Revision 2: Am Min MS 7091

A refined zirconium-in-rutile thermometer

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Abstract. The zirconium-in-rutile thermometer enjoys widespread use, but confidence in its accuracy is limited because experiments were conducted at higher temperatures than many rutile-bearing rocks, and calibration uncertainties have not been quantitatively assessed. Refined calibrations were developed using bootstrap regression to minimize residuals in the natural logarithm of the equilibrium constant, based on experiments only (n=32) and on a combined compilation of experiments and natural data (n=94, total). Rearranging the regression to solve for T, and expressing Zr concentration (C) in ppm (μg/g), the calibrations in the α-quartz stability field are:

Experimental dataset:

$$T\ (°C) = \frac{68740 + 0.441 \cdot P(bars) - 0.114 \ast C(ppm)}{129.76 - R \cdot ln[C(ppm)]} - 273.15$$

Combined dataset:

$$T\ (°C) = \frac{71360 + 0.378 \cdot P(bars) - 0.130 \cdot C(ppm)}{130.66 - R \cdot ln[C(ppm)]} - 273.1$$

Thermodynamics of the quartz-coesite transition as applied to the calibration for α-quartz yields calibrations for the coesite stability field:

Experimental dataset

$$T\ (°C) = \frac{71290 + 0.310 \cdot P(bars) - 0.114 \ast C(ppm)}{128.76 - R \cdot ln[C(ppm)]} - 273.15$$

Combined dataset:

$$T\ (°C) = \frac{73910 + 0.247 \cdot P(bars) - 0.130 \cdot C(ppm)}{129.65 - R \cdot ln[C(ppm)]} - 273.15$$

Propagated temperature uncertainties are ±20-30 °C (2σ) for the experimental dataset calibration, and ±10-15 °C (2σ) for the combined dataset. Compared to previous experimental calibrations, the refined thermometer predicts temperatures up to 40 °C lower for T ≤ 550 °C, and systematically higher temperatures for T > 800 °C. With careful attention to distributions of Zr in rutile grains, precisions of ±5 °C and accuracies ~±15 °C may be possible, although poor understanding of how to select compositions for thermometry will typically lead to larger uncertainties. The ZiR calibration promises continued high-precision and accurate thermometry, and possibly improved thermodynamic properties, but the sources of compositional variability in rutile warrant further scrutiny.

Keywords: Zirconium, rutile, thermometry, bootstrap regression, errors

Introduction

The zirconium-in-rutile thermometer (ZiR), first calibrated empirically (Zack et al., 2004), then experimentally (Watson et al., 2006; Tomkins et al., 2007) is highly precise and has been widely applied. It is based on the temperature sensitive net-transfer reaction:

$$ZrSiO_4 = SiO_2 + ZrO_2 \qquad \textit{Eq. 1}$$

Here, the reference polymorphs are taken to be zircon, α-quartz, and tetragonal-ZrO_2 ("t-ZrO_2"), although other polymorphs for all these compositions are possible (Fig. 1). It is assumed that substitution of Zr in rutile occurs as t-ZrO_2, unlike monoclinic baddeleyite. Most applications of the thermometer prefer the wholly experimental calibration of Tomkins et al. (2007), not least because it directly incorporates pressure dependencies. However, Zr-in-rutile experiments are mostly very high temperature (averaging ~1150 °C), whereas many rutile-bearing rocks form at substantially lower temperatures (Fig. 1). In that context, Watson et al. (2006) used a small set of lower-temperature empirical data to help define the temperature-dependence of the reaction within a thermodynamic formalism.

Since 2007, new experiments (Hofmann et al., 2013) improve the experimental basis of the calibration. More importantly, widespread application of ZiR to natural rocks has resulted in numerous studies that compare, directly or indirectly, temperatures determined using ZiR with temperatures determined from other thermobarometers or from thermodynamically-calculated mineral assemblage diagrams (MAD's or "pseudosections"). These data permit ZiR to be refined over a region of P-T space not accessible to experiments, especially ≤650 °C and with a denser population of moderate to high pressures (Fig. 1). One important result of the current effort is to propagate calibration uncertainties to compositional and pressure-temperature (P-T) conditions of interest so as to assess the possible magnitude of systematic errors, i.e. ZiR accuracy.

In this paper, published measurements of Zr contents in rutile and corresponding P-T conditions are compiled, as determined experimentally (Watson et al., 2006; Ferry and Watson, 2007; Tomkins et al., 2007; Hofmann et al., 2013) and empirically using mineral assemblage diagrams or thermobarometry (see supplemental file for values and sources). The use of empirical data follows the approach of Watson et al. (2006), but with considerably more observations. These data are then regressed using bootstrapped, weighted, linear regressions to refine ZiR and determine calibration uncertainties. Next, uncertainties are propagated in calculated temperatures, corresponding to calibration errors, for a range of typical measured compositions. Lastly, implications of the refined calibration for rocks and for thermodynamic properties are discussed.

Methods

Thermodynamic basis

Equilibrium among zircon, α-quartz, and tetragonal ZrO_2 can be expressed thermodynamically by:

$$\Delta G(P,T) = 0 = \Delta H(1\,bar,T) - T\Delta S(P,T) + P\Delta V(P,T) + RTlnK_{eq} \qquad Eq.\ 2$$

where ΔG is the Gibbs free energy of reaction, T and P are temperature and pressure, ΔH, ΔS, and ΔV are the enthalpy, entropy and volume of reaction (ignoring compressibilities) for the pure endmember minerals, R is the gas constant, and K_{eq} is the equilibrium constant. The equilibrium constant is expressed in terms of activities:

$$K_{eq} = \frac{a_{t-ZrO_2} \cdot a_{\alpha-quartz}}{a_{zircon}} \qquad Eq.3$$

where a_{t-ZrO_2}, $a_{\alpha-quartz}$, and a_{zircon} are the activities of the chemical endmember components of Equation 1, as referenced to the crystalline structures t-ZrO_2, α-quartz, and zircon.

Assuming non-ideal mixing between ZrO_2 and TiO_2 in rutile (Tomkins et al., 2007), this expression can be expanded to:

$$\Delta G(P,T) = 0 = \Delta H(1,T) - T\Delta S(P,T) + P\Delta V(P,T) + W \cdot X_{ZrO_2}\left[X_{ZrO_2} - 2\right] + RTlnK'_{eq} \qquad Eq.\ 4$$

where W is a Margules-type interaction term, and:

$$K'_{eq} = \frac{X_{t-ZrO_2} \cdot a_{\alpha-quartz}}{a_{zircon}} \qquad Eq.5$$

In principle W can depend on P and T, but the current dataset cannot resolve such a dependency and it is assumed to be constant (see Tomkins et al., 2007). While the activity of zircon is essentially 1 if zircon is stable, the activity of α-quartz will be lower at P-T conditions where it is absent or where other SiO_2 polymorphs are stable (e.g., coesite for natural rocks, β-quartz and tridymite for experimental data). Because all experiments and rocks considered in this study contained zircon, a_{zircon} was assumed to be equal to 1.0. For rocks containing α-quartz, $a_{\alpha\text{-quartz}}$ was also assumed to be equal to 1.0. For rocks and experiments with another polymorph of SiO_2 $a_{\alpha\text{-quartz}}$ was calculated using an internally consistent thermodynamic database (Berman and Aranovich, 1996), as implemented using Theriak-Domino (De Capitani and Petrakakis, 2010). Specifically, input consisted of the experimental P-T conditions plus a composition of 100% SiO_2; output included the activities of all SiO_2 polymorphs, including α-quartz (supplemental Table S1). All fit parameters and thermodynamic terms are reported in units of J/mole, bar, and K.

Experimental data

Experimental data were taken from SiO_2-saturated experiments of Watson et al. (2006), Tomkins et al. (2007) and Hofmann et al. (2013). The Zr content used for calibration was taken directly from tables of means (Watson et al., 2006; Hofmann et al., 2013) and the midpoint of bracketing experiments (Tomkins et al., 2007). Few experiments were conducted in the α-quartz stability field, so X_{ZrO2} was multiplied by the (reduced) activity of α-quartz to maintain equilibrium according to Eqs. 2, 3, and 5 (see Ferry and Watson, 2007). The SiO_2-undersaturated (ZrO_2-bearing) experimental results of Ferry and Watson (2007) were omitted partly because they are statistical outliers but also because they were conducted in the t-ZrO_2 stability field (Fig. 1). The thermodynamic properties of t-ZrO_2 are not known sufficiently well to predict $a_{\alpha\text{-quartz}}$ accurately. Errors were assigned according to how the data were originally presented: for the Tomkins et al. (2007) data, errors were treated as brackets with a combined error equal to the sum of squares of the bracket width divided by 4 and the stated measurement uncertainty. For Watson et al. (2006) and Hofmann et al. (2013), each experiment was treated as a separate measurement with reported composition errors. Temperature and pressure uncertainties were set at ±10 °C and ±500 bars (2σ), except for room pressure experiments, where the uncertainty in pressure was set to 0.001 (to avoid computational errors). Three SiO_2-saturated experiments were omitted as statistical outliers, leading to 32 experimental data points between 675 and 1400 °C (median = 1200 °C), and 1 and 30 kbar (median = 10 kbar).

Natural data

Natural data were taken from published data on rocks that all contained rutile, zircon and either quartz or coesite, whose P-T conditions were independently constrained. Including data from rocks generally improves regression statistics because they record much lower temperatures than achievable experimentally, so provide strong leverage on regressed fit parameters and (potentially) thermodynamic properties. For the ZiR calibration, rocks also more densely sample a large range of pressures. However, assigning a Zr content to rutile corresponding to peak metamorphic conditions requires considering processes that can affect the Zr-contents, both during prograde metamorphism and retrograde cooling. The philosophy taken here is that Zr contents of at least some rutile grains reequilibrate during prograde metamorphism (Penniston-Dorland et al., 2018), whereas rutile in high temperature rocks exhibit little reequilibration during cooling below c. 700 °C (Ewing et al., 2013; Kohn et al., 2016). This view warrants additional discussion of how rutile compositions deviate from or correspond with peak P-T conditions:

With respect to prograde formation, thermodynamically-based mineral assemblage diagrams suggest that rutile should form over a limited P-T region (typically c. 10 °C or 200 bars; M. Kohn, unpublished models), and many rocks show rutile inclusions in peak metamorphic minerals. These observations imply that rutile forms prior to the peak of metamorphism, so in principle its chemistry could reflect a prograde rather than peak P-T condition. If so, and if rutile were inert, it would show a very limited range of Zr contents, with generally low concentrations. However, most datasets for rutile in rocks that formed below 700 °C show a large range of Zr contents and relatively high concentrations of Zr in some grains (see original studies cited in Supplemental Table S1). This range of compositions cannot represent diffusional reequilibration because the position-dependent closure temperature (Dodson, 1986) for Zr in rutile is c. 700 °C for the cores of cylindrical grains (assuming typical grain sizes and cooling rates of 50 μm and 10-25 °C/Ma, and diffusion parameters of Cherniak et al., 2007 and Dohmen et al., 2018). Assuming that experimental calibrations of ZiR are even approximately correct, some rutile grains must reequilibrate above the predicted rutile-in reaction along the prograde path (e.g., see Penniston-Dorland et al., 2016) presumably by dissolution-reprecipitation or recrystallization.

Conversely, during cooling, rutile may reequilibrate via diffusion or recrystallization, or simply fail to maintain equilibrium with quartz and zircon because kinetic limitations such as diffusion along grain boundaries ultimately prevent mutual equilibration (e.g., see Ewing et al., 2013; Kohn et al., 2016). This process appears to affect only the outer 10-20 microns of individual crystals in rocks as temperatures decrease below c. 700 °C (Kohn et al., 2016), or creates compositional disparities among crystals for UHT rocks (Ewing et al., 2013; Pape et al., 2016; see also data of Kooijman et al., 2012). Even for UHT rocks, the highest Zr-contents appear broadly consistent (again, assuming experimental calibrations have merit) with a peak metamorphic temperature as determined using phase equilibria. This further suggests that resetting of rutile grains during cooling is not complete.

If the previous discussion holds true, rutile grains with peak metamorphic compositions are likely to occur somewhere in a rock, whereas reequilibration during cooling appears limited to temperatures above c. 700 °C. In that context, potential calibrant samples were omitted if, within thermometric uncertainty, they must have equilibrated at T >700 °C. As one example of this potential reequilibration, in a study of the Main Central Thrust, ZiR temperatures correspond well with thermobarometry at temperatures below 700 °C, but record temperatures of ~690 °C for rocks whose temperatures determined from other thermobarometers was ~750 °C (Kohn, 2008). Similarly, Pauly et al. (2016) report a large proportion of ZiR temperatures of ~740 °C for matrix grains in rocks whose peak metamorphic temperatures exceeded 900 °C. For these reasons, some natural data reported in Watson et al. (2006) were not used: samples from the Adirondacks (T=765 °C) and Lebait (1070 °C). Data for a rock from Santa Catalina were also removed because Watson et al. (2006) report circularity in linking temperature with rutile composition.

Lastly, no rocks were included whose temperatures were ≤450 °C because low-temperature rutile in rutilated quartz veins contains much higher Zr contents than can be consistent with any higher-temperature thermometric extrapolation (Shulaker et al., 2015). The origin of this deviation at low temperature is unclear, and Shulaker et al. (2015) suggest several possible calibration and analytical biases. The independence of Ti contents in quartz on temperature may suggest disequilibrium of the quartz-rutile-(zircon) system at such low temperatures or for this type of occurrence of rutile + quartz.

For natural rutile, the maximum reported Zr concentration was used, assuming (as discussed above) that some rutile grains reequilibrate during prograde metamorphism, and that retrograde reequilibration is small for these relatively low temperature rocks. Uncertainties in Zr content were based on compositional variability reported in each study. This approach probably overestimates uncertainties because it represents the entire range of compositions in a sample, which probably reflect rutile that crystallized over a range of temperatures (e.g., see Penniston-Dorland et al., 2018). For studies that did not directly report compositional standard deviations, uncertainties were calculated from raw measurements, or the quarter range of a reported total compositional range (either reported directly, or calculated based on the reported temperature range using the calibration of Tomkins et al., 2007). If only a single temperature was reported, that study was omitted.

P-T conditions in natural samples assumed published P-T means (excluding any temperature estimates based on ZiR), and errors were based on either standard deviations or, more typically, ranges. If no temperature or pressure uncertainties were recommended, 2σ uncertainties were set at ±50 °C and either ±1000 bars (P<20 kbar) or ±2000 bars (P≥20 kbar). A minimum temperature uncertainty of ±25 °C was assigned (i.e., if reported uncertainties were lower, they were increased to ±25 °C) based on typical minimum errors reported for thermobarometric studies (e.g., see Ferry, 1980). These errors (±25-50 °C; ±1000-2000 bars) are far larger than the calibration uncertainties in a single thermometer or barometer and generally represent the effects of mineral compositional variation in rocks beyond analytical errors (Kohn and Spear, 1991).

In all, 62 data points between 480 and 725 °C (median = 650 °C), and between 3.5 and 31.5 kbar (median = 18.7 kbar) make up the natural sample dataset.

Calculating K_{eq}

For converting Zr concentrations in ppm to mole fractions, the following expression from Tomkins et al. (2007) was used:

$$X_{ZrO_2} = \frac{8768.3 \cdot C_{Zr}}{10^{10} - 4739.3 \cdot C_{Zr}} \qquad Eq. 6$$

where X_{ZrO_2} is mole fraction of ZrO_2 in rutile and C_{Zr} is Zr concentration in ppm (=μg/g). This expression assumes mixing between only ZrO_2 and TiO_2, but even the highest concentrations of other components likely to be encountered (e.g., 1000s of ppm for Cr and 1-2 wt% for Nb; (Zack and Kooijman, 2017) introduce relative uncertainties in X_{t-ZrO_2} of <1%. For coesite-bearing assemblages, $a_{\alpha-quartz}$ was calculated using the thermodynamic database of Berman and

Aranovich (1996) as implemented using de Capitani and Petrakakis (2010). No rocks considered here equilibrated in the stability field of β-quartz or other SiO_2 polymorphs (Fig. 1).

Regressions and thermometers

In principle, uncertainties can be minimized either in $-ln(K'_{eq})$ by using weighted linear regressions, or in T (or 1/T) by using non-linear minimization approaches. Minimization of residuals in $-ln(K'_{eq})$ between models and data was employed in this study because it is computationally straightforward and provides direct estimates of fit parameters that have potential thermodynamic value, and that can be readily incorporated into thermometer calibrations. Because the activity of zircon was assumed to be equal to 1.0, models minimized residuals in $\ln(K'_{eq})$ by regressing a rearranged form of Eq. 4:

$$-ln(K'_{eq}) = -ln(X_{ZrO_2} \cdot a_{\alpha-quartz}) = \frac{a}{R \cdot T(K)} + b + \frac{c \cdot P(bars)}{R \cdot T(K)} + d \cdot \frac{X_{ZrO_2}[X_{ZrO_2} - 2]}{R \cdot T(K)} \qquad Eq.\ 7$$

where a, b, c and d are regressed fit parameters. In comparison with Equation 4, the fit parameters a, b, c, and d would correspond with ΔH, -ΔS/R, ΔV and W of reaction, respectively.

Two calibrations of Eq. 7 were calculated based on experiments-only data (Experimental Model) and on the entire dataset of experiments plus rocks (Combined Model). A simple weighted least squares regression is commonly used for calibrations, but can misrepresent uncertainties and correlations for three reasons: outliers strongly influence the regression, errors occur in independent variables (as well as the dependent variable), and variation does not necessarily follow Gaussian statistics. With respect to Eq. 7, each observation of composition, pressure, and temperature carries uncertainty, so a simple weighted linear regression that minimizes residuals in $-ln(K'_{eq})$ (alone) will underestimate uncertainties and propagated errors.

A bootstrap method was chosen to calibrate Eq. 7 because it reduces sensitivity to outliers and permits simultaneous assessment of uncertainties in independent variables without prior assumptions about the distribution of data. At its core, this method uses a Monte Carlo approach in which a dataset is randomly sampled, with replacement, for a number of datapoints equal to the number of primary observations. For each randomly chosen datum, the value of any parameter with measurement uncertainty is simultaneously sampled randomly within its stated uncertainty.

Each iteration then employs a weighted linear regression to derive a set of regressed parameters. The process is repeated a large number of times, and statistical properties (means, standard deviations, correlations) are calculated.

For the ZiR data, the dataset was randomly sampled with replacement, simultaneously perturbing values of temperature, pressure, and composition in each datum within the range of their assumed uncertainties. That is, comparing any two iterations, the suite of datapoints was not identical (random sampling with replacement) except fortuitously, and the exact values of temperature, pressure, and composition for any one datapoint were not the same (random perturbation). For each iteration, the randomly sampled data were regressed using a simple weighted linear regression to derive values of a, b, c, and d in Eq. 7, and the process was repeated 10,000 times. The means of a, b, c, and d, and their corresponding variance-covariance matrix were calculated from the aggregate values of the 10,000 iterations. These values define the best-fit calibration within the α-quartz stability field.

A thermometer appropriate to the coesite stability field was determined by regressing values of $RT\ln(a_{\alpha-quartz})$ vs. P and T over a grid of P-T conditions in the coesite stability field between 500 and 1000°C and between 25 and 40 kbar. This correction was then added to the calibration of ZiR in the α-quartz stability field. Although applications in the β-quartz stability field are expected to be rare, a similar approach was used to derive a calibration (see Supplemental file) using a P-T grid between 800 and 1200 °C, and 5 to 15 kbar.

Propagated uncertainties in temperature were calculated for assumed compositions and pressure as a byproduct of the bootstrap method. Each Monte Carlo iteration yields a calibration, from which temperatures can be calculated. That is, the 10,000 iterations yield 10,000 possible calibrations. Any assumed Zr concentration and pressure can then be converted into 10,000 estimates of temperature, from which a mean and standard deviation can be calculated. In this study, temperatures were calculated at 15 kbar for assumed Zr contents of 10, 20, 40, 80, 160, 320, 640, and 1280 (corresponding roughly with temperatures ranging from 400 to 800 °C). Propagated errors in temperature for the Tomkins et al. (2007) calibration were calculated using a variance-covariance matrix that was kindly provided by R. Powell (pers. comm., 2019).

Results

Regressed values and 2σ errors for a, b, c, and d parameters, are listed in Table 1 for the Experimental and Combined Models, with the published regression of Tomkins et al. (2007) for comparison. Variance-covariance matrices are provided in the supplemental file.

Table 1. Regression parameters for Tomkins et al. (2007), the Experimental Model, and the Combined Model, with 2σ uncertainties

Parameter[1]	a (J/mole)	b	c (J/bar)	d (J/mole)
Tomkins et al. (2007)[2]	85500±4600	-3.50±0.36	0.476±0.039	10000
Experimental (n=32)	68740±6080	-1.66±0.66	0.441±0.124	65240±37810
Combined (n=94)	71360±37703750	-1.77±0.39	0.378±0.079	74100±33500

[1] Comparison of equations 4 and 7 implies that, if the values for a, b, c, and d have thermodynamic significance, they would correspond with thermodynamic parameters ΔH, ΔS/R, ΔV, and W

[2] The regression parameters from Tomkins et al. (2007) are reversed in sign relative to this study; their published errors are 2σ (R. Powell, pers. comm. 2019).

For the Experimental Model (with 32 data points), a high R^2 value (0.995) indicates the regression is highly significant, but the MSWD as applied to experimental plus natural data is 6.1 (Fig. 2; 3.0 for experimental data alone), indicating scatter beyond measured compositional variability. Watson et al. (2006) and Tomkins et al. (2007) also show excess scatter in their thermometer regressions, especially for data at 30 kbar. For the Combined Model (with 94 data points), a high R^2 value (0.995) also indicates a highly significant regression. The errors on regressed parameters are markedly smaller, although the MSWD is still high (5.4; Fig. 2). The Experimental and Combined Models make almost identical predictions, but the Combined Model has the smallest parameter errors (Table 1) and propagated errors (Table 2). Using values from Table 1, equation 7 can be rearranged to solve for T as a function of P and X_{ZrO_2} for rocks with coexisting rutile, zircon, and α-quartz. For the Experimental Model, the thermometric equation is:

$$T\,(°C) = \frac{68740 + 0.441 \cdot (P-1)(bars) + 65240 \cdot X_{ZrO_2} \cdot \left(X_{ZrO_2} - 2\right)}{13.80 - R \cdot ln\left(X_{ZrO_2}\right)} - 273.15 \qquad Eq.8$$

The corresponding equation for the Combined Model is:

$$T\,(°C) = \frac{71360 + 0.378 \cdot (P-1)(bars) + 74100 \cdot X_{ZrO_2} \cdot \left(X_{ZrO_2} - 2\right)}{14.70 - R \cdot ln\left(X_{ZrO_2}\right)} - 273.15 \qquad Eq.9$$

From the thermodynamics of the quartz-coesite transition, an equation can be calculated for rutile that coexists with zircon and coesite. For the Experimental Model:

$$T\ (°C) = \frac{71290 + 0.310 \cdot (P-1)(bars) + 65240 \cdot X_{ZrO_2} \cdot \left(X_{ZrO_2} - 2\right)}{12.79 - R \cdot ln\left(X_{ZrO_2}\right)} - 273.15 \qquad Eq. 10$$

The corresponding equation for the Combined Model is:

$$T\ (°C) = \frac{73910 + 0.247 \cdot (P-1)(bars) + 74100 \cdot X_{ZrO_2} \cdot \left(X_{ZrO_2} - 2\right)}{13.69 - R \cdot ln\left(X_{ZrO_2}\right)} - 273.15 \qquad Eq. 11$$

As highlighted by Ferry and Watson (2007), for rocks that lack an SiO_2 phase, X_{ZrO2} in the denominator would need to be multiplied by the activity of α-quartz (Eqs. 8, 9) or the activity of coesite (Eqs. 10, 11). Equations 8-11 hold over the entire range of zirconium concentrations. As noted by Tomkins et al. (2007), for nearly all rocks, X_{ZrO2} is very small, and for Equation 6 the conversion between X_{ZrO2} and the concentration of Zr (= C) in ppm (μg/g) simplifies to $X_{ZrO2} \sim C*8768.3/10^{10}$. Making this substitution into the denominators of Equations 8 – 11 requires adding the difference between the natural logarithms of $1x10^{10}$ and 8768.3 (=13.947), multiplied by R (=115.96). The non-ideal interaction term can also be approximated by $-2*W*8768.3/10^{10}$. This approach provides a close approximation of the thermometer as expressed in ppm Zr in rutile, up to ~25,000 ppm:

In the α-quartz field for the Experimental Model:

$$T\ (°C) = \frac{68740 + 0.441 \cdot P(bars) - 0.114 * C(ppm)}{129.76 - R \cdot ln[C(ppm)]} - 273.15 \qquad Eq. 12$$

In the α-quartz field for the Combined Model:

$$T\ (°C) = \frac{71360 + 0.378 \cdot P(bars) - 0.130 \cdot C(ppm)}{130.66 - R \cdot ln[C(ppm)]} - 273.15 \qquad Eq. 13$$

In the coesite field for the Experimental Model:

$$T\ (°C) = \frac{71290 + 0.310 \cdot P(bars) - 0.114 * C(ppm)}{128.76 - R \cdot ln[C(ppm)]} - 273.15 \qquad Eq. 14$$

In the coesite field for the Combined Model:

$$T\ (°C) = \frac{73910 + 0.247 \cdot P(bars) - 0.130 \cdot C(ppm)}{129.65 - R \cdot ln[C(ppm)]} - 273.15 \qquad Eq. 15$$

The regressed parameters (Table 1) can be used to predict T as a function of P and ln(K_{eq}') in comparison to measured T (Fig. 3). The Experimental and Combined Models fit the data almost equally well (Figs. 3A, B), although the Experimental Model shows a slight negative bias for natural rocks (c. 7 °C; Fig. 3B). Intercomparison of predicted temperatures (Fig. 4) shows very slight differences. The quality of fit can be expressed in terms of the MSWD for temperature, which is ~20 for the entire dataset (both models), ~4 for natural data alone, and ~51 for experimental data alone. The experimental data are harder to fit because temperature errors are so small, but uncertainties would have to be increased to ±70 °C to reduce the MSWD to ~1.0. Such an unreasonably large error indicates that the experiments are not mutually reconcilable. The largest deviations between modeled and measured temperatures occur with the experimental data of Tomkins et al. (2007), but there is no systematic behavior with respect to misfit and pressure.

As anticipated by Ferry and Watson (2007) and shown by Tomkins et al. (2007), ΔV of reaction is positive and should cause the original experimental calibration of Watson et al. (2006) to underestimate temperature at high pressure, and overestimate temperature at low pressure. This behavior is evident both for the Tomkins et al. (2007) experiments (e.g., compare 30 kbar vs. 1 bar experiments, Fig. 3C), and for natural data (e.g., selected points at high and low pressure extremes; Fig. 3C).

Not surprisingly, the calibration of Tomkins et al. (2007) fits data well for experiments published in 2006 and 2007 because they were the basis of the calibration. However, it underestimates temperatures for more recent 10 kbar experiments (Hofmann et al., 2013), and overestimates temperatures for most natural data (Fig. 3D). These discrepancies reflect very different values for fit parameter "b" (corresponding mathematically with ΔS/R) compared with the current regressions (Table 1). The regressed parameters for each model can also be used to predict ln(K_{eq}') as a function of T and P for comparison with measured ln(K_{eq}') (Fig. 2). The Combined and Experimental Models fit these data similarly (Fig. 2).

In general, propagated uncertainties in temperature using the Combined Model are ~2.5 times smaller than the Experimental Model (Table 2). The propagated error for the Tomkins et al. (2007) calibration based on their variance-covariance matrix is similar to the refined calibrations, but their regression method differs from this study.

Table 2. Temperatures and propagated temperature uncertainties[†] for different regressions.

Concentration (ppm)	10	20	40	80	160	320	640	1280
Experimental Model								
Temperature (°C)	408	445	487	534	587	647	717	797
±2σ	32	31	31	30	29	28	25	22
Combined Model								
Temperature (°C)	418	455	497	544	597	658	727	807
±2σ	13	12	12	12	11	10	10	10
Tomkins et al. (2007)								
Temperature (°C)	455	491	530	574	622	676	738	808
±2σ*	20	20	20	20	20	20	19	18

[†] Errors in Zr content are not propagated in these calculations.

*Re-regressing the same experimental data as Tomkins et al. (2007) using the bootstrap method of this study approximately doubles this error.

Discussion

The "best" thermometer calibration

Based on statistics, the Combined Model has the smallest uncertainties in regressed parameters and propagated temperature, so would normally be considered preferable. However, assumptions needed to include natural data may render it less accurate than the Experimental Model. Excess scatter (high MSWD) occurs for experimental data, indicating that equilibration and reequilibration systematics are not fully understood. However, a lower MSWD for rocks mainly reflects an assigned temperature uncertainty that exceeds analytical error. For example, the analytical precision of a temperature estimate in a rock using other thermometers can be as low as ±10 °C (2σ; Kohn and Spear, 1991), whereas the minimum temperature uncertainty assigned in this study was ±25 °C, and many uncertainties are ±50 °C. This expansion of errors reflects uncertainties in petrologic models and compositional heterogeneity ("geologic error"; Kohn and Spear, 1991) and indicates that, again, our understanding of equilibration and reequilibration is incomplete. In that context, it is debatable whether rocks provide better constraints on thermometer accuracy. While the author recommends using the Combined Model for calculating temperatures (Eq.'s 9, 11, 13, 15), others may justifiably prefer the Experimental Model (Eq.'s 8, 10, 12, 14).

Propagation of calibration errors

No formal propagation of calibration errors appears to have been reported previously. Tomkins et al. (2007) suggest an overall uncertainty of ±30 °C (2σ), but this seems to be based on observed natural variability, not on calibration errors. The refined regressions imply temperature uncertainties for typical Zr contents of 20-30 °C for the Experimental Model, and 10-15 °C for the Combined Model (Table 2; all uncertainties 2σ). Calculated errors in Table 1 demonstrate that use of data from natural rocks reduces uncertainties by a factor of ~2.5. As in Watson et al. (2006), the use of natural data, even with relatively large P-T uncertainties, constrains the calibration to lower temperatures more tightly than a calibration based on experiments only. The natural data also provide many more data at high pressure, from which pressure-dependencies can be more precisely estimated. In most thermometric regressions, propagated errors in temperature would increase towards the extremes of the data distribution. In the case of ZiR, errors are nearly uniform towards lower temperatures because natural data are dense at lower temperatures, and because a larger change in ln(K_{eq}’) is needed to affect calculated temperature.

The propagated error in temperature using the variance-covariance matrix for the original Tomkins et al. (2007) regression indicates 2σ calibration uncertainties of c. 20 °C over the entire temperature range considered, only slightly higher than the Combined Model. However, the choice of regression model affects the propagated error. For example, application of the bootstrap method to the same experimental data used by Tomkins et al. (2007) results in propagated errors ranging from ±20 °C at T~800 °C to ±40°C for T≤550 °C. The bootstrap method tends to predict higher uncertainty because it makes fewer assumptions regarding data distributions, and it reduces the effects of outliers. Other types of regressions that make more assumptions will indicate smaller uncertainties.

Total temperature uncertainties

The total temperature uncertainty must include the effects of calibration errors and natural compositional variability. Different rocks can exhibit highly different compositional variability within and among rutile grains. In that context, Penniston-Dorland et al. (2018) proposed a method (the “mean-max” method) for identifying the likely range of maximum Zr contents in rutile, which they interpreted to represent compositions corresponding with peak metamorphic conditions. Application of this method to thermometry of rocks from Santa Catalina, California yielded a typical temperature precision of ~±5 °C (2σ). Such a small error reflects clustering of high-Zr data in their rocks and the insensitivity of ZiR thermometry to Zr content (i.e., even large uncertainties in Zr content propagate to small uncertainties in calculated temperature). Together (taking the square root of the sum of the squares), calibration errors plus natural variability would produce a combined error of ±10-15 °C, comparable to the propagated error reported in Ferry and Watson (2007), although smaller than for the calibration of Tomkins et al. (2007). This error represents a best-case scenario for rocks with highly consistent rutile compositions. Rocks with greater variability in rutile composition could have much higher temperature uncertainties.

Comparison to thermodynamic properties

While fit parameters do not necessarily equate to thermodynamic properties, the direct mathematical correspondence between Equations 2 and 7 invites comparison. Because the tetragonal form of ZrO_2 cannot be quenched, its thermodynamic properties are not well known. However, molar volumes of different minerals commonly show rather similar sensitivities to temperature and pressure, so comparison of measured ΔV with fit parameter c is arguably more robust. A decrease in volume of several percent attends the transition from monoclinic to tetragonal ZrO_2 at 1 bar (Patil and Subbarao, 1969). Experiments relevant to estimation of ΔV include measurements of ΔS of transition at 1 bar and 1200 °C (3.69±0.21 J/mol·K; Moriya and Navrotsky, 2006, and the P-T location of a triple point among ZrO_2 polymorphs (530±30 °C at 19.8±2.8 kbar; Block et al., 1985; Fig. 1). Using the Clapeyron relationship ($dP/dT = \Delta S/\Delta V$), and assuming that ΔS does not change appreciably from the 1 bar transition at 1200 °C to the triple point, these data suggest a volume decrease of 0.1 to 0.14 J/bar (5.5±1%). At 675 °C and 14 kbar (the median P-T conditions of the dataset), and using tabulated volumes, compressibilities, and thermal expansivities for baddeleyite, α-quartz, and zircon (Holland and Powell, 1998), calculated ΔV is 0.38±0.02 J/bar. This value is indistinguishable from the regressed values for the Experimental and Combined Models, but falls outside the range reported by Tomkins et al. (2007). If thermodynamic properties of t-ZrO_2 improve, calculation of Zr-in-rutile temperatures may likewise become more accurate.

Implications

Implications for rocks

The refined calibrations yield similar temperatures as the Tomkins et al. (2007) calibration at 700-800 °C but deviations up to 25-35 °C occur at T≤600 °C (Table 2; Fig. 3). That is, new ZiR temperatures will be lower than have been commonly calculated from the Tomkins et al. (2007) calibration for blueschists and low-T eclogites. While this difference should be considered in future studies, many temperature estimates in these rock types have been based on thermodynamically-based mineral assemblage diagrams (MAD's or "pseudosections"), so no change in interpretation is required.

Implications for thermodynamic calculations

The similarity of the Experimental and Combined Models is striking – calculated temperatures are typically different by <10 °C (although differences increase at lower pressure). Yet, temperatures for experiments were directly measured, whereas temperatures for rocks were determined through thermodynamic inversion of mineral compositions and modes. The similarity of temperature estimates for rocks using these two very different approaches indicates that thermodynamic databases and thermobarometers must be broadly consistent with the ZiR experiments. That is, ZiR experiments support the accuracy of other thermodynamic calculations, even though the experiments do not directly constrain those calculations.

The regressed a, b, c, and d parameters are analogous to ΔH, ΔS/R, ΔV and W, respectively. Tomkins et al. (2007) reformulated their regression results for thermodynamic applications (see their Appendix), so some comparison to their regressed values in Table 1 is warranted in a thermodynamic context. The inferred values for ΔH, ΔS and W do not overlap within uncertainty with the values reported in Tomkins et al. (2007) while the values for ΔV are indistinguishable for the Experimental Model, but do not overlap for the Combined Model. Regressed values for W in this study imply substantially greater non-ideality of mixing between ZrO_2 and TiO_2 than originally inferred. This parameter influences calculated T for T>~1200 °C but becomes less relevant at T<~1000 °C. The differences in ΔH and ΔS values between regressions partly reflect their negative correlation (-0.93 to -0.96): any increase in ΔH causes a corresponding decrease in ΔS. So, values for ΔH and ΔS are more compatible than a simple comparison of errors might at first suggest. Nonetheless, the differences in the regressed values for ΔS and the fits to the data are conspicuous (Fig. 3A and 3B vs. 3D). If used in thermodynamic calculations, the parameters derived from the Combined Model are recommended.

Implications for rutile compositional variability

The refined calibrations improve confidence in the accuracy of ZiR thermometry for natural rocks, potentially reducing errors to ~±10-15 °C. Nonetheless, the uncertainties in Zr concentration assigned to samples used for calibration (expressed as percent) are far larger than typically encountered for other thermometers. For example, for Fe-Mg exchange thermometers like garnet-biotite, identifying which compositions to pair typically introduces relative compositional uncertainties of 5%, which propagates to temperature uncertainties of ~25 °C. This level of compositional uncertainty exceeds counting statistics errors (≤~2% relative error for EPMA data, or ±~10 °C) by a factor of 2-3, but is considerably smaller than the total range in Fe-Mg compositions that can be found for a single mineral in a rock (e.g., more than 100% for Mg in some growth-zoned garnets). In practice, we apply petrologic criteria to identify which compositions were most likely in equilibrium (e.g., Kohn and Spear, 2000). These criteria have been developed over decades of research on the growth, diffusive (re)equilibration, recrystallization, and consumption of minerals.

Such a well-established body of research does not yet exist for rutile. Unlike ~5% compositional uncertainties that can attend Fe-Mg thermometry, the average uncertainty assigned to Zr concentrations for the calibration samples was ~20%, indicating substantial data scatter. Some data scatter might reflect micro-inclusions of zircon, which can cause spuriously high Zr analyses and data scatter (Zack et al., 2004; Chalmers et al., 2007). However, not all high-Zr rutile can be explained this way, for example when there are clusters of high-Zr measurements (Penniston-Dorland et al., 2018). Prograde relict grains probably contribute low-Zr outliers. Other possible biases include incomplete equilibration with quartz (high Zr-rutile) or zircon (low-Zr rutile), possibly because of slow diffusion along grain boundaries (see discussions in Taylor-Jones and Powell, 2015; Kohn et al., 2016). These observations imply that we do not understand equilibration of Zr in rocks so well as for major elements like Fe-Mg. Further investigation of compositional variability in rutile is warranted (e.g., Kooijman et al., 2012; Ewing et al., 2013; Kohn et al., 2016; Pape et al., 2016; Penniston-Dorland et al., 2018; Smye et al., 2018), as well as transport of Zr through the rock matrix (Ewing et al., 2013; Kohn et al., 2016), although limitations to transport have been suggested as yet only during retrograde cooling. From the perspective of ZiR alone, incompatibilities between thermometers exceeding ~25 °C are statistically significant, and further thermometric comparisons may provide another route for improving applications to rocks.

Acknowledgements

Thanks are due to many individuals: the NSF reviewer who inadvertently incentivized this study by questioning the accuracy of the Zr-in-rutile thermometer; HP Marshall for help understanding different residual minimization approaches; Roger Powell for providing unpublished variance-covariance matrices; Frank Spear, Keith Putirka, and Andy Smye for providing thorough critical reviews; and Ian Swainson for his editorial patience. Funded by NSF grant OIA1545903.

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Figure captions

Figure 1. Pressure vs. temperature diagram, showing distribution of datapoints used for calibration. Lines depict key stability bounds for polymorphs of SiO_2 and ZrO_2 (baddeleyite, tetragonal ZrO_2, and a second tetragonal form of ZrO_2, "t-II ZrO2").

Figure 2. Visualizations of predicted vs. measured $\ln(K_{eq})$ for the Experimental and Combined Models, showing nearly identical fits to the data. MSWD is calculated as applied to all data (i.e., not just experiments for the Experimental Model).

Figure 3. Visualizations of predicted vs. measured T. Numbers next to symbols are pressure in kbar, except for "1b" (1 bar). (A, B) The Experimental Model and Combined Model both show excellent fits to data, excepting experimental results of Tomkins et al. (2007). There is no systematic behavior in model misfit and pressure for Tomkins et al. (2007) data. (C) Model of Ferry and Watson (2007) shows significant underprediction vs. overprediction of temperature for high-pressure vs. low-pressure data, for both rocks and experiments. (D) Model of Tomkins et al. (2007) shows fairly good fit for experimental data used in the original calibration (Watson et al., 2006; Tomkins et al., 2007), but underprediction for more recent experiments of Hofmann et al. (2013), and overprediction of natural data.

Figure 4. Comparison of predicted temperatures for the Experimental and Combined Models, showing virtually identical predictions over a large range of temperatures (and pressures). The Experimental Model deviates to slightly lower values at low temperature, and slightly higher values at high temperature, giving rise to slightly different regressed values for fit parameters.