) Experimental investigations of the role of H₂O in calc-alkaline differentiation and subduction zone magmatism. *Contrib Mineral Petr* 113:143–166
- Tuttle OF, Bowen NL (1958) Origin of granite in the light of experimental studies in the system NaAlSi₃O₈-KAlSi₃O₈-SiO₂-H₂O. *Geol Soc Am* 74:153
- Ulmer P, Kaegi R, Müntener O (2018) Experimentally Derived Intermediate to Silica-rich Arc Magmas by Fractional and Equilibrium Crystallization at 1.0 GPa: an Evaluation of Phase Relationships, Compositions, Liquid Lines of Descent and Oxygen Fugacity. *J Petrol* 59:11–58
- Walker D, Shibata T, Delong SE (1979) Abyssal tholeiites from the Oceanographer fracture zone. *Contrib Mineral Petr* 70:111–125
- Watson EB (1979) Zircon saturation in felsic liquids: experimental results and applications to trace element geochemistry. *Contrib Mineral Petr* 70:407–419
- Watson EB, Harrison TM (1983) Zircon saturation revisited: temperature and compositions effects in a variety of crustal magma types. *Earth Planet Sc Lett* 64:295–304
- Watson EB, Harrison TM (1984) Accessory minerals and the geochemical evolution of crustal magmatic systems: a summary and prospectus of experimental approaches. *Phys Earth Planet* in 35:19–30
- Weaver JS, Langmuir CH (1990) Calculation of phase equilibrium in mineral-melt systems. *Comput Geosci-UK* 16:1–19
- Zhang Y, Niu YL, Hu Y, Liu JJ, Ye L, Kong JJ, Duan M (2015) The syncollisional granitoid magmatism and continental crust growth in the West Kunlun Orogen, China - Evidence from geochronology and geochemistry of the Arkarz pluton. *Lithos* 245:191–204