

TitaniQ: a titanium-in-quartz geothermometer

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Abstract Titanium is one of many trace elements to substitute for silicon in the mineral quartz. Here, we describe the temperature dependence of that substitution, in the form of a new geothermometer. To calibrate the “TitaniQ” thermometer, we synthesized quartz in the presence of rutile and either aqueous fluid or hydrous silicate melt, at temperatures ranging from 600 to 1,000°C, at 1.0 GPa. The Ti contents of quartz (in ppm by weight) from 13 experiments increase exponentially with reciprocal T as described by:

$$\text{Log}(X_{\text{Ti}}^{\text{qtz}}) = (5.69 \pm 0.02) - \frac{(3765 \pm 24)}{T(K)}.$$

Application of this thermometer is straightforward, typically requiring analysis of only one phase (quartz). This can be accomplished either by EPMA for crystallization temperatures above 600°C, or by SIMS for temperatures down to at least 400°. Resulting temperature estimates are very precise (usually better than $\pm 5^\circ\text{C}$), potentially allowing detailed characterization of thermal histories within individual quartz grains. Although calibrated for quartz crystallized in the presence of rutile, the thermometer can also be applied to rutile-absent systems if TiO_2 activity is constrained.

Introduction

Despite its abundance in the Earth’s crust, the mineral quartz (composed almost entirely of Si and O atoms in the ratio 1:2) has rarely been the target of geochemical study. This is beginning to change, however, due in part to the increasing ease of analyzing trace element concentrations down to the ppm level using ion and laser beam instruments (e.g., Flem et al. 2002; Mueller et al. 2003). In addition, there is increased recognition that the trace element budget and related cathodoluminescence emission properties of quartz may provide valuable petrologic clues to crystallization conditions (e.g., Goetze et al. 2004, 2005; Landtwing and Pettke 2005; Peppard et al. 2001; Watt et al. 1997).

One trace element—titanium—shows special promise in this regard. Concentrations of Ti in metamorphic and igneous quartz are relatively high (ranging from 1 to over 100 ppm) and are thus easily quantified. Furthermore, Ti can substitute for Si without having to be charge balanced by coupled substitution of another element, because of the tetravalent nature of both the Ti and Si cations. Finally, the activity of Ti in many systems is fixed by the presence of a nearly pure TiO_2 phase (typically rutile). Consequently, the chemical potential of Ti, and hence the extent of Ti substitution for Si in quartz, should vary systematically with temperature.

The purpose of this paper is to describe the systematic relation between the Ti content of quartz and its temperature of equilibration, in the form of a titanium-in-quartz geothermometer, which we dubbed (Wark and Watson 2004) the “TitaniQ”. This new geothermometer is based on experiments conducted at temperatures between 600 and 1,000°C, in which

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quartz was equilibrated with rutile in the presence of aqueous fluids and/or silicate melt. Although rutile was present in experiments, the TitaniQ thermometer can be applied to natural systems in which rutile was *not* an equilibrium phase, if Ti activity (relative to that required for rutile saturation) can be estimated. Even when this is not possible, the thermometer predicts a minimum temperature of equilibration that can be accurate to within a few tens of °C.

We expect the TitaniQ to have advantages over many existing geothermometers. Firstly, it should be applicable to a broad range of rock types, due to the abundance of quartz in Earth's continental crust combined with the large range of pressures and temperatures over which quartz is stable. Also, the thermometer is relatively easy to apply because it typically requires analysis of only one phase. In addition, the thermal history recorded by Ti zoning in quartz can often be characterized by cathodoluminescence (CL) imaging, because CL intensity in many quartz crystals is a function of Ti content (Wark and Spear 2005). Finally, one of the strongest attributes of the TitaniQ is its precision: for rocks equilibrated at $T > 500^\circ\text{C}$, temperature uncertainties of $\pm 2^\circ\text{C}$ can be achieved.

Theory

The thermodynamic principles behind our TitaniQ thermometer—like those for the complementary trace-element thermometers, Ti-in-zircon and Zr-in-rutile (Watson et al. 2006)—are straightforward. For quartz in equilibrium with rutile, an exchange reaction can be written:



The equilibrium constant for this reaction, K , is described by

$$K = \frac{a_{\text{TiO}_2}^{\text{qtz}}}{a_{\text{TiO}_2}^{\text{rutile}}}, \quad (2)$$

where a_{TiO_2} is the activity of TiO_2 in each phase. For relatively pure rutile, $a_{\text{TiO}_2, \text{rutile}} \sim 1$. Consequently, $K \sim a_{\text{TiO}_2, \text{quartz}}$ and we can write:

$$\exp\left[\frac{-\Delta G^0}{RT}\right] = a_{\text{TiO}_2}^{\text{qtz}}, \quad (3)$$

where R is the gas constant, T is absolute temperature, and ΔG^0 is the free energy change for reaction (1) when quartz and rutile are in their standard states.

Assuming Henrian behavior (a linear relation between activity and concentration of TiO_2 in quartz),

$$a_{\text{TiO}_2}^{\text{qtz}} = \gamma \cdot X_{\text{TiO}_2}^{\text{qtz}}, \quad (4)$$

where γ is the activity coefficient. Combining the previous two equations, we get

$$\exp\left[\frac{-\Delta G^0}{RT}\right] = \gamma \cdot X_{\text{TiO}_2}^{\text{qtz}}. \quad (5)$$

Assuming constant γ , this equation predicts that the TiO_2 (or Ti) content of quartz that crystallizes in equilibrium with rutile will increase exponentially with $1/T$.

Experimental methods

As summarized in Table 1, experimental calibration was performed by equilibrating finely ground ($<10 \mu\text{m}$) glassy or crystalline SiO_2 (Arkansas quartz) with amorphous TiO_2 powders (Aesar) and a 1 M HF solution or distilled H_2O (up to 30 vol%). In one run, Na_2CO_3 was added (this reacted at run conditions to form an alkali silicate glass); in another, we added rhyolite glass (Lake county obsidian). Finely powdered zircon or ZrO_2 was added to most of the experiments,

Table 1 Summary of experiments and results

Run ID	Fluid type ^a	Capsule type ^b	T (°C)	Duration (h)	ppm Ti in quartz ^c (s.e.)
16	H	Ag	600	114	22 (0.6)
9	H	Ag	650	99	31 (4.0)
79a	H	AuNi	700	118	69 (2.3)
79m	MLC	AuNi	700	118	60 (3.3)
6	H	Ag	750	86	103 (6.0)
87	HF	PtNi	800	120	140 (2.5)
69	H	HDC	875	406	265 (10.4)
50	HF	AuNi	850	168	250 (6.8)
3	H	Ag	850	66	230 (5.3)
83	H	AuNi	900	162	327 (2.7)
68	H	HDC	950	240	413 (15.4)
77a	H	PtNi	1,000	148	522 (5.4)
77 m	MNa	PtNi	1,000	148	526 (4.0)

Note: All experiments were saturated in H_2O or in 1 M HF solution, and contained TiO_2 and ZrO_2 or ZrSiO_4 powders, in addition to excess SiO_2 as glass or as crystalline quartz powder

^a H, H_2O , HF, 1 molar HF solution, MLC, Lake County obsidian (which formed melt phase), MNa, Na_2CO_3 (which formed melt phase)

^b *Ag* thick-walled Ag capsule, *AuNi* Au liner in thick-walled oxidized Ni capsule, *PtNi* Pt liner in thick-walled oxidized Ni capsule, *HDC* Hydrothermal double capsule (see Watson et al. 2006)

^c #16 analyzed by SIMS; all others by EPMA

with the goal of providing data for the Zr-in-rutile and Ti-in-zircon thermometers (Watson et al. 2006). Although some of these utilized a double capsule made of Pt metal (see description in Watson et al. 2006), others were performed in pressure-sealing Ni capsules lined with Au or Pt, or in capsules made of Ag (Fig. 1).

All experiments were performed at 1.0 GPa in a piston-cylinder apparatus, where they were held at T between 600 and 1,000°C for up to 406 h. Experiments were also attempted at lower pressure in piston cylinders (0.5 GPa) and in cold seal furnaces (<0.2 GPa), but none of these yielded quartz of sufficient size to allow accurate analysis of Ti contents. The same was true for low temperatures: we were unable to produce large quartz crystals below 600°C. At the high temperature end, experiments were limited to $T < 1,100^\circ\text{C}$, which is the temperature at which quartz melts in the presence of excess H_2O at 1.0 GPa.

After quenching experiments, capsules were sliced open, vacuum-impregnated with epoxy, and then ground and polished. Suitability for analysis was evaluated using backscattered-electron imaging (BEI; Fig. 2). For reasons described below, the most important criterion for suitability was the presence of large (at least 10 μm diameter), newly grown quartz crystals lacking rutile as inclusions or as a nearby phase. Many experiments failed to meet this criterion and were excluded from consideration.

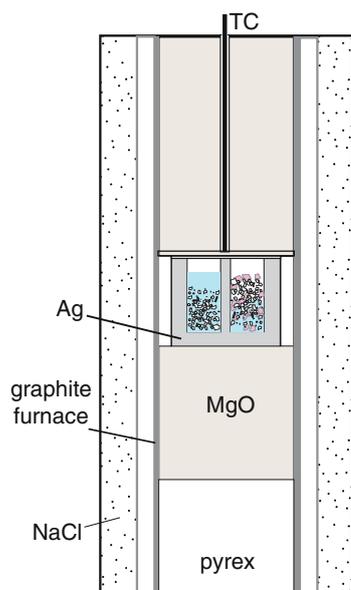


Fig. 1 Schematic diagram of experimental assembly for experiments labeled “Ag” in Table 1. “TC” refers to thermocouple. Capsule is shown with quartz, rutile and water added to left side reservoir, and quartz, rutile, glass, and water in right reservoir. See Watson et al. (2006) for diagrams showing other experiment types

Analytical procedures

EPMA

The Ti content of new quartz in all but one experiment was determined by electron probe microanalysis (EPMA) at Rensselaer, by simultaneously counting Ti K-alpha X-rays using PET crystals on four spectrometers and averaging the results. Although analyses were performed at high current (>100 nA), calibration of Ti (on the mineral rutile) took place at currents of 15 nA or lower (giving roughly 1,500 cps/nA on peak, for each spectrometer), to avoid the pulse-height analyzer (PHA) peak shifts that accompany high count rates. Care was taken to select grains for analysis that had no visible, nearby (within 100 μm) rutile, because its Ti atoms can be excited by the Bremsstrahlung (“braking radiation”) that is produced by elastic interaction of the 15 kV incident electrons with the quartz lattice (e.g., Bastin et al. 1984). This form of secondary fluorescence, which can typically be ignored for routine EPMA work, can generate sufficient Ti K-alpha X-rays to result in erroneously high estimates of Ti concentration. This is illustrated in Fig. 3, which shows the apparent (measured) Ti concentration in nominally Ti-free quartz as the incident beam approaches a contact with rutile.

During the early stage of this project, run products were analyzed on a JEOL 733 “Superprobe”, which yielded detection limits on the order of 20 ppm (for 300 s analyses on peak and on background, at 150 nA current). Recently, we replaced the JEOL instrument with a Cameca SX100 that is specially configured for trace-element work: with four large PET crystals, count rates are roughly twice those on the JEOL, reducing analytical uncertainties by ~30%, and lowering the detection limit to about 15 ppm. This new instrument was used to re-analyze the low-Ti run products (those run at 800°C or below), with the goal of reducing their relatively large uncertainties. This also allowed us to test for instrument bias, by comparing concentrations measured using the two instruments. Concentrations determined using the different instruments were indistinguishable (at two-sigma uncertainty) not only in the low-Ti experimental run products, but also in the highest-T experiment reported (sample ID 77, with ~525 ppm Ti), and in natural quartz (with ~45 ppm Ti) from the rhyolitic Bishop Tuff. Having established no instrumental differences, we report the Cameca results for low-Ti (lower precision) experiments, and the original JEOL results for all others.

Fig. 2 Backscattered-electron images of representative run products from **a** #79 m, with quartz surrounded by glass (“gl”) containing vapor bubbles (“b”) with finely-disseminated rutile (bright phase) **b** #6, where large quartz crystal fragment grown in aqueous fluid is surrounded by quench precipitates (smaller gray pieces) and rutile (bright phase), **c** #77 m, with equant, euhedral quartz crystals surrounded by glass; both rutile (light gray) and zircon (bright) are present in glass and as inclusions in some quartz crystals, **d** #77a, large quartz crystals with rutile (“r”) both as inclusions (bottom of photo) and surrounded by quench precipitate near top of image where it was growing in fluid at time of quench. Bright object in upper right is piece of metal from capsule material

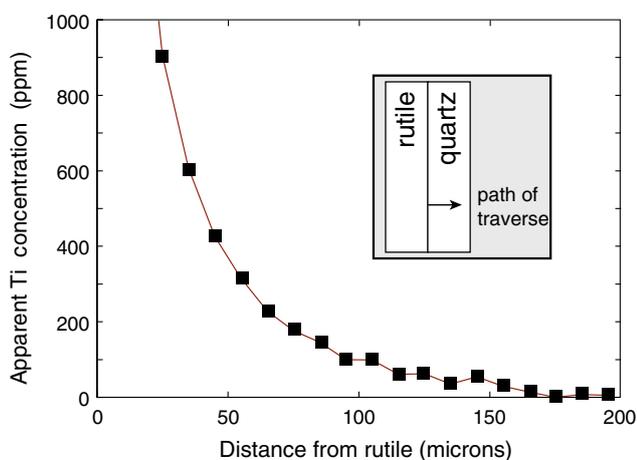
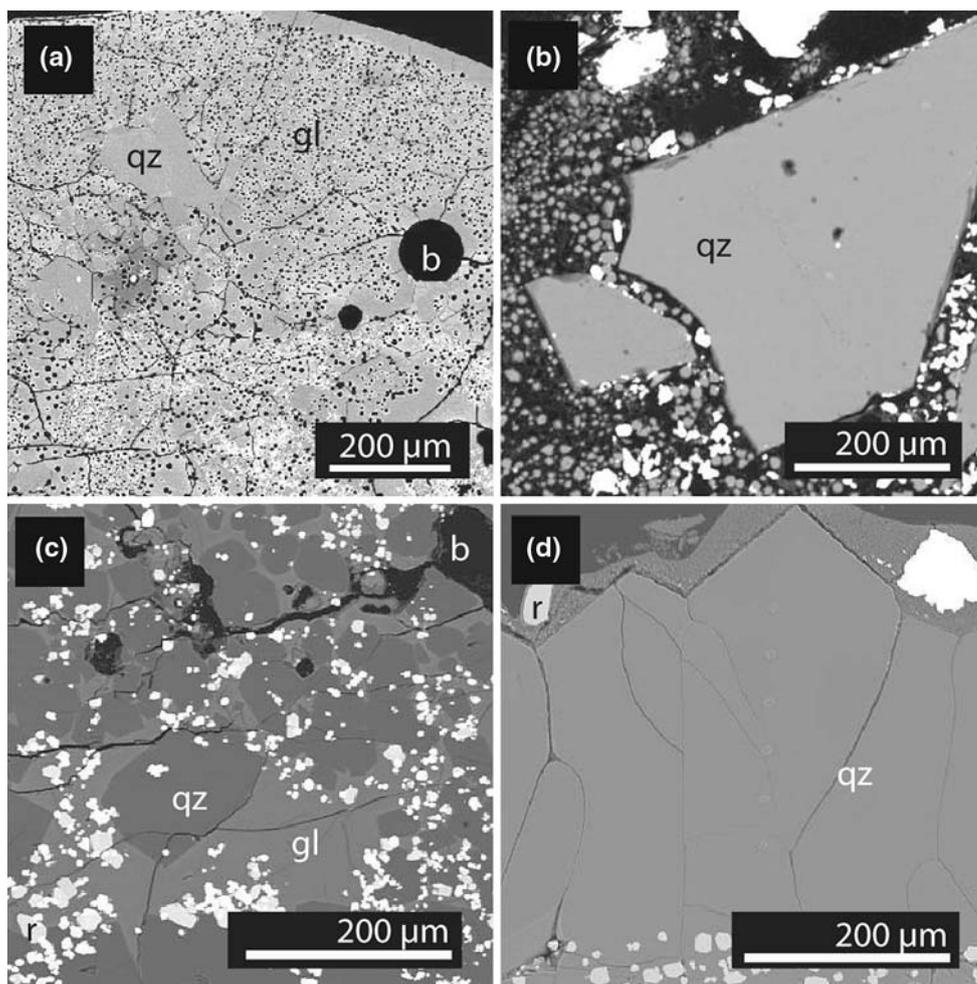


Fig. 3 Plot of apparent Ti concentration (ppm) in nominally Ti-free quartz versus distance (in microns) from artificial interface separating the quartz from a polished rutile surface. EPMA analyses were conducted in traverse oriented orthogonal to the interface (see *inset*), to show the effect of secondary fluorescence of Ti due to the Bremsstrahlung radiation

SIMS

Quartz in the lowest-temperature (600°C) run product, with Ti concentrations below EPMA detection limits, was analyzed using the Cameca *ims 3f* ion microprobe (SIMS) at Woods Hole Oceanographic Institute (WHOI). For most analyses, we used a primary oxygen (O-) beam, a current of 5–10 nA, and a spot size of roughly 10 μm. We measured counts on the ^{48}Ti peak, which were normalized to counts on “reference peak” ^{30}Si . These were compared with $^{48}\text{Ti}/^{30}\text{Si}$ ratios on quartz from run product #87 to calculate Ti concentrations. The Ti content of this “standard” (140 ppm) was determined by EPMA at Rensselaer, thereby assuring an internally consistent data set.

Results

Table 1 summarizes run conditions and results. Excluded from the table are experiments for which the

variation among measured Ti contents exceeded analytical uncertainty by a factor of two or more. While some of this “excess” variation may indicate failure of the experiment to reach equilibrium, it can also be attributed to secondary fluorescence of Ti in rutile by Bremsstrahlung radiation, as described above. This issue becomes particularly important (and problematic) if rutile crystals are intimately mixed with relatively small crystals of quartz. Because rutile crystals below the surface can also contribute to the Ti signal, it is not always possible to avoid this problem by analyzing quartz that appears (in BSE images) to be “rutile-free”.

Results, shown in Fig. 4 as a plot of $\log(X_{\text{Ti}})$ versus $1/T$, support the prediction (Eq. 5) that the Ti content of quartz that was equilibrated with rutile will increase exponentially with reciprocal T . Also consistent with thermodynamic principles is the observation that there is no significant difference between experiments in which the solid phases were separated by silicate melt and those in which H_2O was the separating medium.

A linear regression to the experimental data (with only uncertainties in Ti concentration taken into account, because temperature uncertainties are relatively small), is shown by the solid line in Fig. 4a, and is described by:

$$\log(X_{\text{Ti}}^{\text{qtz}}) = (5.69 \pm 0.02) - \frac{(3765 \pm 24)}{T(\text{K})}, \quad (6)$$

where Ti concentrations in quartz ($X_{\text{Ti,qtz}}$) are in ppm by weight.

The temperature (in degrees Celsius) of quartz crystallization (or re-equilibration) can be calculated by simple rearrangement of Eq. (6), to

$$T(^{\circ}\text{C}) = \frac{-3765}{\log(X_{\text{Ti}}^{\text{qtz}}) - 5.69} - 273. \quad (7)$$

Based only on the calculated uncertainties in slope and intercept, the thermometer is estimated to be accurate to within 5°C (two sigma) (Fig. 5). Of course, the accuracy of an individual application is also based on the accuracy and uncertainty of an individual Ti analysis, which may in turn be a function of calibration errors, inter-laboratory differences between instruments, instrument operating conditions, and quality of specimens and standards.

Regardless of the accuracy of a particular temperature determination using Eq. (7), uncertainties associated with relative thermometry are solely a function of analytical conditions. Calculated analytical uncertainties (two sigma) for EPMA analysis of quartz (Fig. 5b) using a 200 nA beam and 240 s counts on peak and

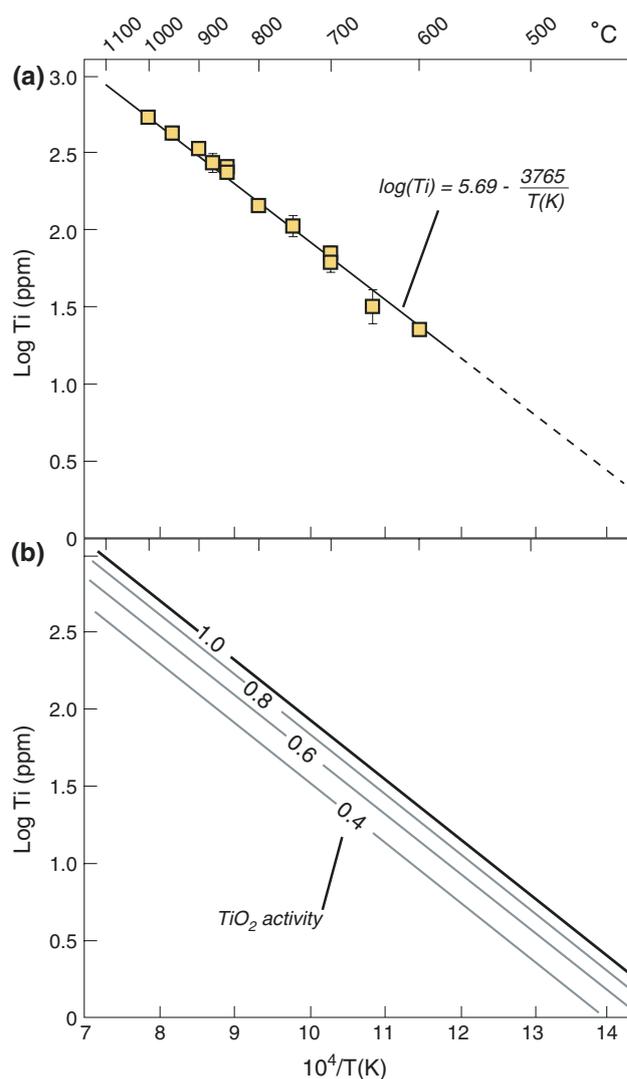


Fig. 4 Plot of Ti concentration [as $\log(\text{Ti})$, ppm] versus reciprocal T (as $10^4/T$, K) for **a** experimental data, with line showing results of linear regression to the data (*dashed portion* showing extrapolation to metamorphic and hydrothermal regimes), and **b** curves applicable to different TiO_2 activity values, as labeled, where $a_{\text{TiO}_2} = 1$ curve corresponds with linear regression shown in **(a)**

background (i.e., conditions suitable for large crystals in which the beam can be broadened) are estimated to be better than $\pm 6^{\circ}\text{C}$ for quartz equilibrated at $T > 750^{\circ}\text{C}$ (corresponding to at least 100 ppm Ti), and better than $\pm 20^{\circ}\text{C}$ for $T \sim 600^{\circ}\text{C}$ (22 ppm). At analytical conditions more suitable for smaller crystals (e.g., 100 nA, 120 s) the uncertainties are somewhat higher ($\pm 12^{\circ}\text{C}$ and $\pm 40^{\circ}\text{C}$ for $T > 750$ and 600°C , respectively). The uncertainty can be reduced dramatically by use of SIMs for quartz crystallized at temperatures between 450 and 800°C : analytical errors are on the order of $1\text{--}2^{\circ}$. This highlights the sensitivity of the

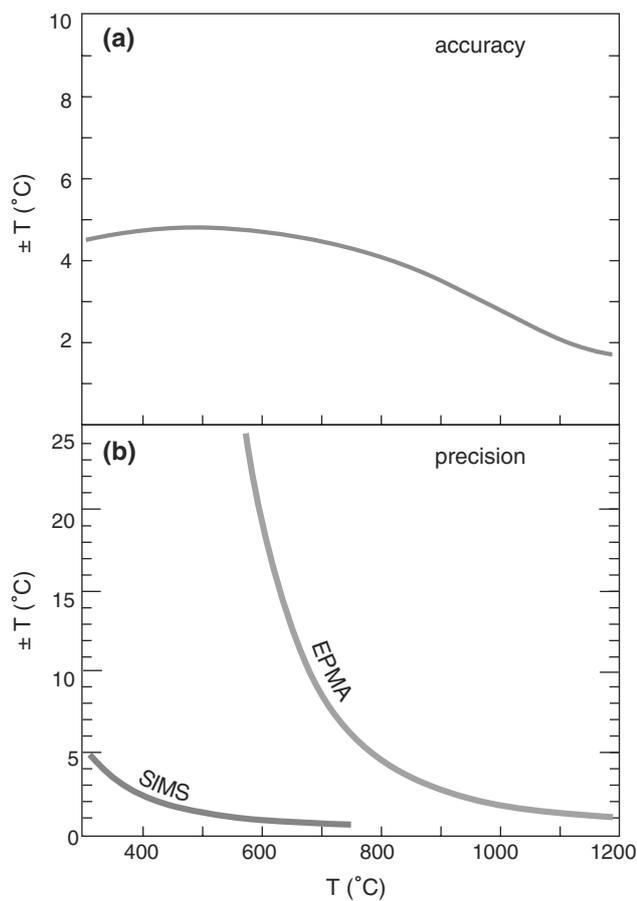


Fig. 5 Plots of estimated 2-sigma **a** accuracy of the TitaniQ thermometer, based on uncertainties in slope and intercept of least-squares regression, and **b** analytical precision of the thermometer, for both electron microprobe (EPMA; for typical 4-spectrometer analysis) and ion microprobe (SIMS) analyses

TitaniQ thermometer: the relatively low uncertainties that can be achieved by EPMA or (even better) by ion probe analyses make it possible to characterize differences in quartz crystallization temperatures (or where modified by diffusion, re-equilibration temperatures) of only a few degrees.

Discussion

In this section we address several issues related to use of the TitaniQ thermometer. First, we consider the possibility of a pressure effect. Next, we discuss application of the thermometer to systems lacking rutile (or some other TiO_2 phase). This is followed by a summary of recent work regarding diffusion of Ti in quartz.

Pressure effect

All of the data on which our calibration is based are from experiments conducted at 1.0 GPa. Several lines of

evidence, however, indicate little pressure effect on the TitaniQ calibration. For example, Si–Ti interdiffusion experiments that were conducted at 1 atm pressure (Cherniak et al. 2004) produce diffusion profiles in quartz from which Ti solubilities can be extracted. As shown by Cherniak et al. (2007), these 1-atm values are close to those predicted from the 1.0 GPa TitaniQ calibration.

Absence of a strong pressure effect is also supported by a close match between temperatures based on the 1.0 GPa TitaniQ calibration and those calculated using a new Zr-in-sphene thermometer (Hayden et al. 2006) for quartz that crystallized in the shallow crust ($P < 0.2$ GPa). For six different sphene-bearing dacites and rhyolites, Zr-in-sphene thermometry yields temperatures ranging from 743 to 763°C. For three of the six samples, TitaniQ temperatures are within nine degrees of the sphene values; in the worst case, the TitaniQ temperature is lower by only 21°C.

Little pressure effect is also indicated by the Ti contents of metamorphic quartz that equilibrated at ~0.5 GPa. Quartz crystals in two rutile-bearing rocks from eastern Vermont, USA (Spear et al. 2002) were analyzed by SIMS at WHOI due to their low Ti contents. Rims of quartz in a garnet-zone rock (#BF53) with biotite, chlorite, muscovite, plagioclase, rutile, and ilmenite, contain 3.8 ppm Ti. This corresponds to a TitaniQ temperature of 464°C, only 21° lower than the peak metamorphic temperature of 485°C of Spear et al. (2002). In a second, staurolite-zone rock (#BF38b) with garnet, amphibole, biotite, plagioclase, and rutile, both staurolite and quartz were formed during a garnet consumption reaction. The quartz produced during reaction surrounds garnet and is recognizable in CL images because it is brighter than most matrix quartz. With 11.4 ppm Ti, the garnet-rimming quartz yields a TitaniQ temperature (using the 1.0 GPa experimental calibration) of 540°C, within 10°C of the ~550°C temperature predicted (F. S. Spear, unpublished data) for the ~0.5 GPa reaction.

Limitations imposed by absence of rutile

The TitaniQ thermometer was calibrated using quartz equilibrated with a pure TiO_2 phase (rutile). This, however, doesn't restrict TitaniQ application to rutile-bearing rocks. The thermometer can be applied even in the absence of rutile if TiO_2 activity of the system (relative to that required to stabilize a pure TiO_2 phase) is known. For rutile-present conditions, $a_{\text{TiO}_2} = 1$; if rutile is absent, $0 < a_{\text{TiO}_2} < 1$. In the latter case, we simply scale by a_{TiO_2} : in a melt, for example, if the concentration of TiO_2 is 75% of the amount

required for rutile saturation, we assume that the Ti concentration in quartz will be reduced by the same factor (0.75) for a given T . Accuracy of this approach rests on the assumption of Henrian behavior (near-linear change in activity with Ti concentration), which is justified by the low Ti concentrations in quartz. Accordingly, the applicable TitaniQ calibration would be defined by a line parallel to the one for the rutile-present case [defined by Eq. (6)], but with an intercept differing by the amount $\log(a_{\text{TiO}_2})$; with values always less than zero, the curve is displaced downward on the plot of $\log(\text{Ti})$ versus $1/T$.

Shown in Fig. 4b are the relevant calibration curves for a_{TiO_2} values of 1.0 [corresponding with Eq. (6)], 0.8, 0.6, and 0.4. Considering the relatively high concentrations of TiO_2 in most rocks, combined with the fact that most rocks contain at least one phase in which Ti is an essential (stoichiometric) component (e.g., rutile, ilmenite, or sphene), these curves likely cover the range expected in most geologic systems. This is supported by the work of Ghent and Stout (1984), who calculated a_{TiO_2} in metamorphic rocks based on compositions of coexisting minerals. Based on their conclusions, the $a_{\text{TiO}_2} = 0.6$ curve is applicable to some metabasites (although most have even higher TiO_2 activities), whereas metapelites would fall close to the $a_{\text{TiO}_2} = 1$ curve. For silicic igneous rocks (which typically do not have rutile as a stable phase, and hence a_{TiO_2} values are usually below one) activities of 0.5 or higher seem to be the norm, based on several rhyolites that we've examined thus far (also see Watson et al. 2006, and discussion below in Applications section).

In practical terms, the equation for calculating temperatures in rutile-undersaturated rocks is:

$$T(^{\circ}\text{C}) = \frac{-3765}{\log \left[\frac{X_{\text{Ti}}^{\text{qtz}}}{a_{\text{TiO}_2}} \right] - 5.69} - 273. \quad (8)$$

Using the wrong a_{TiO_2} value in this equation will, of course, yield invalid temperature estimates. This is shown in Fig. 6, where we have quantified the amount that temperature may be under- or over-estimated in typical rutile-absent crustal rocks. These curves represent a_{TiO_2} values of 0.6 and above, which are considered likely to apply to most crustal assemblages, except those that are exceptionally Ti-poor.

As noted previously, assuming $a_{\text{TiO}_2} = 1$ for a rutile-absent system (which is equivalent to using Eq. (7)) will provide a minimum temperature of equilibration. For rutile-absent metapelites with equilibration temperatures as high as 600°C (amphibolite facies), for example, this leads to underestimation of the equilibration temperature (thick solid line, assuming $a_{\text{TiO}_2} = 0.8$)

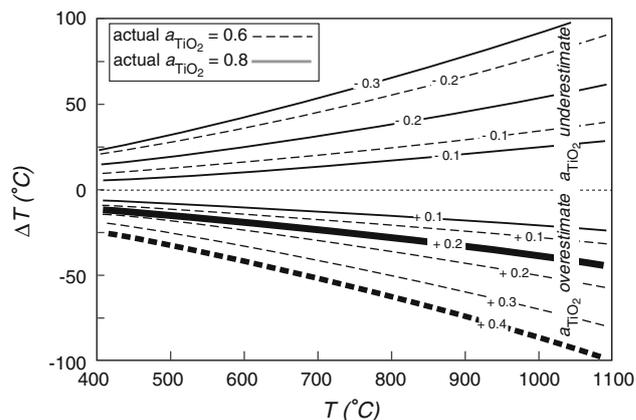


Fig. 6 Plot showing possible error in calculated TitaniQ temperature for rutile-absent systems if the incorrect TiO_2 activity value is used in Eq. (8). Curves in the upper half of diagram show the amount that T can be overestimated if TiO_2 activity is underestimated; lower curves show the amount T can be underestimated if too high a TiO_2 activity value is used. Solid curves represent a system with actual TiO_2 activity of 0.8 (most metapelites are higher); dashed curves represent system with activity of 0.6 (at low end of metabasite range; see text). For each case, the two thick curves show the maximum amount that T might be underestimated by assuming that rutile was present (activity of one) during quartz crystallization, when in fact it was not part of the equilibrium assemblage

by no more than 15°C. For 600°C metabasites (thick dashed line, assuming $a_{\text{TiO}_2} = 0.6$), however, application of the rutile-present curve can yield temperatures low by as much as 40°C. Considering that most metapelites and metabasites studied by Ghent and Stout (1984) had a_{TiO_2} values above 0.8 and 0.6, respectively, the errors cited here are probably on the high side for most metamorphic rocks. In all cases, the errors increase with temperature of equilibration.

If a reasonable estimate of TiO_2 activity can be made, the error in calculated temperature is lower: for most rocks equilibrated at T below 700°C, a ± 0.2 error in a_{TiO_2} estimation yields temperatures off by no more than -30° (in the case that a_{TiO_2} is overestimated) or $+50^{\circ}\text{C}$ (a_{TiO_2} underestimated). If a_{TiO_2} is known to within ± 0.1 , the calculated T will be off by no more than $\pm 20^{\circ}\text{C}$. For quartz equilibrated at temperatures as high as 1,000°C, if a_{TiO_2} can be estimated to within ± 0.1 the T will at most off by no more than 30 or 35°C.

Ti diffusion in quartz

Important to the application of any mineral-chemistry based geothermometer is the assumption that mineral composition has not been modified by diffusion after equilibration at the temperature of interest. For various thermal histories, we can evaluate the likelihood of

Ti diffusion in quartz by applying the Arrhenius relation of Cherniak et al. (2004):

$$D = 7 \times 10^{-8} \exp\left(\frac{-273 \text{ kJ mol}^{-1}}{RT}\right) \text{ m}^2 \text{ s}^{-1}. \quad (9)$$

For 500 and 700°C, for example, diffusivities of Ti in quartz are roughly 3×10^{-26} and $\sim 1.3 \times 10^{-22} \text{ m}^2 \text{ s}^{-1}$, respectively. From these values, we can calculate the “characteristic transport distance” ($[4Dt]^{1/2}$) over which Ti may diffuse (assuming a chemical potential gradient): At 500°C, Ti will diffuse roughly 2 μm in 1 m.y.; at 700°C this distance increases to $\sim 125 \mu\text{m}$ for the same time. This suggests that the scale of diffusive modification will be relatively limited in low- to medium-grade metamorphic rocks. Unless held at peak conditions for several m.y., only the rims of mm-scale quartz grains are likely to record the highest temperatures reached. At granulite facies conditions (900°C), however, the distance increases to 2 mm in 1 m.y., increasing the likelihood that cores of quartz grains will record peak temperatures. The high diffusivities of Ti at $T > 900^\circ\text{C}$ also has implications for exsolution and growth of rutile needles during cooling, as discussed by Cherniak et al. (2007).

Igneous quartz, too, will be affected by diffusion. Sharp gradients in Ti concentration may be “smoothed out” during prolonged phenocryst residence time at magmatic temperatures. Preservation of step-like Ti concentration profiles, on the other hand, indicates short residence time. Steep Ti profiles in quartz from the Bishop Tuff, for example, are interpreted by Wark et al. (2007) to indicate that the quartz crystals acquired these profiles during a heating event that took place shortly before eruption, as discussed further below.

Applications

Considering the large temperature-range over which quartz is stable, the TitaniQ thermometer should be applicable to a wide variety of crustal rocks. The upper limit of application will probably correspond to “dry” (H_2O absent) systems, in which quartz can survive temperatures above 1,000°C. In the presence of excess H_2O , on the other hand, quartz may not survive temperatures higher than the solidus of wet granite.

At the low-temperature extreme, TitaniQ applications will be limited not by the stability of quartz, but by analytical capabilities. Using the electron microprobe, we can characterize (with reasonably low uncertainty) Ti contents on the order of 20 ppm, corresponding to quartz equilibration temperatures of

$\sim 600^\circ\text{C}$ for $a_{\text{TiO}_2} = 1$ (rutile present). Using an ion microprobe, we can analyze down to a few tenths of a ppm, decreasing the lower limit of application to about 400°C.

Based on these considerations, we expect the TitaniQ thermometer to prove useful in studies of metamorphic rocks equilibrated at greenschist facies temperatures and higher, many quartz-bearing igneous rocks, and even some hydrothermal veins. With the goal of demonstrating the diversity of potential applications, in this section we briefly summarize some preliminary TitaniQ results.

Igneous rocks

The TitaniQ thermometer has strong potential for application to quartz-bearing, igneous rocks such as granites and rhyolites. For example, rims of quartz phenocrysts in volcanic rocks can be used to determine magma temperature at the time of eruption. In plutonic rocks, the rims of quartz crystals will likely record final temperature of magma crystallization. Perhaps of even greater value, however, may be the record of thermal events that is preserved by Ti zoning in quartz interiors. Unless subjected to high-temperature metamorphism, only in extraordinary circumstances would igneous zoning be eliminated by diffusion: even if a quartz phenocryst were held at magmatic temperature ($\sim 750^\circ\text{C}$) for 100,000 years, for example, Ti would diffuse only $\sim 100 \mu\text{m}$.

Most silicic, quartz-bearing magmas are relatively Ti-rich, and have at least one phase in which Ti is a stoichiometric component, such as ilmenite or sphene (titanite). Rutile, however, is rarely (if ever) part of the equilibrium assemblage, so TiO_2 activity must be estimated before one can apply Eq. (8). One approach is to calculate a_{TiO_2} directly from equilibria among coexisting, equilibrium phases—although this may require that temperature already be known. Similarly, if the Ti content of quartz rims is known, and if temperature can be estimated independently (from FeTi oxide thermometry, for example), one can solve for a_{TiO_2} in Eq. (8).

By establishing TiO_2 activity, it may then be possible to extract thermal histories from Ti zoning profiles in quartz, assuming that a_{TiO_2} did not change significantly during quartz crystallization. It may also be possible to apply that same a_{TiO_2} value to estimate temperature in other rocks with similar melt composition and with the same mineral assemblage, if that assemblage serves to fix a_{TiO_2} . This highlights an important principle of TitaniQ application to low-variance, silicic igneous systems: as long as the equilibrium mineral assemblage

remains the same (albeit allowing some compositional variation), activity of TiO_2 may be relatively “buffered” at some fixed value despite temperature changes. With fixed a_{TiO_2} , any temperature increase will result in more of the Ti-essential minerals (in this case ilmenite) going into solution, increasing the Ti content of the melt and of the coexisting quartz [according to Eq. (8)] in which Ti is a trace constituent.

For systems in which a_{TiO_2} cannot be determined, it may still be possible to determine temperature of crystallization, if the Ti contents of quartz and of the melt from which it crystallized can be established. We use the Hayden et al. (2005) relation that expresses TiO_2 solubility in rhyolite as a function of T:

$$\text{Log}(X_{\text{Ti,melt,sat}}) = 7.95 - 5305/T(\text{K}) + 0.124 \cdot \text{FM}, \quad (10)$$

where $X_{\text{Ti,melt,sat}}$ is the concentration (ppm) of Ti in the melt required for rutile saturation, and FM is the melt composition parameter ($[(\text{Na} + \text{K} + 2(\text{Ca} + \text{Fe} + \text{Mg}))/\text{Al}] \times 1/\text{Si}$) used by Ryerson and Watson (1987), in which the chemical symbols are the anhydrous cation fractions in the melt. Assuming Henrian behavior, we can express TiO_2 activity as the ratio of measured Ti to the calculated saturation value of Ti in the melt (Eq. 10) or in quartz crystallized from that melt (Eq. 6). Accordingly,

$$a_{\text{TiO}_2} = \frac{X_{\text{Ti,melt,meas}}}{X_{\text{Ti,melt,sat}}} = \frac{X_{\text{Ti,qtz,meas}}}{X_{\text{Ti,qtz,sat}}}. \quad (11)$$

Rearranging, we get

$$X_{\text{Ti,melt,sat}} = \frac{(X_{\text{Ti,melt,meas}} \times X_{\text{Ti,qtz,sat}})}{X_{\text{Ti,qtz,meas}}}. \quad (12)$$

Substituting this expression for $X_{\text{Ti,melt,sat}}$ in Eq. (10), and replacing $X_{\text{Ti,qtz,sat}}$ using the expression in Eq. (6), we get an equation for T that based solely on the Ti content of quartz and on the Ti content and FM value of its host glass:

$$T(\text{K}) = \frac{1540}{(2.26 - \log\left(\frac{X_{\text{Ti,melt,meas}}}{X_{\text{Ti,qtz,meas}}}\right) + 0.124 \times \text{FM})}. \quad (13)$$

Unfortunately, relatively large errors are associated with this approach due to the similarity of the slopes for the equations describing Ti solubility in quartz and in melt. Consequently, calculated temperatures are highly sensitive to uncertainty in the measured Ti concentrations. To estimate temperature to within $\sim \pm 5^\circ\text{C}$, for example, the concentrations of Ti in both

the quartz and glass have to be known to within 1% of their equilibrium values.

Application example: Bishop Tuff

One example of using the TitaniQ thermometer to document the thermal evolution of a silicic magma system is the recent study (Wark et al. 2007) of the 0.76 Ma Bishop Tuff, which was deposited during the eruption of $\sim 650 \text{ km}^3$ of magma from the Long Valley Caldera (California). As first shown by Peppard et al. (2001), cores and rims of late-erupted quartz phenocrysts (Fig. 7a) could be distinguished by differences in CL emission intensity (rims appear much brighter), whereas no core-to-rim differences were discernable in early-erupted quartz. Wark et al. (2007) showed that these differences correlate with Ti content of quartz: bright rims on late-erupted quartz contain, on average, about 95 ppm Ti; dark-CL cores contain roughly 55 ppm Ti.

As in most igneous systems, rutile was not part of the equilibrium mineral assemblage in the Bishop magma. Consequently, TiO_2 activity had to be determined before temperatures of quartz crystallization could be calculated using Eq. (8). Both approaches outlined above gave approximately the same result. Using published FeTi oxide compositions (and temperatures based on FeTi oxide thermometry), Wark et al. (2007) estimated TiO_2 activities for the entire eruptive sequence of Bishop Tuff from the relation $[2 \text{ ilmenite} = \text{ulvospinel} + \text{TiO}_2]$. For 22 oxide pairs representing a temperature range of almost 100°C , calculated TiO_2 activities average 0.63 ± 0.03 . This is in good agreement with a value of 0.6, which was determined empirically to provide the best match between TitaniQ temperatures (for quartz rims) and independently determined FeTi oxide temperatures for the entire eruption sequence.

Using a value of 0.6 for a_{TiO_2} , the rimward increase of Ti content (from ~ 55 to 95 ppm) in late-erupted quartz was interpreted to document heating of deep Bishop magma from about 740°C to 810°C , presumably due to recharge by injection of hot, mafic melts. The contact separating the high-Ti (bright-CL) rims from the low-Ti (dark) cores truncates internal CL zoning in many phenocrysts, presumably indicating that high-temperature rim growth was preceded by partial dissolution. The contact is also abrupt, with Ti concentrations in some crystals increasing more than 40 ppm across a distance of $<10 \mu\text{m}$. Based on modeling of Ti diffusion, Wark et al. (2007) suggested that preservation of this steep concentration gradient requires that the high-temperature rims grew only a short time (100's of years at most) before the 0.76 Ma eruption.

Fig. 7 Examples of TitaniQ applications (see text), including **a** CL image of quartz phenocryst from late-erupted Bishop Tuff, showing bright-CL rim with Ti contents of roughly 90 ppm, and dark-CL core with Ti contents of ~55 ppm; **b** transmitted-light and **c** CL image of quartz in granulite from Enderby Land, Antarctica; and **d** CL image of quartz vein from Butte ore deposit. In all CL images, brightest regions correspond with highest Ti contents. Note rutile needles exsolved from Enderby quartz in **(b)**, and dark-CL, Ti-depletion haloes where rutile needles (not visible) intersect the surface of the polished section in **(c)**

Metamorphic rocks

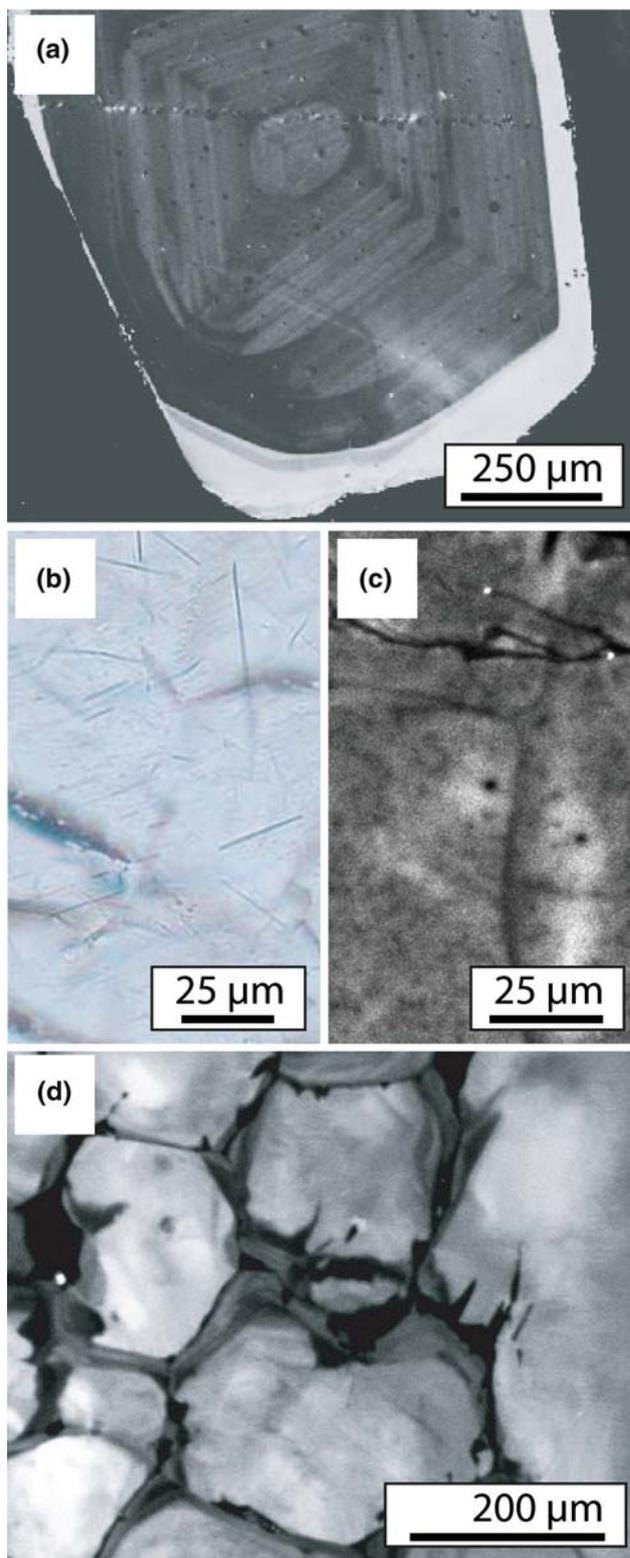
Because quartz is stable over a broad range of pressures and temperatures, it can be found in metamorphic assemblages of virtually all grades. This, coupled with the relatively high Ti activity (and common presence of rutile) in many metamorphic rocks (Ghent and Stout 1984) provides fertile ground for new TitaniQ applications. Some metamorphic quartz is even zoned with respect to Ti content, presumably because it records multiple metamorphic events.

Application example: UHT quartz

With the goal of evaluating application of the TitaniQ thermometer to high-grade metamorphic rocks, we analyzed quartz in an Archaean, sapphirine-bearing, “ultra-high temperature” (UHT) granulite from Enderby Land, East Antarctica. Metamorphic temperatures of 1,000°C (and higher) have been proposed for these Napier Complex rocks by several authors (e.g., Ellis 1980; Grew 1980; Harley 1987; Harley and Motoyoshi 2000). Like quartz from other high-grade assemblages, the Enderby quartz that we analyzed is littered with fine (sub-micron), oriented needles of exsolved rutile (Fig. 7b, c) spaced roughly 25 µm apart. To characterize the Ti content of peak-temperature, pre-exsolution quartz, we averaged 26 randomly located EPMA analyses that were performed using a beam diameter of 50 µm. The resulting value of 516 ppm Ti yields a TitaniQ temperature of 992°C, consistent with the high temperatures estimated by others, and with Ti-in-zircon temperatures (Watson et al. 2006) of ~995°C recorded by co-existing, metamorphic zircons, in which we measured maximum Ti concentrations of ~100 ppm (unpublished data).

Hydrothermal (vein) quartz

Another TitaniQ application that shows promise is the determination of quartz crystallization temperatures in ore deposits. Considering that a practical lower limit of



the TitaniQ thermometer is roughly 400°C, application will probably be restricted to veins in magmatic-hydrothermal systems. Several epithermal vein samples that we attempted to analyze had Ti contents

below our detection limit, including hydrothermal vein quartz from Silverton, Colorado, as well as samples of open-fill quartz that was intergrown with coarse rutile needles from other locations.

Application example: Butte vein quartz

Quartz that precipitated with rutile in some veins at the Butte (Montana) porphyry deposit have fluid-inclusion temperatures in excess of 500° (Rusk et al. 2004), making it ripe for potential application of the TitaniQ thermometer. Indeed, Rusk and Reed (2002) and Rusk et al. (2006) used CL to interpret ore deposition history, and noted a correlation of CL intensity and Ti content with temperature of vein formation. TitaniQ thermometry confirms this: in one veinlet bordered by potassic alteration (biotite-K-feld-musc) the interiors of individual crystals of vein quartz exhibit strong CL emission intensity (Fig. 7d), with Ti contents as high as 36 ppm. CL emission intensity is relatively uniform over 75% of the exposed area in each grain, but decreases sharply near the rims, as does Ti content (to ~15 ppm). TitaniQ temperatures—which overlap temperatures determined using the Zr-in-rutile thermometer of Watson et al. (2006)—record the crystallization of quartz in this vein as temperature dropped at least 75° from a peak near 645°C.

Summary

The TitaniQ (Titanium-in-Quartz) thermometer, as described by Eqs. (7) and (8), offers advantages over many other thermometers in use today: (1) it is simple to use because it usually requires analysis of only one phase; (2) quartz is stable over a broad P and T range, and hence the TitaniQ should be applicable to many rock types; (3) intensity of CL emissions often correlates with Ti concentration, allowing the possibility of “mapping” temperature domains; and (4) temperature estimates are very precise: for quartz precipitated at $T > 500^\circ\text{C}$, for example, temperature uncertainties of $\pm 2^\circ\text{C}$ can be achieved. Although our practical lower limit of application is now roughly 400°C, it may eventually be possible to apply the TitaniQ to quartz crystallized at T as low as 300°C using analytical procedures that are optimized for sub-ppm Ti concentrations.

Despite its promise, the TitaniQ thermometer also has potential to be misused. Care must be taken, for example, to either (a) establish rutile as an equilibrium phase or (b) determine TiO_2 activity of the system before applying the thermometer using Eq. (8), because

application of the $a_{\text{TiO}_2} = 1$ curve (Eq. 7) to a rutile-absent system will provide only a minimum value for temperature of equilibration. Temperature overestimates, on the other hand, can result from EPMA analyses of quartz in close (<100 μm) vicinity of a Ti-bearing mineral phase, if the Bremsstrahlung radiation causes secondary fluorescence and an artificially high Ti X-ray signal. With careful attention to these considerations, however, we expect the TitaniQ to prove robust in a variety of rock types.

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