

New thermodynamic models and revised calibrations for the Ti-in-zircon and Zr-in-rutile thermometers

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Abstract The models recognize that ZrSiO_4 , ZrTiO_4 , and TiSiO_4 , but not ZrO_2 or TiO_2 , are independently variable phase components in zircon. Accordingly, the equilibrium controlling the Zr content of rutile coexisting with zircon is $\text{ZrSiO}_4 = \text{ZrO}_2$ (in rutile) + SiO_2 . The equilibrium controlling the Ti content of zircon is either $\text{ZrSiO}_4 + \text{TiO}_2 = \text{ZrTiO}_4 + \text{SiO}_2$ or $\text{TiO}_2 + \text{SiO}_2 = \text{TiSiO}_4$, depending whether Ti substitutes for Si or Zr. The Zr content of rutile thus depends on the activity of SiO_2 (a_{SiO_2}) as well as T , and the Ti content of zircon depends on a_{SiO_2} and a_{TiO_2} as well as T . New and published experimental data confirm the predicted increase in the Zr content of rutile with decreasing a_{SiO_2} , and unequivocally demonstrate that the Ti content of zircon increases with decreasing a_{SiO_2} . The substitution of Ti in zircon therefore is primarily for Si. Assuming a constant effect of P , unit a_{ZrSiO_4} , and that a_{ZrO_2} and a_{ZrTiO_4} are proportional to ppm Zr in rutile and ppm Ti in zircon, $[\log(\text{ppm Zr-in-rutile}) + \log a_{\text{SiO}_2}] = A_1 + B_1/T(\text{K})$ and $[\log(\text{ppm Ti-in-zircon}) + \log a_{\text{SiO}_2} - \log a_{\text{TiO}_2}] = A_2 + B_2/T$, where the A and B are constants. The constants were derived from published and new data from experiments with a_{SiO_2} buffered by either quartz or zircon + zirconia, from experiments with a_{SiO_2} defined by the Zr content of rutile, and from well-characterized natural samples. Results are $A_1 = 7.420 \pm 0.105$;

$B_1 = -4,530 \pm 111$; $A_2 = 5.711 \pm 0.072$; $B_2 = -4,800 \pm 86$ with activity referenced to α -quartz and rutile at P and T of interest. The zircon thermometer may now be applied to rocks without quartz and/or rutile, and the rutile thermometer applied to rocks without quartz, provided that a_{SiO_2} and a_{TiO_2} are estimated. Maximum uncertainties introduced to zircon and rutile thermometry by unconstrained a_{SiO_2} and a_{TiO_2} can be quantitatively assessed and are ≈ 60 to 70°C at 750°C . A preliminary assessment of the dependence of the two thermometers on P predicts that an uncertainty of ± 1 GPa introduces an additional uncertainty at 750°C of $\approx 50^\circ\text{C}$ for the Ti-in-zircon thermometer and of ≈ 70 to 80°C for the Zr-in-rutile thermometer.

Introduction

The Ti content of zircon coexisting with rutile or other Ti-rich phases and the Zr content of rutile coexisting with zircon or other Zr-rich phases has a strong dependence on temperature (T) (Degeling 2003; Troitzsch and Ellis 2004, 2005; Zack et al. 2004; Watson et al. 2006). Zircon and rutile are common trace minerals, and thermometers based on the Ti content of zircon and the Zr content of rutile have wide application to igneous and metamorphic rocks and ore deposits. The thermometers can be applied to individual grains, and they provide estimates of crystallization T for minerals removed from their original petrologic context such as detrital zircon and rutile.

Because of the importance of zircon and rutile thermometers, it is essential to develop sound thermodynamic models for the substitution of Ti in zircon and of Zr in rutile and to calibrate the models as accurately as possible. In an earlier treatment, Watson et al. (2006) derived

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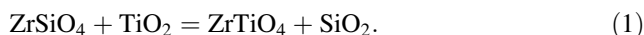
the temperature dependencies of Ti solubility in zircon and of Zr solubility in rutile by equating the chemical potentials of TiO_2 and ZrO_2 in coexisting phases. This oversimplified approach leads to useful diagrams, but fails to represent the effects of variations in the activities of all the components involved in the relevant substitutions. The problem is resolved by recognizing that TiO_2 and ZrO_2 are not valid phase components in zircon because they cannot be independently varied in a zircon solid solution. Components such as ZrSiO_4 , ZrTiO_4 , and TiSiO_4 , on the other hand, are valid. For the Zr-in-rutile thermometer, Watson et al. (2006) assumed that the activity of ZrO_2 was buffered by the coexistence of zircon and quartz, but this condition was not always met in their experiments. Here we present and calibrate new thermodynamic models based on appropriate independently variable phase components in zircon. As anticipated by others (Degeling 2003; Watson et al. 2006), the new analysis predicts that the solubility of Zr in rutile coexisting with zircon depends on the activity of SiO_2 (a_{SiO_2}) as well as on T , and that the solubility of Ti in zircon depends not only on T and a_{TiO_2} but also on a_{SiO_2} . The predicted dependence of the thermometers on a_{SiO_2} is verified by new and published experimental data (Watson et al. 2006; this study). Calibrations of the new thermodynamic models for the zircon and rutile thermometers explicitly incorporate their dependencies on a_{SiO_2} , and, in the case of the zircon thermometer, on a_{TiO_2} . The revised calibrations of the Ti-in-zircon and Zr-in-rutile thermometers extend their application to occurrences without quartz and, in the case of the zircon thermometer, without rutile as well. In cases where a_{SiO_2} and/or a_{TiO_2} are unconstrained, as in the study of some out-of-context zircons, the corresponding uncertainty in T may be estimated from the revised calibrations.

Thermodynamic analysis

Ti-in-zircon thermometer

Because the solubility of Ti in zircon is extremely limited, electron microprobe analyses of Ti-bearing zircons cannot conclusively detect a compensating deficit in either Zr or Si. The circumstantial evidence for replacement of Si by Ti, however, is compelling. Titanium replaces Si in quartz (Wark and Watson 2006). There are no Ti-rich minerals in which Ti is in eightfold coordination with oxygen, as is the case for Zr in zircon. On the basis of molecular dynamics simulations, Harrison et al. (2005) concluded that $\approx 95\%$ of Ti in zircon is in the Si site, and that this proportion is independent of T . This

strongly suggests that ZrTiO_4 is the appropriate phase component, and that the solubility of Ti in zircon is governed by the equilibrium:



At equilibrium,

$$\Delta\bar{H}_1^0 - T\Delta\bar{S}_1^0 + P\Delta\bar{V}_1^0 + RT\ln a_{\text{ZrTiO}_4} + RT\ln a_{\text{SiO}_2} - RT\ln a_{\text{ZrSiO}_4} - RT\ln a_{\text{TiO}_2} = 0. \quad (2)$$

Assuming $a_{\text{ZrSiO}_4} \approx 1$ and $a_{\text{ZrTiO}_4} \approx k_1(\text{ppm Ti-in-zircon})$, where k_1 is the product of a Henry's Law constant that relates a_{ZrTiO_4} to X_{ZrTiO_4} and the factor that converts ppm Ti to X_{ZrTiO_4} , and rearranging,

$$\begin{aligned} & [\log(\text{ppm Ti-in-zircon}) + \log a_{\text{SiO}_2} - \log a_{\text{TiO}_2}] \\ & = (\Delta\bar{S}_1^0/2.303R - \log k_1) - (\Delta\bar{H}_1^0 + P\Delta\bar{V}_1^0)/2.303RT. \end{aligned} \quad (3)$$

The approximations, $a_{\text{ZrTiO}_4} \approx 1$ and $a_{\text{ZrTiO}_4} \approx k_1(\text{ppm Ti-in-zircon})$, are excellent because the mole fraction of the Ti component is <0.006 in the zircons analyzed by Watson et al. (2006) and used in the calibration of the Ti-in-zircon thermometer. Equation (3) predicts that $[\log(\text{ppm Zr-in-zircon}) + \log a_{\text{SiO}_2} - \log a_{\text{TiO}_2}]$ should define a linear relation with $1/T$ whose slope is $-(\Delta\bar{H}_1^0 + P\Delta\bar{V}_1^0)/2.303R$ and whose intercept is $(\Delta\bar{S}_1^0/2.303R - \log k_1)$. Further, Eq. (3) predicts simple dependencies of $\log(\text{ppm Ti-in-zircon})$ on $\log a_{\text{SiO}_2}$ and $\log a_{\text{TiO}_2}$ at constant P and T :

$$[\partial \log(\text{ppm Ti-in-zircon}) / \partial \log a_{\text{SiO}_2}]_{P,T,a_{\text{TiO}_2}} = -1; \quad (4)$$

$$[\partial \log(\text{ppm Ti-in-zircon}) / \partial \log a_{\text{TiO}_2}]_{P,T,a_{\text{SiO}_2}} = +1. \quad (5)$$

In circumstances where both $\log a_{\text{SiO}_2}$ and $\log a_{\text{TiO}_2}$ are <1 but identical, the quantitative effects of reduced a_{SiO_2} and a_{TiO_2} are predicted to exactly compensate.

On the other hand, if Ti substitutes for Zr in zircon (Speer 1982), TiSiO_4 is the appropriate phase component, and the solubility of Ti in zircon is governed by the equilibrium:



At equilibrium,

$$\Delta\bar{H}_6^0 - T\Delta\bar{S}_6^0 + P\Delta\bar{V}_6^0 + RT\ln a_{\text{TiSiO}_4} - RT\ln a_{\text{SiO}_2} - RT\ln a_{\text{TiO}_2} = 0. \quad (7)$$

Making the same assumptions as before,

$$[\log(\text{ppm Ti-in-zircon}) - \log a_{\text{SiO}_2} - \log a_{\text{TiO}_2}] \\ = (\Delta \bar{S}_6^0 / 2.303R - \log k_6) - (\Delta \bar{H}_6^0 + P\Delta \bar{V}_6^0) / 2.303RT, \quad (8)$$

where k_6 relates ppm Ti-in-zircon to a_{TiSiO_4} . Equation (8) predicts that

$$[\partial \log(\text{ppm Ti-in-zircon}) / \partial \log a_{\text{SiO}_2}]_{P,T,a_{\text{TiO}_2}} = +1. \quad (9)$$

The question whether Ti substitutes primarily for Si or Zr in zircon was resolved by experiments that equilibrated zircon with rutile and either quartz or zirconia at 1.0 GPa and 1,050°C. Zirconia rather than baddeleyite is used to refer to crystalline ZrO_2 because the P – T conditions of the experiments of Watson et al. (2006) span the stability fields of both tetragonal and monoclinic ZrO_2 (Troitzsch and Ellis 2004, 2005). The presence of quartz buffers a_{SiO_2} at the maximum possible value. Zircon coexisting with rutile and β -quartz at 1.0 GPa and 1,050°C contains 108 ± 23 ppm Ti (Run 66, Table 2 of Watson et al. 2006). The minimum possible value of a_{SiO_2} consistent with zircon stability is that buffered by zircon + zirconia. The value of $\log a_{\text{SiO}_2}$ defined by zircon + zirconia at 1.0 GPa and 1,050°C, corrected for the measured 0.146 X_{TiO_2} in zirconia using Raoult's Law (Run 101, Table 1), is -0.469 (calculated from the Berman 1988 database, updated 1992, assuming zirconia has thermodynamic properties not significantly different from baddeleyite). The Ti content of zircon coexisting with rutile and zirconia at 1.0 GPa and 1,050°C then should be 318 ± 68 ppm if Ti substitutes for Si (Eq. 4) or 37 ± 8 ppm if Ti substitutes for Zr (Eq. 9). The measured value of 368 ± 28 ppm (Run 101, Table 1) clearly demonstrates: (a) the significant dependence of the Ti content of zircon on a_{SiO_2} , (b) that Ti primarily or entirely substitutes for Si rather than Zr in zircon, and (c) that Eq. (3) quantitatively represents the dependence of the zircon thermometer on a_{SiO_2} within error of measurement.

Zr-in-rutile thermometer

Generalizing the analysis of Degeling (2003), the solubility of Zr in rutile coexisting with zircon is governed by the equilibrium:



At equilibrium,

$$\Delta \bar{H}_{10}^0 - T\Delta \bar{S}_{10}^0 + P\Delta \bar{V}_{10}^0 + RT \ln a_{\text{ZrO}_2} \\ + RT \ln a_{\text{SiO}_2} - RT \ln a_{\text{ZrSiO}_4} = 0. \quad (11)$$

Making the same assumptions as before,

$$[\log(\text{ppm Zr-in-rutile}) + \log a_{\text{SiO}_2}] \\ = (\Delta \bar{S}_{10}^0 / 2.303R - \log k_{10}) - (\Delta \bar{H}_{10}^0 + P\Delta \bar{V}_{10}^0) / 2.303RT. \quad (12)$$

The approximation, $a_{\text{ZrO}_2} \approx k_{10}(\text{ppm Zr-in-rutile})$, may not be as good as the corresponding assumption for the Ti-in-zircon thermometer because the mole fraction of the ZrO_2 component in rutile can be as high as 0.09 at 1,450°C (calculated from data in Watson et al. 2006). Equation (12) predicts that $[\log(\text{ppm Zr-in-rutile}) + \log a_{\text{SiO}_2}]$ should define a linear relation with $1/T$ whose slope is $-(\Delta \bar{H}_{10}^0 + P\Delta \bar{V}_{10}^0) / 2.303R$ and whose intercept is $(\Delta \bar{S}_{10}^0 / 2.303R - \log k_{10})$. Further, Eq. (12) predicts that

$$[\partial \log(\text{ppm Zr-in-rutile}) / \partial \log a_{\text{SiO}_2}]_{P,T} = -1. \quad (13)$$

The predicted dependence of the Zr content of rutile on a_{SiO_2} is qualitatively confirmed by new and published experimental data for rutile coexisting with zircon and either quartz, zirconia, or quartz- and zirconia-undersaturated silicate melt. Rutile coexisting with zircon at 800°C, 1.0 GPa, and the maximum possible a_{SiO_2} buffered by quartz contains $1,697 \pm 56$ ppm Zr while rutile equilibrated with zircon and quartz-undersaturated melt at the same P – T

Table 1 New experimental data for coexisting zircon, rutile, and zirconia

Run	P (GPa)	T (°C)	ppm Ti in zircon	ppm Zr in rutile	wt% TiO_2 in zirconia	X_{TiO_2} in zirconia
23	1.0	1,300	NA	$94,050 \pm 100$	NA	0.183 ^a
49	1.0	1,400	NA	$103,700 \pm 800$	NA	0.194 ^a
52	1.0	1,350	NA	$101,100 \pm 1,600$	NA	0.189 ^a
70	1.0	1,280	NA	$63,400 \pm 800$	NA	0.181 ^a
101	1.0	1,050	368 ± 28	NA	10.0 ± 0.3	0.146 ^b

NA not analyzed. Uncertainties are ± 2 standard errors

^a Estimated from data in Troitzsch and Ellis (2004)

^b Calculated from measured wt% TiO_2

conditions contains significantly more Zr, $2,411 \pm 176$ ppm (Runs QT13 and 87a, Table 4 of Watson et al. 2006). Rutile coexisting with zircon at $1,350^\circ\text{C}$, 1.0 GPa, and the minimum possible a_{SiO_2} buffered by zircon + zirconia contains $101,100 \pm 1,600$ ppm Zr while rutile equilibrated with zircon and zirconia-undersaturated melt at the same P – T conditions, contains significantly less Zr, $63,100 \pm 1,542$ ppm (Run 71, Table 4 of Watson et al. 2006, and Run 52, Table 1).

Revised calibrations for the Ti-in-zircon and Zr-in-rutile thermometers

Zr-in-rutile thermometer

The Zr-in-rutile thermometer is considered first because results are then used to calibrate the Ti-in-zircon thermometer. Assuming $P\Delta\bar{V}_{10}^0 \approx \text{constant}$, the linear relationship between $[\log(\text{ppm Zr-in-rutile}) + \log a_{\text{SiO}_2}]$ and $1/T(\text{K})$, expected from Eq. (12), was quantitatively calibrated from data in Tables 4 and 5 of Watson et al. (2006) and new experimental results (Table 1). Data used in the calibration are represented as circles in Fig. 1. The reference state adopted for a_{SiO_2} was α -quartz at P and T of interest in anticipation of the numerous applications of the thermometer to rocks with zircon, rutile and α -quartz (e.g., Spear et al. 2006). Seven calibration points (black circles with number or “QTi” designations, Fig. 1) are from published experiments in which rutile + zircon + quartz was stable (Table 4 of Watson et al. 2006). For experiments in the α -quartz stability field, $\log a_{\text{SiO}_2} = 0$ (Runs QT13, QT14, QT15); for those in the β -quartz stability field, $\log a_{\text{SiO}_2} = -0.005$ to -0.010 , calculated from the Berman (1988, updated 1992) database (Runs 56b, 62a, 68a, 69a). Four calibration points (unfilled circles, Fig. 1) are from new experiments in which rutile + zircon + zirconia was stable (Runs 23, 49, 52, 70 in Table 1). Values of a_{SiO_2} buffered by zircon + zirconia were calculated as described earlier but with X_{TiO_2} in zirconia linearly extrapolated from data in Troitzsch and Ellis (2004) for $1,300$ and $1,500^\circ\text{C}$ at 2.0 GPa and for $1,300^\circ\text{C}$ at 1.5 GPa. The absence or very small amount of zirconium titanate, $(\text{Zr,Ti})_2\text{O}_4$, in these experiments and in Runs 57 (Watson et al. 2006) and 101 (Table 1) could be explained in two ways. First, the low abundance of zirconium titanate could have resulted from its difficulty in nucleating at $P < 1.2$ GPa in piston-cylinder experiments (Troitzsch et al. 2004), in which case rutile + zirconia represents a metastable equilibrium. Second, the low abundance of zirconium titanate could be explained by the requirement of oxygen fugacity at or above the hematite–magnetite buffer for zirconium titanate stability (Troitzsch and Ellis 2004),

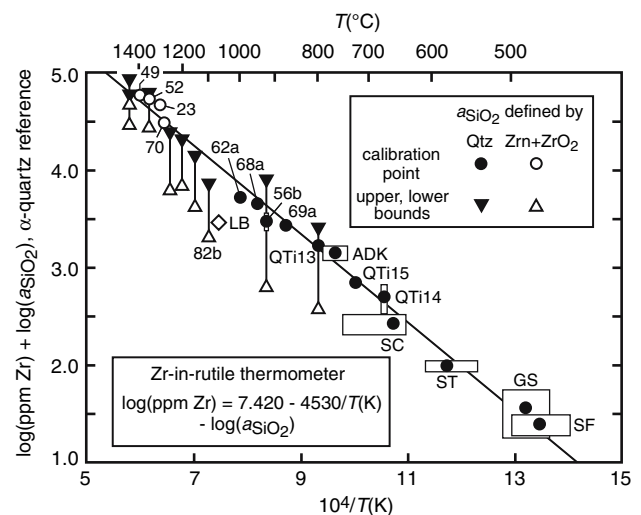


Fig. 1 Calibration of the Zr-in-rutile thermometer based on data from experiments and natural samples in Watson et al. (2006) and on experimental results in Table 1. Line is a least-squares fit to the calibration points, using: (1) natural samples with rutile, zircon, and quartz (black circles with letter designations: ADK Adirondack migmatite, SC Santa Catalina migmatite, ST Stillup Tal schist, GS Vermont greenschist, SF Sifnos blueschist); (2) experiments with rutile, zircon, and quartz (black circles with number or “QTi” designations); (3) experiments with rutile, zircon, and zirconia (unfilled circles). Where larger than the symbol, error for each calibration point is represented by a rectangle whose half-height corresponds to twice the standard error of measurement of the Zr content of rutile and whose width is either $\pm 5^\circ\text{C}$ (experiments) or the reported range of possible T (natural samples). Data for Labait harzburgite (LB) and experiments with unbuffered a_{SiO_2} (paired triangles connected with vertical line) not used in the calibration. Upper bounds for experiments with unbuffered a_{SiO_2} (downward-pointing black triangles) defined by fictive equilibrium with quartz (Qtz); lower bounds for experiments with unbuffered a_{SiO_2} (upward-pointing unfilled triangles) defined by fictive equilibrium with zircon (Zrn) and zirconia (ZrO_2)

in which case rutile + zirconia represents a stable equilibrium. An additional five calibration points are from data in Table 5 of Watson et al. (2006) for natural occurrences of rutile + zircon + α -quartz ($\log a_{\text{SiO}_2} = 0$). A linear fit to the 16 data points, over the range $T = 470$ – $1,400^\circ\text{C}$, gives the quantitative calibration of the Zr-in-rutile thermometer in Fig. 1:

$$\log(\text{ppm Zr-in-rutile}) = (7.420 \pm 0.105) - (4530 \pm 111)/T(\text{K}) - \log a_{\text{SiO}_2}. \quad (14)$$

Uncertainties are 95% confidence intervals. The least-squares fit considered uncertainties both in the Zr content of rutile and in $1/T$. Because the sources of error in the calibration points based on experiments and in those based on data for natural samples are so different, we did not feel justified in weighting the calibration points.

The datum for the Labait harzburgite was not used because, after the correction for reduced a_{SiO_2} was made

($\log a_{\text{SiO}_2} = -0.643$ based on forsterite + enstatite equilibrium at 3.0 GPa and 1,070°C), the datum fell well off the trend defined by the calibration points (LB, Fig. 1). Likewise data for nine experiments that contained neither quartz nor zirconia (and hence with undefined a_{SiO_2}) from Table 4 of Watson et al. (2006) were not used in the calibration. Results for each experiment are represented by the nine pairs of opposed triangles connected by vertical lines in Fig. 1. The downward pointing black triangle of each pair represents the plotting position for the average measured Zr content of rutile plus two standard errors if a_{SiO_2} was the maximum possible value defined by a fictive equilibrium with quartz. The upward pointing unfilled triangle of each pair represents the plotting position for the average measured Zr content of rutile minus two standard errors if a_{SiO_2} was the minimum possible value defined by a fictive equilibrium with zirconia. Ideally, each pair of opposed triangles should bracket the calibration curve.

Where larger than the symbols, error for each datum used in the calibration in Fig. 1 is represented by a rectangle whose half-height corresponds to twice the standard error of measurement of the Zr content of rutile and whose width is either $\pm 5^\circ\text{C}$ (experiments) or the reported range of possible T (natural samples). The calibration line passes within error of measurement through data for all natural samples (except the Labait harzburgite) and seven of the experimental calibration points. The line just misses the points for the other four calibration experiments (Runs 23, 52, 56b, 62a). The line also passes between the brackets or close to the upper bracket for all but one of the experiments with undefined a_{SiO_2} . The entire bracket of the one exception (Run 82b, Fig. 1) lies significantly below the calibration curve for unknown reasons.

The 95% confidence envelope for the calibration of the linear relationship between $[\log(\text{ppm Zr-in-rutile}) + \log a_{\text{SiO}_2}]$ and $1/T$ is illustrated by the gray band in Fig. 2 over the range of values covered by the calibration points. For a given value of $[\log(\text{ppm Zr-in-rutile}) + \log a_{\text{SiO}_2}]$ the uncertainty in estimated T introduced by uncertainty in the linear fit to the data alone is $\pm 14^\circ$ at 500°C, $\pm 13^\circ$ at 750°C, and $\pm 30^\circ$ at 1,100°C at the 95% confidence level.

Ti-in-zircon thermometer

Assuming $P\Delta\bar{V}_1^0 \approx \text{constant}$, the linear relationship between $[\log(\text{ppm Zr-in-Zircon}) + \log a_{\text{SiO}_2} - \log a_{\text{TiO}_2}]$, and $1/T(\text{K})$, expected from Eq. (3), was quantitatively calibrated from data in Tables 2 and 3 of Watson et al. (2006) and the results of one new experiment (Table 1). Data used in the calibration are represented as circles in Fig. 3. The reference states adopted for a_{SiO_2} and a_{TiO_2} were α -quartz and rutile at P and T of interest. For all calibration points, a value of X_{ZrO_2} in rutile was estimated from Eq. (14). The

value of a_{TiO_2} was then calculated as $1 - X_{\text{ZrO}_2}$, assuming Raoult's Law. One calibration point (black circle, Fig. 3) is from a published experiment in which zircon + rutile + β -quartz was stable (Run 66, Table 2 of Watson et al. 2006) with $\log a_{\text{SiO}_2}$ buffered by β -quartz calculated as described previously. Two calibration points (unfilled circles, Fig. 3) are from experiments in which zircon + rutile + zirconia was stable (Run 101, Table 1; Run 57, Table 2 and Fig. 2a of Watson et al. 2006) with $\log a_{\text{SiO}_2}$ buffered by zircon + zirconia calculated as described previously. Four calibration points (gray circles, Fig. 2) are from experiments that contained zircon + rutile but with unbuffered a_{SiO_2} (Runs 58, 63, 65, 71 in Table 2 of Watson et al. 2006). A value of $\log a_{\text{SiO}_2}$ for each experiment was computed from the measured Zr content of rutile (Table 4 of Watson et al. 2006) and Eq. (14); two small but physically impossible positive calculated values of $\log a_{\text{SiO}_2}$ were reassigned a value of zero. An additional four calibration points are from data in Table 3 of Watson et al. (2006) for natural occurrences of zircon + rutile + α -quartz ($\log a_{\text{SiO}_2} = 0$). A linear fit to the 11 data points, over the range $T = 580$ – $1,400^\circ\text{C}$, gives the quantitative calibration of the Ti-in-zircon thermometer in Fig. 3:

$$\log(\text{ppm Ti-in-zircon}) = (5.711 \pm 0.072) - (4800 \pm 86)/T(\text{K}) - \log a_{\text{SiO}_2} + \log a_{\text{TiO}_2}. \quad (15)$$

Uncertainties are 95% confidence intervals. The least-squares fit considered uncertainties both in the Ti content

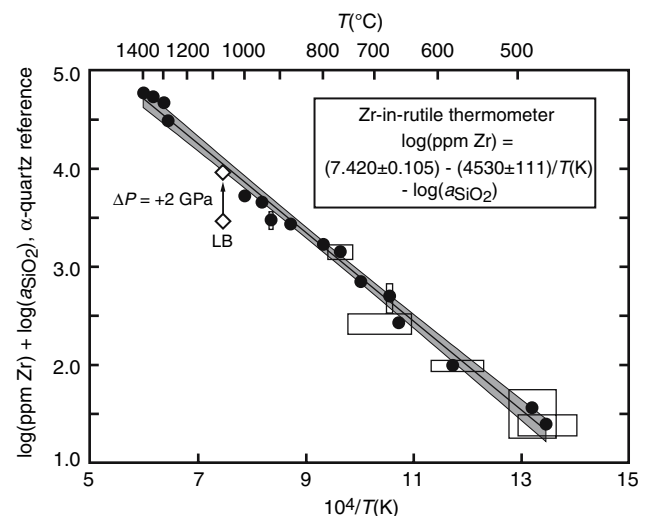


Fig. 2 Calibration of the Zr-in-rutile thermometer as in Fig. 1 showing the 95% confidence envelope for the linear fit to the data (gray band). Calibration points (black circles) are shown without distinguishing the type of data they represent. Rectangles are the same as in Fig. 1. The two diamonds illustrate how the datum for rutile from the Labait harzburgite is shifted by a preliminary pressure correction of 2 GPa (see text)

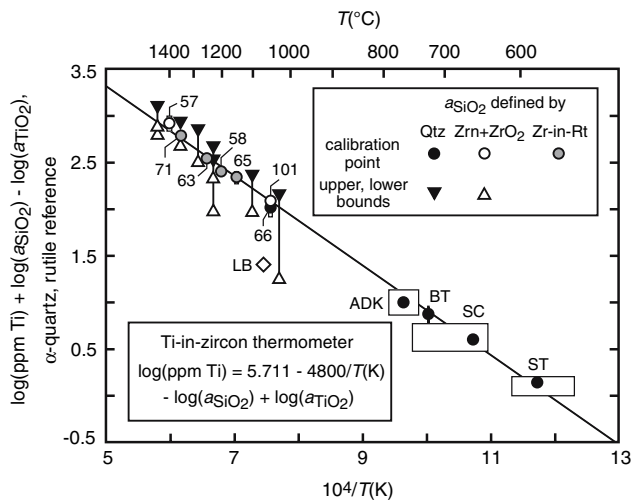


Fig. 3 Calibration of the Ti-in-zircon thermometer based on data from experiments and natural samples in Watson et al. (2006) and on experimental results in Table 1. Format, symbols, and abbreviations are as in Fig. 1. Line is a least-squares fit to the calibration points, using: (1) natural samples with zircon, rutile, and quartz (black circles with letter designations; BT Bishop tuff); (2) one experiment with zircon, rutile, and quartz (filled circle, Run 66); (3) experiments with zircon, rutile, and zirconia (open circles, Runs 57 and 101); (4) experiments with unbuffered a_{SiO_2} defined by the Zr content of rutile (Rt) (gray circles). Rectangles have the same meaning as in Fig. 1 except that the vertical dimension of rectangles for natural samples represents the total measured range in the Ti content of zircon and that the horizontal dimension of the rectangle for Run 57 represents $\pm 10^\circ\text{C}$. Data for Labait harzburgite (LB) and experiments with unbuffered and undefined a_{SiO_2} not used in the calibration

of zircon and in $1/T$, and the calibration points were not weighted.

The datum for the Labait harzburgite was not used because, after the correction for reduced a_{SiO_2} was made (as described previously), the datum fell well off the trend defined by the calibration points (LB, Fig. 3). Likewise, the datum for one experiment without quartz or zirconia but for which $\log a_{\text{SiO}_2}$ was calculated from Eq. (14) (Run 73, Table 2 of Watson et al. 2006) was not used because it also fell well off the trend defined by the calibration points. There are seven experiments in Table 2 of Watson et al. (2006) that contained zircon + rutile but neither quartz nor zirconia and for which no measured values of the Zr content of the rutile were reported. For these experiments a_{SiO_2} is neither buffered nor defined by mineral equilibria. Results for each of the seven experiments and for Run 73 are represented by the eight pairs of opposed triangles connected by vertical lines in Fig. 3. The downward pointing black triangle of each pair represents the plotting position for the average measured Ti content of zircon plus two standard errors if a_{SiO_2} was the maximum possible value defined by a fictive equilibrium with quartz. The upward pointing unfilled triangle represents the plotting

position for the average measured Ti content of zircon minus two standard errors if a_{SiO_2} was the minimum possible value defined by a fictive equilibrium with zirconia.

The rectangles in Fig. 3 have the same meaning as those in Fig. 1 except that the vertical dimension of the rectangles for natural samples represents the total measured range in the Ti content of zircon and that the horizontal dimension of the rectangle for Run 57 represents $\pm 10^\circ\text{C}$. The calibration line passes within error of measurement through data for all natural samples (except the Labait harzburgite) and through all experimental calibration points. In addition, the line passes between the brackets for Run 73 and for all of the experiments with undefined a_{SiO_2} .

The 95% confidence envelope for the calibration of the linear relationship between $[\log(\text{ppm Zr-in-Zircon}) + \log a_{\text{SiO}_2} - \log a_{\text{TiO}_2}]$, and $1/T$ is illustrated by the gray band in Fig. 4 over the range of values covered by the calibration points. For a given value of $[\log(\text{ppm Zr-in-Zircon}) + \log a_{\text{SiO}_2} - \log a_{\text{TiO}_2}]$, the uncertainty in estimated T introduced by uncertainty in the linear fit to the data alone is $\pm 12^\circ$ at 600°C , $\pm 11^\circ$ at 750°C , and $\pm 16^\circ$ at $1,100^\circ\text{C}$ at the 95% confidence level.

Discussion and applications

Comparison of revised and published calibrations

The calibration of the Ti-in-zircon thermometer by Watson et al. (2006) suggested that there was a slight inconsistency between calibration points based on experimental data and points derived from the Ti contents of zircon in natural samples (thin dashed and solid lines in their Fig. 4). Once the dependency of the thermometer on a_{SiO_2} is explicitly taken into account, however, there is (with the exception of the datum for the Labait harzburgite) full consistency between experimental and natural data within error of measurement (Fig. 3).

The new calibrations of the Ti-in-zircon and Zr-in-rutile thermometers in Figs. 1, 2, 3, and 4 are remarkably similar to those derived by Watson et al. (2006). For example, Ti contents of zircon that record 1,100, 750, and 600°C using the calibration of Watson et al. (2006) record 1,138, 756, and 597°C with the revised calibration, assuming $a_{\text{SiO}_2} = a_{\text{TiO}_2} = 1$. The Zr contents of rutile that record 1,100, 750, and 500°C using the calibration of Watson et al. (2006) record 1,093, 750, and 502°C with the revised calibration for $a_{\text{SiO}_2} = 1$. The good agreement is explained if many of the experiments conducted by Watson et al. (2006) with zircon and rutile in the presence of hydrous silicate melt were close to quartz saturation. Except for an added uncertainty over the values of a_{SiO_2} , a_{TiO_2} , and P , the T s estimated for zircons from Jack

Hills, Australia, by Watson and Harrison (2005) and the conclusions drawn from them do not require significant revision. The uncertainty over a_{SiO_2} and a_{TiO_2} is probably not significant both because quartz is the most common mineral inclusion in the Jack Hills zircons, and because reduced activities of SiO_2 (absence of quartz) and TiO_2 (absence of rutile) compensate for one another in terms of their effect on calculated T . For example, if $a_{\text{SiO}_2} = 0.5$ and $a_{\text{TiO}_2} = 0.5$ (not unrealistic for a ‘mafic’ granitoid melt such as a tonalite), then T recorded by the Ti-in-zircon thermometer will be the same as if both quartz and rutile were present. In another recent study, T s estimated from rutile coexisting with α -quartz and zircon in blueschists by Spear et al. (2006) likewise do not require significant revision.

Activities of SiO_2 and TiO_2

For rocks that contain zircon, rutile, and quartz, for out-of-context zircons that contain rutile and quartz inclusions, and for out-of-context rutiles that contain zircon and quartz inclusions, Figs. 1, 2, 3, and 4 may be applied directly to measured Ti contents of zircon and Zr contents of rutile. If estimated values of T lie in the stability field for β -quartz, a correction for the α -quartz reference state may be made, but it is very small (<0.03 log units for $T \leq 1,300^\circ\text{C}$) and not significant in most applications.

In the case of rocks that lack quartz and/or rutile, and for which values of a_{SiO_2} and a_{TiO_2} may be independently estimated from mineral equilibria, accurate estimates of T can still be made from Eqs. (14) and (15) or from Figs. 1, 2, 3, and 4. The Ti-in-zircon thermometer may additionally be accurately applied to rocks without quartz and rutile if only the difference ($\log a_{\text{SiO}_2} - \log a_{\text{TiO}_2}$) is independently defined (e.g., by the orthopyroxene-ilmenite equilibrium in mafic igneous rocks). The revised calibrations of the Ti-in-zircon and Zr-in-rutile thermometers make them more generally useful by extending their application to rocks devoid of quartz and, in the case of the zircon thermometer, devoid of rutile.

For rocks and out-of-context zircons and rutiles with undefined a_{SiO_2} and a_{TiO_2} , Eqs. (14) and (15) allow estimates of maximum plausible additional uncertainties in calculated T introduced by the undefined activities. Values of a_{TiO_2} in silicic melts at appropriate magmatic T s are rarely below ≈ 0.5 and typically 0.6–0.9 (Watson et al. 2006; Hayden et al. 2007). Zircons with Ti contents that record $T = 750^\circ\text{C}$ under conditions of $a_{\text{TiO}_2} = 1$ record $T = 820^\circ\text{C}$ for $a_{\text{TiO}_2} = 0.5$. In applications to typical rutile-free crustal rocks or out-of-context zircons, the assumption of $a_{\text{TiO}_2} = 1$ leads to T estimates using Eq. (15) that may be too low by up to $\approx 70^\circ\text{C}$. The common occurrence of albite and the uncommon occurrence of nepheline indicate that

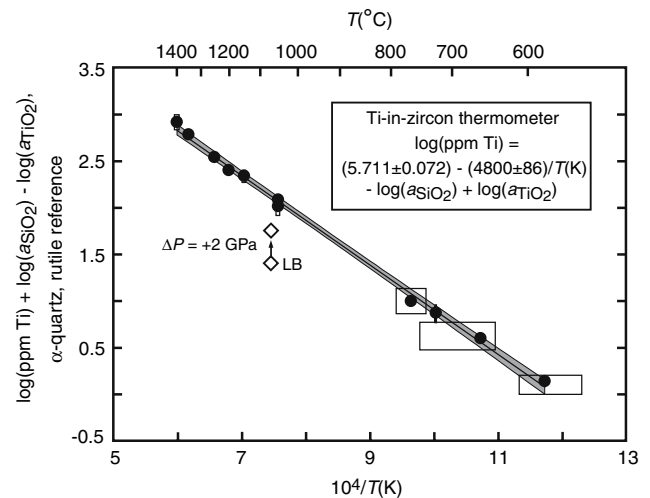


Fig. 4 Calibration of the Ti-in-zircon thermometer as in Fig. 3 showing the 95% confidence envelope for the linear fit to the data (gray band). Calibration points (black circles) are shown without distinguishing the type of data they represent. Rectangles are the same as in Fig. 3. The two diamonds illustrate how the datum for zircon from the Labait harzburgite is shifted by a preliminary pressure correction of 2 GPa (see text)

a_{SiO_2} in most crustal rocks is also not usually less than ≈ 0.5 (calculated from Berman's 1988 database, updated 1992). Zircons with Ti contents and rutiles with Zr contents that record $T = 750^\circ\text{C}$ under conditions of $a_{\text{SiO}_2} = 1$ record $T = 688$ and 685°C , respectively, for $a_{\text{SiO}_2} = 0.5$. In applications to typical quartz-free crustal rocks or out-of-context zircons and rutile, the assumption of $a_{\text{SiO}_2} = 1$

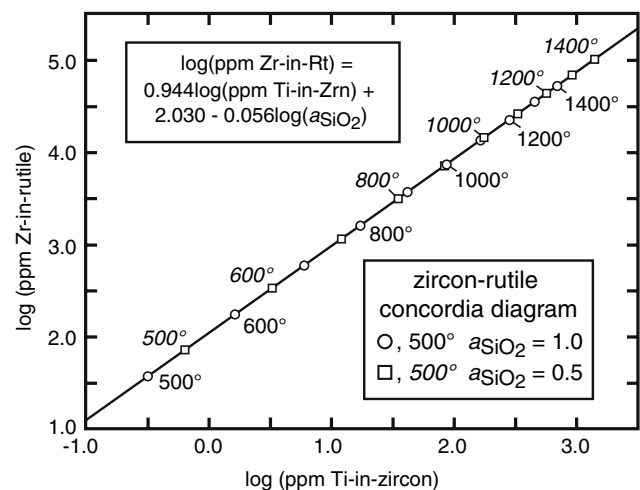


Fig. 5 The Ti contents of zircon and Zr contents of rutile coexisting at equilibrium predicted by Eqs. (14) and (15) with $a_{\text{TiO}_2} \approx 1$ and $P \approx 1$ GPa. Values of T are marked off at 100° intervals from 500 to $1,400^\circ\text{C}$ for $a_{\text{SiO}_2} = 1$ (circles, numbers in normal type) and $a_{\text{SiO}_2} = 0.5$ (squares, numbers in italics). Regardless of a_{SiO_2} , the diagram can be used to test for equilibrium between coexisting zircon and rutile and to estimate the approximate T of equilibration

leads to T estimates using Eqs. (14) and (15) that may be too high by up to ≈ 60 to 70°C . Errors introduced by unknown values of a_{SiO_2} and a_{TiO_2} are in addition to those introduced by calibration of the thermometers themselves (Figs. 2, 4) and by possible equilibration at P significantly different from ≈ 1 GPa (next section). The effects of reduced a_{SiO_2} and a_{TiO_2} compensate, but the degree to which this occurs is difficult to quantitatively evaluate in individual rutile- and quartz-free rocks or out-of-context zircons.

Dependence of the thermometers on pressure

A preliminary evaluation of the dependence of the Ti-in-zircon and Zr-in-rutile thermometers on P is derived from Eqs. (3) and (12):

$$[\partial \log(\text{ppm Ti-in-zircon}) / \partial P]_{T, a_{\text{SiO}_2}, a_{\text{TiO}_2}} = -\Delta \bar{V}_1^0 / 2.303RT; \quad (16)$$

$$[\partial \log(\text{ppm Zr-in-rutile}) / \partial P]_{T, a_{\text{SiO}_2}} = -\Delta \bar{V}_{10}^0 / 2.303RT. \quad (17)$$

Approximate values of $\Delta \bar{V}_1^0 = 4.51 \text{ cm}^3$ and $\Delta \bar{V}_{10}^0 = 6.27 \text{ cm}^3$ ($1 \text{ cm}^3 = 1 \text{ kJ/GPa}$) were computed from 25°C and 1 bar molar volume data for zircon, rutile and α -quartz in Holland and Powell (1998), for ZrO_2 with the rutile structure cited in Degeling (2003), and for ZrTiO_4 in Troitzsch and Ellis (2004). The value of $\Delta \bar{V}_1^0$ is less reliable than the value of $\Delta \bar{V}_{10}^0$ because the molar volume used for ZrTiO_4 does not refer to the compound in the zircon structure. Eqs. (16) and (17) predict that both the Ti content of zircon coexisting with quartz and rutile and the Zr content of rutile coexisting with zircon and quartz decrease with increasing P at constant T , a_{SiO_2} and a_{TiO_2} . The predicted pressure dependence of the Zr content in rutile coexisting with zircon and quartz is fully consistent with the experimental data of Degeling (2003). Isopleths of the Ti content of zircon coexisting with rutile and quartz and of the Zr content of rutile coexisting with zircon and quartz will both have positive slopes on a P – T diagram.

The calibrations of the Ti-in-zircon and Zr-in-rutile thermometers in Figs. 1, 2, 3, and 4 are most appropriately considered as referring to $P \approx 1$ GPa because (a) all but two experiments used for calibration were conducted at 1 GPa (the exceptions are Run 63 at 1.2 GPa and Run 62a at 1.4 GPa) and (b) the estimated P of equilibration of all but two natural samples used in the calibrations was 1.0 ± 0.5 GPa (samples GS and BT equilibrated at lower P). The magnitude of the pressure dependence of the thermometers is illustrated by considering coexisting zircon

with a Ti content and rutile with a Zr content defined by crystallization at $T = 750^\circ\text{C}$ in the presence of quartz. If the zircon and rutile equilibrated at 2 GPa rather than 1 GPa, T estimated from Figs. 1, 2, 3, and 4 is 702°C for the zircon and 681°C for the rutile. If the zircon and rutile equilibrated at 1 bar rather than 1 GPa, T estimated from Figs. 1, 2, 3 to 4 is 803°C for the zircon and 830°C for the rutile. An approximate measure of the pressure dependence of the Ti-in-zircon and Zr-in-rutile thermometers therefore is 50°C/GPa and 70 – 80°C/GPa , respectively. The uncertainties introduced in any application of the thermometers to conditions of unknown P are in addition to those introduced by uncertainties of the calibration itself (Figs. 2, 4) and to those introduced by unknown values of a_{SiO_2} and a_{TiO_2} . More thorough assessment of the pressure dependence of the Zr-in-rutile thermometer is forthcoming (Tompkins et al. 2007); a more accurate assessment of the pressure dependence of the Ti-in-zircon thermometer awaits new experimental data for the Ti content of zircon coexisting with rutile and quartz at $P \neq 1$ GPa.

The unexpectedly low Ti content of zircon and Zr content of rutile from the Labait harzburgite in Figs. 1, 2, 3, and 4, at least in part, can be explained by the rock's equilibration at ≈ 3 GPa (Lee and Rudnick 1999). Equations (16) and (17) were used to correct mineral compositions reported by Watson et al. (2006) for equilibration at 2 GPa higher than appropriate for the calibrations in Figs. 1, 2, 3, and 4. The pressure-corrected rutile composition brings the datum for the Labait harzburgite into registry with the calibration of the Zr-in-rutile thermometer (Fig. 2). The pressure-corrected zircon composition, on the other hand, brings the datum for the Labait harzburgite closer to but not in registry with the calibration of the Ti-in-zircon thermometer (Fig. 4). The dependence of the Ti-in-zircon thermometer on P therefore may be underestimated by the preliminary correction.

Effect of elements other than Zr, Ti, and Si in zircon

Zircon may deviate from a $\text{Zr}(\text{Si}, \text{Ti})\text{O}_4$ solid solution by incorporation of other elements such as Hf, U, and Th (Speer 1982). These substitutions will affect applications of both the Ti-in-zircon and Zr-in-rutile thermometers to the extent that a_{ZrSiO_4} is significantly reduced below the value of 1 assumed in the calibrations (Figs. 1, 2, 3, 4; Eqs. 14, 15). The effect may be quantitatively corrected for by calculating the mole fraction of the ZrSiO_4 component of zircon from a mineral analysis and appropriately assuming Raoult's Law ($a_{\text{ZrSiO}_4} = X_{\text{ZrSiO}_4}$). The value of $\log(a_{\text{ZrSiO}_4})$ then would be added to the right-hand sides of Eqs. (14) and (15) or subtracted from the value of the ordinate of Figs. 1, 2, 3 and 4.

The substitution of cations other than Zr, Si, and Ti in zircon may also affect k_1 , the constant that relates a_{ZrSiO_4} to (ppm Ti-in-zircon). The magnitude of the affect, however, is not possible to evaluate at this time.

Zircon-rutile equilibrium

In the case of rocks with both zircon and rutile, zircons with rutile inclusions, and rutiles with zircon inclusions, $a_{\text{TiO}_2} \approx 1$, and simultaneous application of Eqs. (14) and (15), in principle, can be used to eliminate the dependencies of the zircon and rutile thermometers on a_{SiO_2} . Subtracting Eq. (14) from Eq. (15),

$$\log[(\text{ppm Zr-in-rutile})/(\text{ppm Ti-in-zircon})] = (1.709 \pm 0.127) + (270 \pm 140)/T(\text{K}). \quad (18)$$

Unfortunately, the very small temperature dependence of [(ppm Zr-in-rutile)/(ppm Ti-in-zircon)] precludes meaningful application of the zircon-rutile thermometer. Given representative uncertainties in measurement of the Ti content of zircon and of the Zr content of rutile, uncertainties in values of T estimated from Eq. (18) can be $>1,000^\circ\text{C}$. The small temperature dependence of [(ppm Zr-in-rutile)/(ppm Ti-in-zircon)] in Eq. (18) results from the nearly identical slopes of the best-fit lines in Figs. 1, 2, 3, and 4.

There are, nevertheless, useful applications of the zircon-rutile equilibrium. If $a_{\text{TiO}_2} \approx 1$ defined by the presence of rutile, the Ti content of zircon and the Zr content of rutile are related at equilibrium, through Eqs. (14) and (15), by

$$\log(\text{ppm Zr-in-rutile}) = 0.944\log(\text{ppm Ti-in-zircon}) + 2.030 - 0.056\log a_{\text{SiO}_2}. \quad (19)$$

For $a_{\text{SiO}_2} \geq 0.5$, Eq. (19) defines essentially a single line (Fig. 5). Figure 5 is a kind of concordia diagram that allows for straightforward assessment of whether coexisting zircon and rutile are in equilibrium at $P \approx 1$ GPa. Zircon-rutile pairs that plot off of concordia will yield an inaccurate Ti-in-zircon T , an inaccurate Zr-in-rutile T , or both. The concordia line can be marked off with T for a given a_{SiO_2} ; results are illustrated in Fig. 5 for $a_{\text{SiO}_2} = 1$ (circles, values of T in normal type) and $a_{\text{SiO}_2} = 0.5$ (squares, values of T in italics). For zircon-rutile pairs that are concordant within error of measurement on Fig. 5, T may be approximately estimated even if a_{SiO_2} is unknown.

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