Grain-boundary diffusion rates inferred from grain-size variations of quartz in metacherts from a contact aureole

TAKAMOTO OKUDAIRA¹,*, HIKARU BANDO¹, AND KENTA YOSHIDA²

¹Department of Geosciences, Osaka City University, Osaka 558-8585, Japan
²Department of Mineralogy and Petrology, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

*E-mail: oku@sci.osaka-cu.ac.jp

Running title: Grain-boundary diffusion in quartz aggregates
ABSTRACT

We evaluate a temperature-dependent coefficient for grain-boundary diffusion in quartz aggregates using grain size data from a contact aureole, based on the coupling of a numerical model for the temperature–time history of the contact aureole with a model for the kinetics of diffusion-controlled grain growth. The metachert samples were collected from the contact aureole of the Hanase–Bessho quartz diorite at Hanase Pass, Kyoto, Japan. The quartz grain sizes vary systematically with distance from the quartz diorite. We calculated the temperature–time history using a one-dimensional thermal model, validated by peak metamorphic temperature estimates that are based on the degree of graphitization of carbonaceous material in metapelites, as characterized by Raman microspectroscopy. To minimize the sum of the squares of the errors between the measured and calculated grain sizes, based on the normal grain growth law together with the temperature–time history, we estimated the activation energy and pre-exponential factor in the α-quartz field to be 208 kJ/mol and $1.1 \times 10^{-8}$ m$^2$/s, respectively, assuming a grain boundary width of 1 nm. The grain-boundary diffusion rates for temperatures in the greenschist and amphibolite facies are similar to those determined in natural or laboratory grain coarsening experiments, but differ significantly from those determined in diffusion experiments. During grain-size-sensitive deformation, ‘effective’ grain-boundary
diffusion rates may be intermediate between the rates of diffusion along and across the
grain boundary, and would be higher than the grain-boundary diffusion rates estimated by
grain coarsening experiments, and lower than those by tracer diffusion experiments.

**Keywords:** Grain-boundary diffusion, quartz aggregates, grain sizes, contact aureole,
normal grain growth

**INTRODUCTION**

Understanding and predicting the rheological behavior of many common crustal rocks
requires knowledge of the mechanical properties of quartz crystals and aggregates,
because quartz is one of the most abundant rock-forming minerals in the Earth’s
continental crust. Diffusion contributes to most of the important deformation mechanisms,
including grain-size-sensitive diffusion creep/grain-boundary sliding and insensitive
dislocation creep (e.g., Okudaira and Shigematsu 2012). In order to evaluate the relative
importance of these different mechanisms for quartz deformation, the diffusion kinetics
of the major ionic species in quartz crystals and aggregates must first be known.

The grain-boundary (or bulk) diffusion coefficients of Si or O have been estimated
from tracer diffusion experiments (Farver and Yund 1991a, 2000a), and from natural or
laboratory grain-coarsening experiments (Joesten 1983, 1991; Tullis and Yund 1982).
According to Farver and Yund (2000a), based on the data obtained by isotopic tracer $(^{30}\text{Si})$ and standard step-scan analysis using an ion microprobe, the temperature dependence of silicon bulk diffusion in novaculite for hydrothermal experiments at 600–800 °C and 150 MPa confining pressure, and dry experiments at 800–1100 °C and 1 atm (in a stream of dry N$_2$), respectively, is described by the Arrhenius parameters $D_0 = 3.7 \times 10^{-10}$ m$^2$/s and $E = 137 \pm 18$ kJ/mol, and $D_0 = 6.2 \times 10^{-9}$ m$^2$/s and $E = 178 \pm 38$ kJ/mol. Assuming volume diffusion to be negligible (i.e., type C kinetics; Saal et al. 1990), the measured bulk diffusion rates ($D_{\text{bulk}}$) can be related to grain-boundary diffusion rates ($D_{gb}$) through the expression $D_{\text{bulk}} = \tau D_{gb} \delta/d$, where $\tau$, the tortuosity factor, represents the ratio of the true path length to the length of the measured profile (e.g. Watson 1991), $\delta$ is the grain-boundary width, and $d$ the average grain size. The value of $\tau$ depends on the grain geometries, and estimates typically range from 1.5 to 2.0 (e.g., Farver and Yund 2000a).

On the other hand, variations in the grain-sizes of quartz in five nodular chert samples from the Christmas Mountains contact aureole were matched by a normal grain growth model in which the temperature dependence of the Arrhenius function, along a temperature–time history, was calculated by one-dimensional thermal modeling (Joesten 1983). Assuming a grain boundary width of 1 nm, the data permit the coefficient for the
grain-boundary diffusion of oxygen in quartz aggregates to be estimated as $D = 8.07 \times 10^{-10} \exp(-210 \times 10^{3}/RT)$ for the temperature range of 600–1000 °C. Tullis and Yund (1982) determined grain growth rates for quartz aggregates between 800 °C and 1000 °C at 200–1500 MPa, and based on the data from a grain-growth experiment of Tullis and Yund (1982), Joesten (1991) recalculated the values of $D_0$ and $E$ as $5.23 \times 10^{-7}$ m$^2$/s and 282 kJ/mol, respectively.

The values of the grain-boundary diffusion coefficients extrapolated to the conditions of greenschist to granulite facies (~300–900 °C) are $\sim 10^{-19}$ to $10^{-12}$ m$^2$/s (wet experiment of Farver and Yund 2000a), $\sim 10^{-21}$ to $10^{-13}$ m$^2$/s (dry experiment of Farver and Yund 2000a), $\sim 10^{-29}$ to $10^{-19}$ m$^2$/s (Joesten 1983), and $\sim 10^{-30}$ to $10^{-18}$ m$^2$/s (Joesten 1991, based on the data of Tullis and Yund 1982); there is a significant difference between the coefficients for a quartz aggregate calculated from diffusion and grain-coarsening experiments.

The phenomenological, isothermal kinetic grain-growth equation is given by

$$d^n - d_0^n = K_0 \exp(-E/RT)t$$  \hspace{1cm} (1)

where $d$ is the average grain size (m) at time $t$ (s), $d_0$ is the initial grain size, $n$ is the kinetic
grain-growth exponent, $K_0$ is a pre-exponential constant (m$^n$/s), $E$ is the activation energy for grain growth (J/mol), $R$ is the gas constant (J/mol/K), and $T$ is temperature (K). Where pores and impurities are absent, theoretical considerations predict a value of $n = 2$ in a pure single-phase system, and the grain growth is controlled by the diffusion of atoms across the grain boundary (e.g., Joesten 1991 and references therein). Thus, grain growth is a diffusional process, and the analysis of natural or laboratory coarsening experiments can yield values for the grain-boundary diffusion coefficients.

The intrusion of a quartz diorite (2.6 × 1.6 km in surface area) in the Hanase–Bessho area, Kyoto, Japan, produced an extensive contact aureole (Fig. 1; Kiji et al. 2000; Kimura et al. 1998, 2001). Thermally metamorphosed rocks derived from chert, mudstone, and sandstone crop out along a roadside, and extend 1600 m normal to the contact with the quartz diorite. The average grain-size of quartz in the cherts increases systematically towards the quartz diorite contact. In our study of these cherts, similar to the analysis of Joesten (1983), we evaluate the temperature-dependent coefficient for grain-boundary diffusion in the quartz aggregates, using grain-size data from the contact aureole. We also couple a numerical model of the temperature–time history of the contact aureole with a model of the kinetics of diffusion-controlled grain growth.
METHODS AND SAMPLES

Method

Isothermal grain growth in a single-phase aggregate can be described by an equation of the following form (Joesten 1983, 1991; Rubie 1986):

\[ d^2 - d_0^2 = \frac{8 \gamma V_m D_0}{RT} \frac{1}{\delta} \exp\left(-\frac{E}{RT}\right) t \]  \hspace{1cm} (2)

where \( \gamma \) is the surface energy (J/m\(^2\)), \( V_m \) is the molar volume (m\(^3\)/mol), \( D_0 \) is the pre-exponential factor (m\(^2\)/s), and \( \delta \) is the grain-boundary width (m). When temperature is a function of time, such as in a contact aureole, rocks at any point in the aureole experience a heating–cooling cycle, the magnitude and duration of this cycle are functions of the distance from the intrusive contact, and all terms in \( T \) are included within the time integral, so that

\[ d^2 - d_0^2 = \frac{8 \gamma V_m D_0}{RT} \frac{1}{\delta} \int_{t_0}^{t} \frac{1}{T(t)} \exp\left(-\frac{E}{RT(t)}\right) dt \]  \hspace{1cm} (3)

The grain size at a given distance from the intrusive contact is a function of both temperature and time. For thermally activated grain growth, all the information relating to
the temperature dependent behavior of the system is included within the temperature–time integral. The temperature–time integral at a given distance from the contact can be evaluated numerically using a thermal model for the contact aureole. Assuming a constant duration of grain growth of quartz at any distance from the intrusive contact, the average temperature at a given distance from the contact can be calculated by dividing the $T–t$ integral by the duration of grain growth; i.e., the average temperature over time. If the grain-growth exponent of 2 is independent of temperature, it can be used to obtain first-order approximations of the activation energy and the pre-exponential factor for quartz grain growth, which can be determined from the slope of an Arrhenius plot of $\ln[(d^2 - d_0^2)T]$ versus $1/T$. In this case, $T$ means the average temperature at a given distance from the intrusive contact, as defined by dividing time-integrated temperatures by a particular period at any point in the aureole. Furthermore, we calculate the values of the activation energy and pre-exponential factor more precisely, to minimize the sum of the squares of the errors between the measured and calculated grain sizes, using Equation 3 along with the temperature–time history.

We evaluate the temperature–time history of the contact aureole with a one-dimensional thermal model, assuming a sheet-like shape for the intrusion. A one-dimensional heat transfer equation can be written as
\[
\frac{\partial T}{\partial t} = \frac{K}{\rho_m C_m} \frac{\partial^2 T}{\partial x^2} + \frac{A}{\rho_m C_m}
\]  
(4)

where \(\rho_m\) is the density of the rock (kg/m\(^3\)), \(C_m\) is the specific heat of the rock (J/kg/K), \(K\) is the thermal conductivity (W/m/K), \(x\) is a horizontal coordinate (m) measured from the center of the quartz diorite body, and \(A\) is the heat produced by radioactive elements (W/m\(^3\)). Equation 4 was solved numerically using an explicit finite-difference method with an array spacing (\(\Delta x\)) of 10 m and a time step (\(\Delta t\)) of \(3.15 \times 10^7\) s. The production of heat during crystallization of the magma (i.e., latent heat) has been calculated to be continuous linear functions of temperature during the interval of crystallization between the liquidus and solidus temperatures. The production of heat was incorporated into the numerical model using an effective heat capacity (\(C^*\)) and an effective thermal diffusivity \((\kappa^*)\) for rocks undergoing these reactions (e.g., Hanson and Barton 1989). The effective thermal diffusivity is then calculated from

\[
\kappa^* = \frac{K}{\rho_m C^*}
\]  
(5)

where \(C^*\) is defined by
\[ C^* = C_m + \left[ \frac{\Delta H_{magma}}{(T_{liq} - T_{sol})} \right] \] (6)

where \( \Delta H_{magma} \) is the enthalpy of the crystallizing magma (J/kg), \( T_{liq} \) is the liquidus temperature, and \( T_{sol} \) is the solidus temperature. The values of parameters used in the numerical simulation are listed in Table 1. In this study, we assumed no magmatic convection or recharge.

**Samples**

We collected metachert samples from the contact aureole around the Late Cretaceous Hanase–Bessho quartz diorite (Kiji et al. 2000). The quartz diorite is massive and medium-grained, and it is composed mainly of plagioclase, quartz, hornblende, biotite, and K-feldspar, with minor amounts of titanite, opaque minerals, and apatite. The SiO\textsubscript{2} content of the bulk-rock is ~66–67 wt.% (Kiji et al. 2000). The quartz diorite has steeply dipping contacts with country rocks (Kimura et al. 2001), and is likely to be a sheet-like or tabular intrusion. The contact aureole has a width of up to around 1 km, and it is recognized on the basis of the occurrence of metamorphic biotite in the metasediments.

Away from the contact aureole, the rocks are characterized by the mineral assemblage
muscovite + chlorite. Samples next to the intrusive contact (~180 m) contain cordierite that is partially or totally pinitized, and the characteristic assemblage is cordierite + biotite. Along the road where our samples were taken, biotite is present up to 710 m from the intrusive contact. We could not collect metachert samples close to the intrusive contact along the main road, and for this reason, the four samples closest to the intrusive contact had to be collected from a different area.

**Grain size analysis**

The grain sizes of the recrystallized quartz were measured using the image analysis software ImageJ. Each grain size was calculated as the equivalent circular diameter of a grain, and the mean grain size was calculated as the arithmetic mean of the log of grain sizes, or in other words, the geometric mean grain size. We analyzed optical photomicrographs to measure the grain sizes of quartz in sample A. The grain boundaries of minerals were manually traced on photomicrographs taken under plane and crossed-polarized light. To measure the grain sizes of fine-grained quartz in some samples, we analyzed secondary-electron images obtained with a scanning electron microscope (SEM) at the Department of Geosciences, Osaka City University, Japan. We used 200–900 grains in each sample to measure the mean grain size of the quartz. The
modal amounts of minerals were also determined during the analysis, and the analytical results are listed in Table 2.

RESULTS

Results of thermal modeling

Results of the thermal modeling are shown in Figure 2; the temperature profiles are shown for each elapsed time, as well as the maximum temperature experienced by a rock at any position in the aureole. The results of the thermal modeling have been verified by temperature estimates based on the degree of graphitization of carbonaceous material in the metapelites using Raman microspectroscopy (e.g., Aoya et al. 2010; Beyssac et al. 2002). The degree of graphitization of the carbonaceous material is not affected by retrogression, and it records the peak metamorphic conditions. The spectroscopy was carried out with the laser Raman spectrometer (JASCO NRS-3100) at Kyoto University, Japan, using the 514.5 nm line of an Ar–ion laser at 20–30 × 10⁻³ W, and a spot size of 1 µm on the sample surface. We analyzed the relative area of the defect band, i.e., the D1/(G + D1 + D2) peak area ratio (R2 ratio), where D1, D2, and G bands occur at 1350, 1620, and 1580 cm⁻¹, respectively, and calculated the peak temperature with the equation

\[ T (°C) = -445 \times R2 + 641 \] (Beyssac et al. 2002). Although the degree of graphitization of
carbonaceous material would be affected by not only the temperature but also the duration of the temperature, the relationship between temperature and the degree of graphitization of carbonaceous material for regional metamorphic rocks (Beyssac et al. 2002) is applicable to contact metamorphic aureoles (Aoya et al. 2010). The calculated temperatures for the metapelites (see Table 3) are 570 ± 32 °C (182 m from the contact), 536 ± 34 °C (573 m), 471 ± 25 °C (1136 m), and 470 ± 32 °C (1400 m). The results (see Fig. 2b) are comparable to the maximum temperatures obtained by thermal modeling, indicating that the temperature profiles calculated by the model are suitable for studying the thermal structure and temperature–time (T–t) history of the rocks around the Hanase–Bessho quartz diorite. In this thermal model, the duration of the high-temperature conditions is a minimum estimate, because we do not consider magmatic convection or recharge. Consequently, the diffusion rates estimated for the inferred T–t history are maximum estimates.

Results of grain size analysis

The quartz grains studied are polygonal and equigranular (Fig. 3a), and there are no microstructures indicative of internal plasticity. The grain size distributions of the quartz in the metacherts are log-normal (Fig. 3b), and the results of quartz grain-size
measurements are shown in Figure 4 and Table 2. The quartz grain size increases towards the intrusive contact, but the observed data do not fit the expected exponential variation with distance from the contact, and the grain growth of quartz near the contact seems to have been inhibited. The modal amounts of second-phase minerals (mainly sheet silicates and carbonaceous materials) in the metacherts near the contact are approximately 3–4 vol.% (Table 2), slightly more than in the other samples, except for sample 110331-22. This result suggests that the presence of second-phase minerals has an effect on the grain growth kinetics of the first-phase quartz, resulting in the pinning or dragging of quartz grain boundaries, with the pinning process ensuring that the grain size remains small. The grain size of the first-phase mineral is strongly dependent on the grain size ($d_p$ in microns) and volume fraction ($f_p$) of the second-phase minerals: the ratio $d_p/f_p$ is referred to as the Zener parameter or Zener ratio, $Z$ (e.g., Brodhag et al. 2011; Herwegh et al. 2011). At low $Z$ values, grain growth of the first-phase mineral is controlled by the pinning effect of the second-phase minerals (i.e., second-phase controlled coarsening regime) and the upper limit of $Z$ values of this regime increases with increasing temperature. The effect of the second-phase minerals on normal grain growth of the first-phase mineral is smaller at lower temperatures than at higher temperatures. In samples collected farther from the intrusion contact, the second-phase minerals are several microns in size, and their $Z$
values are calculated to be ~10^2–10^3 µm, suggesting a negligible effect of the second phases on grain growth of the first phase (e.g., Herwegh et al. 2011; Okudaira et al. 2010). In samples from near the intrusion contact, the grain sizes of the second-phase minerals are large (up to ~10–20 µm) and the calculated Z values are ~10^2–10^3 µm, which are similar to the Z values of samples collected farther from the contact. Because the Z values of samples from near the intrusion contact (i.e., high-temperature samples) may fall within the field of the second-phase controlled coarsening regime, the effect of the second phases on grain growth of the first-phase quartz would be higher than in other samples, although to an unknown degree.

DISCUSSION

Estimates of activation energy and the pre-exponential factor

To obtain first-order approximations of the values of the activation energy and the pre-exponential factor, we have constructed an Arrhenius plot of \( \ln[(d^2 - d_0^2)/T] \) for metachert data and reciprocal temperatures, as shown in Figure 5. The growth period in this case is 25 \( \times \) 10^3 years, a figure that was chosen arbitrarily as the period during which the temperatures at the center of the intrusion fell to 500 °C (see Fig. 2), after which time the temperature profiles are nearly constant. The solid line in this figure is a linear least
squares fit for the 17 data given by \( \ln[(d^2 - d_0^2)T] = 11.123 - 19698/T \) \( (r^2 = 0.87772) \). The activation energy for quartz grain growth is 163.8 ± 15.8 kJ/mol. Assuming a grain boundary width of 1 nm, the pre-exponential factor is estimated to be \( 1.2 \times 10^{-11} \text{ m}^2/\text{s} \).

Excluding three samples (open circles in Fig. 5) near the intrusion contact when estimating the activation energy and the pre-exponential factor, a linear least squares fit for the remaining 14 data points yields \( \ln[(d^2 - d_0^2)T] = 17.919 - 24638/T \) \( (r^2 = 0.91442) \). The activation energy and the pre-exponential factor are 204.8 ± 18.1 kJ/mol and \( 1.1 \times 10^{-8} \text{ m}^2/\text{s} \), respectively.

To estimate the values of the activation energy and the pre-exponential factor more precisely, we calculated quartz grain sizes using Equation 3, together with the temperature–time history, in order to make comparisons with measured grain sizes (Fig. 6). To minimize the sum of the squares of the errors between the calculated and measured grain sizes, the values of the activation energy and pre-exponential factor, respectively, should be 132 kJ/mol and \( 4.8 \times 10^{-14} \text{ m}^2/\text{s} \). We obtained a grain-boundary diffusion rate of \( D_{gb} = 4.8 \times 10^{-14} \exp(-132/RT) \). The value of the activation energy agrees with the value of 137 ± 18 kJ/mol, determined by Farver and Yund (2000) for the bulk diffusion of silicon or grain-boundary diffusion in wet quartz aggregates. The pre-exponential factor differs significantly from the figure of \( 2.2 \times 10^{-6} \text{ m}^2/\text{s} \) that is given by Farver and Yund.
(2000a) for experimental grain-boundary diffusion in wet quartz aggregates, assuming a
tortuosity factor \( \tau = 1.7 \) and a ratio of grain-boundary width to grain size \( \delta/d = 0.0001 \).

Excluding three samples (open circles in Fig. 6) near the intrusion contact, the activation
energy and pre-exponential factor are 208 kJ/mol and \( 1.1 \times 10^{-8} \text{ m}^2/\text{s} \), respectively. The
value of the activation energy agrees with the value of 210 kJ/mol reported by Joesten
(1983).

The values for the activation energy and pre-exponential factor of quartz grain
coarsening that we have determined may be controlled by silicon grain-boundary
diffusion. When water is present, Farver and Yund (2000a) suggested that grain-boundary
diffusion accommodated processes in quartz aggregates will most likely be rate-limited
by the transport of silicon, because the rate of oxygen grain-boundary diffusion is greater
than silicon grain-boundary diffusion by a factor of about 2. The metachert samples
studied here contain small amounts of sheet silicates (muscovite, chlorite, and/or biotite),
and therefore at least trace amounts of water or water-related species were present at the
time of contact metamorphism.

The volume diffusion coefficients of O in \( \alpha \)- and \( \beta \)-quartz under hydrothermal
conditions are significantly different (Fig. 7; Farver and Yund 1991b; Giletti and Yund
1984), and then the grain-boundary diffusion coefficients of Si may be different between
the stability fields of $\alpha$- and $\beta$-quartz. In the present study, quartz in samples from near the intrusion contact (within ~180 m) does not show the expected exponential variation in grain size with distance from the contact. Given that the temperature conditions of the $\alpha$–$\beta$ transition in quartz at a confining pressure of 200–300 MPa are 630–650 °C (Shen et al. 1993), at least near the metamorphic peak, the growth of quartz grains in these samples must have occurred in the $\beta$-quartz field. The suppression of grain growth may have resulted from the fact that the grain-boundary diffusion coefficients for the $\beta$-quartz field are different from those for the $\alpha$-quartz field. In the $\beta$-quartz field, the volume diffusion rates of O calculated using diffusion coefficients for $\beta$-quartz are slower than those calculated using diffusion coefficients for $\alpha$-quartz, because the extrapolated volume diffusion rates of O in $\alpha$- and $\beta$-quartz for the entire temperature range, as calculated from diffusion rates for experimental temperature range (see Fig. 7), cross over near the temperature of the $\alpha$–$\beta$ transition (Farver and Yund 1991b; Giletti and Yund 1984). Therefore, in the $\beta$-quartz field, the grain-boundary diffusion rates of Si calculated using grain-boundary diffusion coefficients for $\beta$-quartz are likely to be slower than those calculated using diffusion coefficients for $\alpha$-quartz. The grain size of quartz in $\beta$-quartz aggregates is larger when calculated using the grain-boundary diffusion coefficients for the $\alpha$-quartz field, than when calculated with diffusion coefficients for the $\beta$-quartz field.
This means that the difference between the grain size of quartz in samples from near the intrusion contact and the expected exponential variation with distance from the contact can be attributed to the difference in the grain-boundary diffusion coefficients of Si in the \( \alpha \) - and \( \beta \)-quartz fields. However, because no previous experiment has considered grain-boundary diffusion in the \( \alpha \)-quartz field, we cannot conclude that the grain-boundary diffusion coefficient of Si differs between the \( \alpha \) - and \( \beta \)-quartz fields.

The calculated grain size variations, using the \( T-t \) history and different diffusion rates, are shown in Figure 6 in order to compare them with the measured grain size variations. The calculated grain size variations, using the values for \( D_0 \) and \( E \) for the bulk diffusion of silicon, given by Farver and Yund (2000a), are much larger than the measured grain size variations, suggesting that the Farver and Yund (2000a) values of \( D_0 \) and \( E \) cannot be applicable to the grain coarsening of quartz in natural quartz aggregates under the conditions of the greenschist and amphibolite facies.

**Grain-boundary diffusion rates in quartz aggregates**

Figure 7 shows the diffusion rates for quartz aggregates estimated in this study and previous studies. In this figure, the grain-boundary width is assumed to be 1 nm. Using our estimated values of the activation energy and pre-exponential factor, the
grain-boundary diffusion rates for temperatures in the greenschist and amphibolite facies are similar to those of Joesten (1983), as well as those of Tullis and Yund (1982), whose values have been recalculated by Joesten (1991), but they differ significantly from those of Farver and Yund (2000a) (Fig. 7). The grain-boundary diffusion rates estimated from studies of grain coarsening (Joesten 1983; Tullis and Yund 1982; this study) are about four to six orders of magnitude smaller than the silicon grain-boundary diffusion rates determined by Farver and Yund (2000a). The difference between the measured silicon grain-boundary diffusion rates and the values obtained from grain coarsening studies may be due to several factors.

The results from experimental studies typically yield a grain coarsening exponent significantly greater than 2, indicating that abnormal grain growth has occurred, possibly because of grain-boundary drag due to the presence of secondary phases, pores, or contaminants, or possibly because the coarsening is by an Ostwald ripening mechanism instead of normal grain growth (Farver and Yund 2000a). In either case, the apparent grain-boundary diffusion rates estimated from the grain coarsening experiments would be much slower than the true value. However, judging from the values of the coefficient of determination ($r^2$) for least squares regression to fit the data, a kinetic grain-growth exponent ($n$) of 2 is the most suitable for the present data set, rather than $n = 3$ or 4,
suggesting that normal grain growth is the most likely control of quartz grain sizes in the contact aureole.

As described above, the volume diffusion rate of O is much lower in $\alpha$-quartz than in $\beta$-quartz (Fig. 7; Farver and Yund 1991b; Giletti and Yund 1984). The grain-boundary diffusion rates estimated by Farver and Yund (2000a) were measured in the $\beta$-quartz field, whereas those of the present study were estimated mainly in the $\alpha$-quartz field. Consequently, the difference between the two sets of grain-boundary diffusion rates can be attributed to differences in the diffusion coefficients in the $\alpha$- and $\beta$-quartz fields. However, if the grain-boundary diffusion rates in the $\beta$-quartz field are much higher than those in the $\alpha$-quartz field, then we would expect the grain size of quartz in samples from near the intrusion contact to be much larger than in samples farther from the contact, yet this is not the case. Furthermore, the difference in grain-boundary diffusion rates between Farver and Yund (2000a) and the present study is much larger than the difference in the volume diffusion rate of O between $\alpha$- and $\beta$-quartz. The grain-boundary diffusion rates measured in the $\beta$-quartz field, in grain-coarsening experiments (Joesten 1991; Tullis and Yund 1982), differ significantly from those of Farver and Yund (2000a). Thus, the difference between the grain-boundary diffusion rates of Farver and Yund (2000a) and those of the present study cannot be attributed to differences in the grain-boundary rates.
between α- and β-quartz.

Dohmen and Milke (2010) summarized Si grain-boundary diffusion data for quartz (Farver and Yund 2000a), Mg$_2$SiO$_4$ polymorphs (Farver and Yund 2000b; Shimojuku et al. 2009), and MgSiO$_2$ perovskite (Yamazaki et al. 2000). While the diffusion properties of grain boundaries in Mg$_2$SiO$_4$ and MgSiO$_3$ high-pressure phases are nearly identical when pressure dependence is considered, the data for quartz are strikingly different, with grain-boundary diffusion rates of quartz being 4–5 orders of magnitude higher than those of Mg$_2$SiO$_4$ and MgSiO$_3$ high-pressure phases. This difference may be related to the different grain-boundary structures and the diffusion mechanism of Si (due to the presence of Mg), or related to effectively wet grain boundaries even in nominally dry studies. Dohmen and Milke (2010) reported that the water contents of the natural novaculite samples analyzed by Farver and Yund (2000a) were not measured before or after the experiments. Even in the dry experiment (in a N$_2$ stream), water might have initially been present along grain boundaries in the samples, thereby influencing Si diffusivity. Since hydrogen is an incompatible element in most minerals, it is likely to become concentrated along grain boundaries, strongly affecting the grain boundary structure. In fact, based on the experimentally determined growth rates of wollastonite reaction rims between quartz and calcite (where small amounts of water are always
present), the grain boundary diffusion rates of SiO$_2$ are $10^{-16}$ to $10^{-14}$ m$^2$/s at 850 to 1000 $^\circ$C, assuming a grain boundary width $\delta = 1$ nm (Milke and Heinrich 2002). These rates are comparable to those reported for Si bulk diffusion in dry and wet experiments performed by Farver and Yund (2000a), whereas Milke and Wirth (2003) reported diffusion rates of $10^{-16}$ to $6 \times 10^{-18}$ m$^2$/s (950 to 850 $^\circ$C) for SiO$_2$ in wollastonite rims from completely dry experiments in a CO$_2$ atmosphere, being almost two orders of magnitude lower than the rates obtained by Milke and Heinrich (2002). However, in the metachert samples studied here, small amounts of sheet silicates are observed (e.g., muscovite, chlorite, and/or biotite), suggesting that at least trace amounts of water or water-related phases were present at the time of contact metamorphism. Thus, the difference between the grain-boundary diffusion rates of Farver and Yund (2000a) and those of the present study cannot be attributed to differences in the amount of water at grain boundaries.

In natural rocks, the grain-boundary width ranges from several to tens of nanometers (Nakashima 1995). The effective grain boundary width is a poorly constrained measure that acts in opposite directions in the derivation of diffusion coefficients from grain coarsening or diffusion experiments. Grain-boundary diffusion rates depend on the factor $D_{gb}/\delta$ in grain coarsening experiments, whereas the grain-boundary diffusion coefficient
is estimated by the relation $D_{\text{bulk}} = \tau D_{gb} \delta / d$ in tracer diffusion experiments. When the grain boundary width is 10 nm, $D_{gb}$ for grain coarsening experiments increases by an order of magnitude, and that for tracer diffusion experiments decreases by an order of magnitude; consequently, the difference in diffusion rate between them decreases by two orders of magnitude. The rate-limiting jump distance is greater across the boundary than along the boundary, which means that $D_{gb}$ for transport perpendicular to the boundary may be much smaller than $D_{gb}$ parallel to the boundary (Farver and Yund 2000a; Ricoult and Kohlstedt 1983). Diffusion rates measured in grain coarsening experiments are controlled by diffusion in a moving boundary (diffusion across the boundary), whereas the rates obtained from tracer diffusion experiments are related to diffusion along the grain boundary (Ricoult and Kohlstedt 1983). In other words, the diffusion rates inferred from coarsening experiments (Joesten 1983, 1991; Tullis and Yund 1982; this study) are lower than those in tracer diffusion experiments (Farver and Yund 2000a).

In the Ag/Au system, the ratio of diffusion rate along the grain boundary to that across the grain boundary varies according to the misorientation angles between neighboring grains, and is less than ~20 (Ma and Balluffi 1993). Based on an analysis of spinel formation between single crystals of periclase and sapphire, Keller et al. (2010) reported that ionic mobility in a polycrystal depends on grain-boundary structures, such as
misorientations between neighboring grains, and that diffusion rates should be low at
low-angle grain boundaries with misorientation angles of <15°. They suggested that grain
boundary diffusion in spinel varies by one order of magnitude as the misorientation
changes from 0° to 60°. For metals and silicates, since the ratio of diffusion rate along the
grain boundary to that across the grain boundary varies by one order of magnitude, it
seems that anisotropic diffusion at grain boundaries is an important factor in explaining
the large difference between the measured silicon grain-boundary diffusion rate and that
obtained from grain coarsening studies, although other factors also contribute to the
difference.

Grain-size-sensitive creep (diffusion creep or grain-boundary sliding) is governed by
diffusion along grain boundaries, which depends on $D_{gb} \delta$ (e.g., Poirier 1985), and is rate
limited by the diffusion of Si along the grain boundary, if the slowest-diffusing species is
rate controlling (Raj 1982). During deformation, grain-size-sensitive creep and grain
growth occur simultaneously (e.g., Platt and Behr 2011), suggesting that diffusion across
grain boundaries operates effectively. If the difference between grain-boundary diffusion
rates estimated by grain coarsening experiments and by diffusion experiments is caused
mainly by the difference in diffusion rates across and along grain boundaries, then grain
growth and deformation would be governed by the different temperature-dependent
coefficients for grain-boundary diffusion in quartz aggregates. In this case, the ‘effective’
grain-boundary diffusion rate may be intermediate between the rates of diffusion along
and across the grain boundary, and would be higher than the grain-boundary diffusion rate
estimated by grain coarsening experiments, and lower than that estimated by tracer
diffusion experiments.

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REFERENCES CITED

Aoya, M., Kouketsu, Y., Endo, S., Shimizu, H., Mizukami, T., Nakamura, D., and Wallis,
S. (2010) Extending the applicability of the Raman carbonaceous-material
geothermometer using data from contact metamorphic rocks. Journal of Metamorphic
Geology, 28, 895–914.

nuclear micro-analysis methods. Physics of the Earth and Planetary Interiors, 97,
145–162.

carbonaceous material in metasediments: a new geothermometer. Journal of
Metamorphic Geology, 20, 859–871.

contact metamorphic carbonate rocks: The role of different physical interactions

boundaries, mathematical models, and experimental data. Reviews in Mineralogy and
Geochemistry, 72, 921–970.

natural, fine-grained, quartz aggregates. Geochimica et Cosmochimica Acta, 55,
1597–1607.

Dependence on temperature and water fugacity. Chemical Geology, 90, 55–70.


Journal of Geology, 90, 301–318.


FIGURE CAPTIONS

FIGURE 1. Geological map for the Hanase–Bessho quartz diorite and surrounding areas. The map was compiled during this study with the help of data from Kimura et al. (1998, 2001). Localities of metachert samples (solid circles) and metapelite samples (open circles) are shown. Numbers with a dash denote samples 120322-#, and those without a dash, samples 110331-#.

FIGURE 2. Temperature profiles showing the thermal evolution in and around the Hanase–Bessho quartz diorite after its intrusion. (a) Temperature profiles from 0 to 24 kyr (2 kyr intervals). (b) Maximum temperatures experienced after the intrusion. The temperatures are estimated from the degree of graphitization of carbonaceous material in metapelites, using Raman microspectroscopy.

FIGURE 3. Microstructures of the metacherts. (a) Photomicrographs of samples 120322-02 (crossed-polarized light) and 110331-15 (back-scattered electron image, shadow mode). (b) Grain size distribution of quartz grain sizes for samples 120322-02 and 110331-15.

FIGURE 4. Grain size variation plotted against the distance from the intrusive contact.

FIGURE 5. Arrhenius plot of $\ln[(d^2 - d_0^2)/T]$ versus $1/T$. The solid lines (1) and (2) are linear least squares fits for 17 data points (solid circles + open circles) and for 14 data points.
points (solid circles), respectively. See the text for details.

**Figure 6.** Calculated and measured grain size variations. $D_{Si, \text{bulk}}$ (wet, FY00), $D_{Si, \text{bulk}}$ (dry, FY00), $D_{gb}$ (J83), and “this study” represent, respectively, the grain size variations using the values of activation energy and pre-exponential factor from Farver and Yund (2000a) for hydrothermal and dry experiments, Joesten (1983), and as estimated by us in this study. The curves (1) and (2) show calculated grain size variations using the values of 17 metachert samples and of 14 samples that excluded three samples near the intrusion contact (open circles), respectively.

**Figure 7.** Comparison of grain-boundary or bulk diffusion rates for quartz aggregates obtained in the present study and in previous studies. $D_{Si,\text{gb or bulk}}$ (wet, FY00), $D_{Si,\text{gb or bulk}}$ (dry, FY00), $D_{gb}$ (TY82), $D_{gb}$ (J83), and “this study” denote, respectively, the diffusion rates calculated using the values of activation energy and pre-exponential factor from Farver and Yund (2000a) for hydrothermal and dry experiments, Tullis and Yund (1982), with their values recalculated by Joesten (1991), Joesten (1983), and as estimated by us in this paper. Silicon grain-boundary diffusion rates ($D_{Si,gb}$) were estimated using the relation $D_{Si,\text{bulk}} = \tau D_{Si,gb} \delta/d$, where $D_{Si,\text{bulk}}$ is the silicon bulk diffusion rate, $\tau$ is the tortuosity factor (1.7), $\delta$ the grain-boundary width (1 nm), and $d$ the average grain size (10 µm). Diffusion rates represented by thick lines are those calculated for the experimental
temperature range, and those represented by thin lines are the extrapolated rates for the entire temperature range. The labels “this study, 17” and “this study, 14” represent diffusion rates calculated using the activation energy and the pre-exponential factor estimated based on 17 metachert samples and on 14 samples (excluding three samples from near the intrusion contact), respectively. Also shown are the volume diffusion rates of O in $\alpha$- and $\beta$-quartz under hydrothermal conditions (Farver and Yund 1991b; Giletti and Yund 1984), and of Si in $\beta$-quartz (Béjina and Jaoul 1996).
Chert facies

Quartz diorite and tonalite of the San-yo Zone

Siliceous mudstone facies

Mixed rock facies

Black mudstone facies

Granite porphyry, quartz porphyry and aplite

Greenstone facies

Fault

Complex boundary

Figure 1
Figure 3

(a) Microstructure

(b) Grain size distribution
\[ \text{Ln} [(d^2 - d_0^2) \frac{T}{T}] = 11.123 - 19698 x \frac{1}{T} \quad (r^2 = 0.87772) \]

\[ \text{Ln} [(d^2 - d_0^2) \frac{T}{T}] = 17.919 - 24638 x \frac{1}{T} \quad (r^2 = 0.91442) \]
Figure 6

- Log (grain size, μm) vs. Distance from contact (m)

- Curves:
  - $D_{Si, bulk}$ (wet, FY00)
  - $D_{Si, bulk}$ (dry, FY00)
  - $D_{gb}$ (this study)
  - $D_{gb}$ (J83)

- Data points for $D_{gb}$ (this study) and $D_{gb}$ (J83) with error bars.
Figure 7

α-quartz (O)
β-quartz (O)
β-quartz (Si)

$D_{Si, gb}$ (wet, FY00)
$D_{Si, gb}$ (dry, FY00)
$D_{gb}$ (TY82)
$D_{gb}$ (J83)
$D_{gb}$ (this study, 17)
$D_{gb}$ (this study, 14)
<table>
<thead>
<tr>
<th>Parameters used in the thermal modeling</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of rock ((\rho_m))</td>
<td>2750 kg/m(^3) ([1])</td>
</tr>
<tr>
<td>Specific heat of rock ((C_m))</td>
<td>880 J/kg/K ([1])</td>
</tr>
<tr>
<td>Thermal conductivity ((K))</td>
<td>2.8 W/m/K ([1])</td>
</tr>
<tr>
<td>Heat produced by radioactive elements ((A))</td>
<td>(2.64 \times 10^{-6} \text{ W/m}^3) ([1])</td>
</tr>
<tr>
<td>Initial temperature of the intrusion ((T_{int}))</td>
<td>950 °C</td>
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<tr>
<td>Solidus temperature of the intrusion ((T_{sol}))</td>
<td>750 °C ([2])</td>
</tr>
<tr>
<td>Liquidus temperature of the intrusion ((T_{liq}))</td>
<td>1050 °C ([2])</td>
</tr>
<tr>
<td>Initial temperature of the country rocks</td>
<td>350 °C</td>
</tr>
<tr>
<td>Enthalpy of crystallizing magma ((\Delta H_{magma}))</td>
<td>(3.35 \times 10^{5} \text{ J/kg}) ([3, 4])</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters used in the grain growth modeling</th>
<th></th>
</tr>
</thead>
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<tr>
<td>Surface free energy ((\gamma)) of quartz</td>
<td>0.4 J/m(^2) ([5])</td>
</tr>
<tr>
<td>Molar volume ((V)) of quartz</td>
<td>(2.269 \times 10^{-5} \text{ m}^3/\text{mol}) ([6])</td>
</tr>
<tr>
<td>Grain-boundary width ((\delta))</td>
<td>(1 \times 10^{-9} \text{ m})</td>
</tr>
</tbody>
</table>

| Sample        | Distance* (m) | N  | Grain size (µm) | –1 σ/+1 σ | 2nd-phases (vol.%)
|---------------|---------------|----|----------------|-----------|----------------------
| 120322-02     | 1             | 208| 59.0           | 26.6/4836 | 3.0                  |
| 120322-01     | 27            | 356| 40.9           | 15.4/24.9 | 4.2                  |
| 120322-04     | 100           | 356| 40.3           | 16.0/26.6 | 2.3                  |
| 120322-03     | 191           | 298| 58.6           | 22.6/36.7 | 0.9                  |
| 110331-04     | 250           | 617| 40.3           | 18.7/34.7 | 0.5                  |
| 110331-05     | 400           | 856| 52.9           | 24.7/46.4 | 0.1                  |
| 110331-06     | 508           | 509| 32.9           | 14.1/24.7 | 1.9                  |
| 110331-08     | 683           | 625| 21.0           | 8.0/13.1  | 1.4                  |
| 110331-10     | 717           | 533| 24.2           | 10.3/17.8 | 0.3                  |
| 110331-11     | 750           | 499| 22.3           | 8.4/13.4  | 0.7                  |
| 110331-12     | 850           | 671| 11.8           | 3.7/5.5   | 0.8                  |
| 110331-22     | 925           | 614| 9.0            | 3.0/4.4   | 7.2                  |
| 110331-20     | 967           | 881| 9.2            | 3.2/4.9   | 1.7                  |
| 110331-18     | 1267          | 700| 6.6            | 3.0/5.5   | 1.6                  |
| 110331-17     | 1317          | 475| 8.0            | 3.1/5.0   | 0.2                  |
| 110331-16     | 1333          | 564| 9.2            | 3.5/5.6   | 0.8                  |
| 110331-15     | 1400          | 665| 7.6            | 2.7/4.3   | 0.1                  |

* Distance is measured from the intrusion contact.
### Table 3

Mean R2 values and estimated temperatures by Raman spectral analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Distance* (m)</th>
<th>N</th>
<th>R2 ratio (±1 σ)</th>
<th>$T^{[1]}$ (°C)</th>
<th>$T^{[2]}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110331-02</td>
<td>182</td>
<td>28</td>
<td>0.138±0.073</td>
<td>570±32</td>
<td>578±41</td>
</tr>
<tr>
<td>110331-07</td>
<td>573</td>
<td>28</td>
<td>0.222±0.076</td>
<td>536±34</td>
<td>537±38</td>
</tr>
<tr>
<td>110331-19</td>
<td>1136</td>
<td>13</td>
<td>0.375±0.057</td>
<td>471±25</td>
<td>463±27</td>
</tr>
<tr>
<td>120530-03</td>
<td>1400</td>
<td>26</td>
<td>0.376±0.071</td>
<td>470±32</td>
<td>461±33</td>
</tr>
</tbody>
</table>

* Distance is measured from the intrusion contact.