Taking mylonites’ temperatures

Matthew J. Kohn, C.J. Northrup
Department of Geosciences, Boise State University, Boise, Idaho 83725, USA

ABSTRACT
We measured titanium-in-quartz (TitaniQ) temperatures by ion microprobe for three deformed rocks having different quartz microstructure to assess the possibility of constraining the temperature of mylonitization directly from dynamically recrystallized quartz grains. Calibration via ion microprobe indicates analytical precisions and accuracies of ±2 °C and ±10 °C, respectively (2σ). High- versus low-temperature mylonites yield high versus low Ti concentrations and temperatures that are consistent with other field studies of mylonites that have similar microstructures; these observations imply that TitaniQ accurately measures dynamic recrystallization temperatures. Variations in temperature in a single domain exceed analytical errors, implying that one microstructure in a rock can reflect different temperatures and, presumably, strain rates. Combined with paleopiezometric and phase-equilibrium estimates of differential stress and water fugacity, strain rates may be estimated.

INTRODUCTION
Titanium-in-quartz thermometry, or “TitaniQ,” in principle allows precise and accurate determination of quartz crystallization temperatures based on the Ti content of quartz as buffered by either rutile or Ti-buffering assemblages (Wark and Watson, 2006). This thermometer was experimentally calibrated between 1000 °C and 600 °C, and most published applications involve igneous rocks within that temperature range (e.g., Wark and Watson, 2006; Wark et al., 2007). However, applications to lower temperatures hold promise both for general metamorphic studies where other thermometers are scarce, and for deformed rocks, where quartz microstructures are diagnostic of deformation mechanisms. For analyses collected by ion microprobe and temperatures of 300–500 °C, counting statistics are nonlimiting (~±2 °C, 2σ; Table 1), and the principal sources of error at temperatures ≤400 °C are systematic and arise from down-temperature extrapolation of the calibration (~±4–5 °C at 400 °C; Wark and Watson, 2006), and from incomplete knowledge of the activity of TiO₂ (aTiO₂) in rocks that lack rutile. Yet, even maximal errors on aTiO₂ (e.g., ±0.20, 2σ) yield temperature errors of only ~±10 °C at likely conditions of mylonitization. Compared to phase-equilibrium and cation-exchange thermometer errors of ±25–50 °C (Ferry, 1980; Kohn and Spear, 1991; Worley and Powell, 2000), TitaniQ affords superior thermometric resolution, especially for resolving relative temperature differences in a single sample where aTiO₂ is assumed constant, and uncertainties reflect counting statistics alone. Experimentally determined Ti-diffusion rates in quartz (Cherniak et al., 2007) further imply that, for a time scale of 1 m.y., characteristic length scales for diffusion at 300–500 °C are only 0.001–2 μm. Thus, quartz grains that reequilibrate during recrystallization below ~500 °C will undoubtedly retain their compositions.

Mylonites present one potential application of TitaniQ, both because quartz microstructures change progressively with decreasing temperature (or increasing strain rate), and because typical temperatures of mylonitization (~500 °C to ~250 °C) are not readily estimated by cation-exchange thermometers or mineral equilibria. Better temperature estimates for lower temperatures hold promise both for general metamorphic studies where other thermometers are scarce, and for deformed rocks, where quartz microstructures are diagnostic of deformation mechanisms. For applications to lower temperatures, TitaniQ may yield high versus low Ti concentrations and temperatures that are consistent with other field studies of mylonites that have similar microstructures; these observations imply that TitaniQ accurately measures dynamic recrystallization temperatures.

SAMPLES AND METHODS
Samples analyzed included metapelite from the basal shear zone of the composite Caledonian allochthon in northern Norway, and granitic...

TABLE 1. TITANIUM CONCENTRATIONS (PPM), ERRORS, AND ESTIMATED TEMPERATURES OF MYLONITES

<table>
<thead>
<tr>
<th>Sample</th>
<th>aTiO₂ (±2σ)</th>
<th>Ti (ppm, ±1σ)</th>
<th>T (°C, ±2σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>94-SC-9 A2</td>
<td>1.0 ± 0.0</td>
<td>5.65 ± 0.04</td>
<td>489 ± 1</td>
</tr>
<tr>
<td>1.0 ± 0.0</td>
<td>6.15 ± 0.04</td>
<td>495 ± 1</td>
<td></td>
</tr>
<tr>
<td>1.0 ± 0.0</td>
<td>4.89 ± 0.03</td>
<td>480 ± 1</td>
<td></td>
</tr>
<tr>
<td>1.0 ± 0.0</td>
<td>8.38 ± 0.13</td>
<td>517 ± 2</td>
<td></td>
</tr>
<tr>
<td>1.0 ± 0.0</td>
<td>6.99 ± 0.05</td>
<td>504 ± 1</td>
<td></td>
</tr>
<tr>
<td>1.0 ± 0.0</td>
<td>5.36 ± 0.22</td>
<td>486 ± 5</td>
<td></td>
</tr>
<tr>
<td>94-SC-9 A1</td>
<td>1.0 ± 0.0</td>
<td>7.98 ± 0.09</td>
<td>513 ± 1</td>
</tr>
<tr>
<td>1.0 ± 0.0</td>
<td>4.29 ± 0.13</td>
<td>471 ± 2</td>
<td></td>
</tr>
<tr>
<td>1.0 ± 0.0</td>
<td>7.81 ± 0.06</td>
<td>512 ± 1</td>
<td></td>
</tr>
<tr>
<td>1.0 ± 0.0</td>
<td>6.29 ± 0.13</td>
<td>496 ± 1</td>
<td></td>
</tr>
<tr>
<td>1.0 ± 0.0</td>
<td>3.34 ± 0.10</td>
<td>456 ± 2</td>
<td></td>
</tr>
<tr>
<td>CC8–9-2</td>
<td>0.8 ± 0.2</td>
<td>0.208 ± 0.003</td>
<td>327 ± 1</td>
</tr>
<tr>
<td>0.8 ± 0.2</td>
<td>0.061 ± 0.003</td>
<td>280 ± 3</td>
<td></td>
</tr>
<tr>
<td>CC8–3–2 A2</td>
<td>0.8 ± 0.2</td>
<td>56.4 ± 1.8</td>
<td>707 ± 7*</td>
</tr>
<tr>
<td>0.8 ± 0.2</td>
<td>49.9 ± 0.9</td>
<td>694 ± 4*</td>
<td></td>
</tr>
<tr>
<td>0.8 ± 0.2</td>
<td>1.70 ± 0.05</td>
<td>429 ± 3</td>
<td></td>
</tr>
<tr>
<td>0.8 ± 0.2</td>
<td>2.65 ± 0.23</td>
<td>455 ± 10</td>
<td></td>
</tr>
<tr>
<td>0.8 ± 0.2</td>
<td>2.40 ± 0.30</td>
<td>449 ± 13</td>
<td></td>
</tr>
</tbody>
</table>

*Relict grain. Errors are analytical precision only and do not account for aTiO₂ uncertainty (which is ±13 °C for recrystallized grains in CC8–3–2, and ±8 °C for CC6–9–2, 2σ). Data for 94-SC-9 A1 are from a pressure shadow. For relict igneous grains in CC8–3–2 A2, decreasing assumed aTiO₂ to 0.6 would increase calculated temperature by 33 °C.

where m, n, and A are material constants, fH₂O is water fugacity, σ is differential stress, and Q is activation energy. A particular deformation microstructure or viscosity can be produced by a range of T-ε pairs, e.g., higher-T-higher-ε, or lower-T-lower-ε. Deformation microstructures have been studied experimentally (e.g., Hirth and Tullis, 1992) and compared with those produced at geologic conditions (e.g., Hirth et al., 2001). More precise temperatures of natural deformation would not only constrain natural strain rates but also allow better estimates of rock viscosities.

Here, we show the first applications of TitaniQ to mylonites exhibiting characteristic microstructures ranging from high-T coarse-grained quartz (≥100 μm diameter) to low-T fine-grained quartz (<10 μm diameter). These data show that Ti contents of quartz do change during mylonitization, allowing precise and accurate temperature estimates. These data establish the basis for more precise estimation of strain rates in future studies.
dioritic mylonite from the Cougar Creek Complex in the accreted terranes of the Blue Mountains province of Oregon and Idaho, United States. We attempted to sample rocks that were deformed at high temperature (94SC-9, \(T > 475 \, ^\circ\text{C}\)) and intermediate to low temperature (CC8–3–2, CC6–9–2; \(T \leq 400 \, ^\circ\text{C}\)), where relative temperature assignment was based mainly on the deformation microstructures in quartz. Metapelitic sample 94SC-9 contained garnet, indicative of amphibolite-facies temperatures (~475 °C or higher), and rutile, fixing the activity of TiO₂ at 1.0. Quartz occurred mainly in pressure shadows next to garnet and as quartz ribbons in the matrix. Quartz in both settings within this sample consisted of polycrystalline aggregates of coarse (≥100 µm diameter), equant, recrystallized grains with polygonal boundaries, consistent with upper regime 3 of Hirth and Tullis (1992) or postdeformation annealing. We analyzed quartz from both settings, but temperatures overlapped, and we present images only from the quartz ribbons (Fig. 1; Table 1 contains all data).

The metagranitic-dioritic rocks were metamorphosed at amphibolite-facies conditions, then sheared and hydrated in the greenschist facies. This shearing produced core-and-mantle microstructures in quartz. Well-developed subgrains occur in the larger relict “core” grains. Strong grain shape preferred orientation (GSPO) and lattice preferred orientation (LPO; judging from the gypsum plate effect) occur in the fine-grained dynamically recrystallized quartz comprising the “mantle” (Figs. 2 and 3). Quartz deformation microstructures in the metagranitic-dioritic samples appear most consistent with the regime 2–3 boundary (CC6–9–2; Fig. 2) and with lower regime 2 (CC8–3–2; Fig. 3) of Hirth and Tullis (1992).

Rutile was not present in the Cougar Creek (CC) metagranites–diorites, so \(a_{\text{TiO}} < 1.0\), but comparison to rocks of similar bulk composition suggest high \(a_{\text{TiO}}\) at conditions of mylonitization. Many granites have \(a_{\text{TiO}} \geq 0.6\) (e.g., Wark and Watson, 2006; Wark et al., 2007), and felsic rocks at amphibolite-facies conditions have \(a_{\text{TiO}} \geq 0.8\) (Ghent and Stout, 1984). Thus, we expected high \(a_{\text{TiO}}\) at least ≥0.6 and probably ≥0.8, and assigned a high, but relatively uncertain value of 0.8 ± 0.2 (2\(\sigma\)).

Methods are described more completely in the GSA Data Repository1, but they briefly involved four steps: (1) selecting characteristic microstructures in polished thin sections via petrographic microscope, (2) imaging those areas by using a scanning electron microscope (SEM)—mounted cathodoluminescence (CL) detector at the University of Idaho’s Center for Electron Microscopy and Microanalysis, (3) drilling out areas that exhibited variations in CL character among different quartz grains and remounting in 0.25 in. (6.35 mm) outer diameter (O.D.) stainless steel cylinders, and (4) analyzing the remounted subsamples for Ti contents with an ion microprobe at Lawrence Livermore National Laboratory. Ion microprobe analyses were standardized against two experimental run products and one natural sample of quartz, the Ti contents of which were determined by electron microprobe, as well as with Herkimer “diamond,” a low-temperature quartz (150–200 °C; Smith, 2006; so presumably ≤5.5 ppb Ti) that served as a Ti “blank.” Analyses for concentrations ≥1 ppm were collected with a spot ~10 × 15 µm in diameter. For concentrations less than 1 ppm, a larger, 150 × 250 µm, area was first rastered to eliminate minor surface contamination of Ti, then reanalyzed in its center with the 10 × 15 µm spot. Precisions were typically ±2%–3% (2\(\sigma\)), yielding precisions ±2 °C (2\(\sigma\)) for \(T \leq 500 \, ^\circ\text{C}\). Some analyses showed greater variation, reflecting minor compositional inhomogeneities.

1GSA Data Repository item 2009011, analytical methods, Ti standardization, and paleopiezometry regression, is available online at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

Figure 1. (A) Photomicrograph and (B–C) cathodoluminescence images of sample 94SC9, showing recrystallized quartz in a quartz-rich band. TitaniQ temperatures range from ~480 °C to 520 °C, suggesting that quartz deforms and recrystallizes over this temperature range in this rock. Scale bars are 100 µm. Grt—garnet.

Figure 2. (A) Photomicrograph and (B) cathodoluminescence image of sample CC6–9–2, showing complete recrystallization. TitaniQ temperatures are ~300 °C. Scale bar is 100 µm.
RESULTS

As expected, temperatures determined from the coarser recrystallized grains of quartz (94SC9; >475 °C; Fig. 1) were higher than those determined from finer recrystallized grains (≤450 °C; Figs. 2–3; Table 1). Sample CC6–9–2, with uniformly nonluminescent quartz, yielded the lowest TitaniQ temperatures, ~300 °C (Fig. 2). In sample CC8–3–2 (Fig. 3), in which a relict “core” quartz grain abutted a zone of much finer-grained dynamically recrystallized “mantle” quartz, the relict grain preserved high metamorphic to low igneous temperatures (~700 °C), whereas the recrystallized quartz preserved much lower temperatures (≤450 °C). This temperature difference correlates well with strongly luminescent relict quartz and nonluminescent recrystallized quartz (Fig. 3), further suggesting that CL luminescence provides chemical information about quartz recrystallization independent of optical observations. For example, in contrast to Figures 1–3, some samples contained 10–15-µm-diameter quartz grains with highly luminescent cores (e.g., Fig. DR1 [see footnote 1]); these observations indicate incomplete chemical equilibration and, possibly, a subgrain rotation deformation mechanism. Temperature precisions of ±2 °C fall well below the differences in temperature recorded by different quartz grains or domains (10–50 °C), even within a single mylonite zone.

DISCUSSION

In general, assumed highest-temperature microstructures of sample 94SC9 correspond with higher Ti contents and hence higher TitaniQ temperatures than the Cougar Creek samples (Figs. 1–3), implying that Ti contents of quartz in mylonites can reequilibrate during shearing and record the temperature of mylonitization. Sample CC8–3–2 (Fig. 3) provides the strongest within-sample evidence for this conclusion: higher versus lower luminescence corresponds texturally with relict versus recrystallized quartz, and with higher versus lower Ti contents and TitaniQ temperatures. These data suggest that future studies of Ti in quartz can yield precise temperatures of mylonitization. However, sample CC6–9–2, with a regime 2–3 microstructure, recorded a much lower temperature than CC8–3–2, which showed a lower regime 2 microstructure; this observation emphasizes the importance of other factors such as strain rate in determining microstructures, rather than temperature alone.

The strain rate can be quantified from constitutive relations for quartz deformation (e.g., Hirth et al., 2001; Eq. 1), if appropriate differential stress (σ) and water fugacity are assigned. Differential stress can be estimated from its correlation with recrystallized quartz grain size (Twiss, 1977; Stipp and Tullis, 2003; Stipp et al., 2006). Error estimation, however, requires re-regressing experimental data (Stipp and Tullis, 2003; Stipp et al., 2006) to account for errors in both grain size (D, in µm) and differential stress (σ, in MPa; see the Data Repository). Such a regression yields the following paleopiezometry equation (errors are 95% confidence, $r^2 = 0.9132$):

$$\log_{10}(\sigma) = (2.89 \pm 0.09) - (0.84 \pm 0.10)\log_{10}(D).$$

Water fugacity depends on temperature, which can be measured precisely with TitaniQ, and pressure, which may be estimated from phase equilibria or assumed geotherms.

For illustration, we assumed $f_{H_2O} = 400 \pm 100$ MPa (assuming typical thermal gradients, and presence of water during shearing and rehydration), and estimated both the strain rate and its uncertainty for the Cougar Creek samples. Optically determined estimates of quartz grain sizes are 45 ± 5 µm in sample CC6–9–2 and 7 ± 2 µm in sample CC8–3–2, implying $\sigma = 29 \pm 11$ MPa for CC6–9–2 and 140 ± 40 MPa for CC8–3–2; errors in the experimental regression and in the grain-size measurements contribute ~±11 MPa and ±2 MPa, respectively, for sample CC8–3–2, and ±15 MPa and ±35 MPa, respectively, for sample CC8–3–2. Using the expression of Hirth et al. (2001), estimated strain rates are ~1 $\times 10^{-15}$ s$^{-1}$ for CC6–9–2 and ~3 $\times 10^{-15}$ s$^{-1}$ for CC8–3–2, with uncertainties of about one and a half orders of magnitude. The equation of Hirth et al. (2001) contributes the largest source of error (over an order of magnitude). In contrast, variations in measured temperature (±15–25 °C) and grain size (±2–5 µm) each contribute maximal errors of about a factor of 2–3; temperature measurement precision (±2 °C) contributes only an ~10% error. Thus, the strain rate equation itself is currently the main source of uncertainty, contributing at least 10 times the error introduced by temperature and differential stress estimates.

Interestingly, the finer grain size in sample CC8–3–2 compared to CC6–9–2 might have been interpreted microstructurally as resulting from a lower temperature but instead appears to reflect an approximately four orders of magnitude higher strain rate at higher temperature and differential stress. This counterintuitive result emphasizes the importance of direct temperature determination, e.g., by TitaniQ. Note that sample CC8–3–2 is dominated by coarse feldspar and quartz porphyroclasts, with intervening bands of recrystallized quartz (Fig. 3; Fig. DR1). Thus, the high strain rate between rigid, possibly rotating grains may represent highly localized, hand-sample-scale strain, not regional strain (Holyoke and Tullis, 2006).
In sum, TitaniQ improves temperature estimates significantly in mylonites, with an unparalleled measurement precision of ±2 °C for ion microprobe analysis. Advances in our understanding of crustal rheology are no longer limited by temperature or differential stress estimates, but rather by our understanding of the functional dependence of strain rate on these parameters.

ACKNOWLEDGMENTS
This material is based upon work supported by the National Science Foundation under grant EAR-0439733 (to Kohn), and by Boise State University. We thank Doug Phinney, Tom Williams, and Ian Hutcheon for technical help with the ion microprobe and cathodoluminescence (CL) imaging, Joe Pyle and Jay Thomas for providing Ti measurements on quartz standards, and Jay Thomas and E. Bruce Watson for providing experimental quartz for calibrating the ion microprobe. Samples from the Cougar Creek Complex were originally collected by G. Kurz, and he is thanked for providing the geologic context for this study. Jan Tullis and two anonymous reviewers provided incisive reviews that greatly improved the original manuscript.

REFERENCES CITED

Manuscript received 23 April 2008
Revised manuscript received 11 September 2008
Manuscript accepted 13 September 2008
Printed in USA