Kinetics of pressure solution creep in quartz: theoretical considerations

Ichiko Shimizu

Geological Institute, Faculty of Science, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

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Abstract

The kinetics of pressure solution creep are formulated using chemical potentials generalized to nonhydrostatic states. Solving a coupling equation of diffusion and reaction on a spherical quartz grain with diameter \( d \) and grain boundary width \( w \), the flow law of pressure solution creep is derived. As extreme cases, the flow law becomes:

\[
\dot{\varepsilon} = \left( \alpha v_\text{SiO}_2 K D w \right) \left( v_\text{H}_2\text{O} RT d^3 \right)^{-1} \sigma
\]

for the diffusion-controlled case and becomes:

\[
\dot{\varepsilon} = \left( \beta v_\text{SiO}_2 k_+ (v_\text{H}_2\text{O} RT d)^{-1} \right) \sigma
\]

for the reaction-controlled case, where \( \dot{\varepsilon} \) is strain rate, \( \sigma \) is deviatoric stress, \( v \) is the molar volume, \( D \) is the diffusion coefficient through a wet grain boundary, \( K \) is the equilibrium constant, \( k_+ \) is the rate constant of dissolution, \( R \) is the gas constant, \( T \) is temperature, and \( \alpha \) and \( \beta \) are shape factors.

Using the reaction constants determined by Rimstidt and Barnes (1980) and the grain boundary diffusion coefficients estimated by Nakashima (1995), the strain rate of pressure solution creep in metamorphic conditions for quartzose rocks is estimated as \( 10^{-9} \sim 10^{-13}, 10^{-8} \sim 10^{-11}, \) and \( 10^{-7} \sim 10^{-11} \) s\(^{-1} \) at 150, 250, and 350°C, respectively. These values, compared with the duration of regional metamorphism, suggest rapid pressure solution and dewatering in subduction zones followed by fluid-absent metamorphism.

1. Introduction

Pressure solution has been considered as an important process in deformation during metamorphism (Ramsay, 1977) and compaction during diagenesis (Angevine and Turcotte, 1983; James et al., 1986; Tada and Siever, 1989). Microstructures indicating pressure solution such as truncated fossils and mineral grains (McClay, 1977), stylolites (Bathurst, 1971), and discrete crenulation cleavage (Gray, 1979) have been reported in the literature. Dissolved material is transported by diffusion through intergranular channels and redeposited in pores, cracks and pressure shadows (Elliott, 1973; Durney, 1976). Diffusional transfer of silica across a number of grains may be responsible for metamorphic layering and mineral segregation (Robin, 1979; Sawyer and Robin, 1986; Shimizu, 1988a; Potdevin and Caron, 1986). Despite the common observations of pressure solution phenomena in orogenic and metamorphic belts, its causes and mechanisms are not well understood. In the 1970's the nonhydrostatic thermodynamic theory of Gibbs (1906), followed by Kamb (1959, 1961a), was introduced to this subject by Durney (1972) and Paterson (1973), with special attention to diffusional mass transfer in solid–fluid systems. They proposed that the driving force of pressure solution is not “pressure” but differential stress in solids. A similar

Idea was proposed by Elliott (1973), who considered that pressure solution in geology is essentially identical with Coble creep in material sciences (Coble, 1963), but differs in that the former process is greatly enhanced by an aqueous grain-boundary film. This concept of pressure solution is close to the “fluid phase transport” model of Stocker and Ashby (1973). Owing to these works and kinetic considerations by Rutter (1976), the pressure solution and redeposition process was recognized as an important creep mechanism in crustal deformation (McClay, 1977). Nevertheless, the driving force of pressure solution was not clearly established, since the Gibbs–Kamb theory was still in debate (Kumazawa, 1961, 1963; Kamb, 1961b; Ostapenko, 1975). Furthermore, the Gibbs–Kamb theory is not satisfactory for dealing with the kinetics of pressure solution, because the theory postulates a local equilibrium condition between solids and solutes in surrounding fluids; therefore it cannot be used for the reaction-limited kinetics (Paterson, 1973).

Recently, nonequilibrium thermodynamics has been introduced to this subject (Lehner and Bataille, 1984; Lehner, 1990). Shimizu (1992a,b) explained apparent conflicts between pre-existing thermodynamic theories, and formulated the chemical potential ($\mu^+$) for phase transition of a solid at a stressed surface as:

$$\mu^+ = -\tau \nu + f$$

where $\nu$ is the molar volume, $f$ is the molar Helmholtz free energy, $\sigma_{ij}$ is the stress tensor in the solid, $a_i$ is the growth direction vector, $n_i$ is the outward unit normal on the surface. The tensor summation convention is used throughout this paper. If shear stress on the surface is zero, the above is reduced to the Gibbs–Kamb expression:

$$\mu^+ = -\sigma_{ij} n_i a_j$$

where $\sigma_{ij}$ is normal stress (positive for tensional stress). In an isotropic viscous fluid, the stress tensor ($\tilde{\sigma}_{ij}$) is written as:

$$\tilde{\sigma}_{ij} = -p \delta_{ij} + \sigma'_{ij}$$

where $p$ is the hydrostatic pressure component of the stress, $\delta_{ij}$ is Kronecker’s delta, and $\sigma'_{ij}$ is the viscous stress tensor. The chemical potential ($\tilde{\mu}$) for diffusion of a solute in the isotropic viscous fluid is given by Shimizu (1988b) as:

$$\tilde{\mu} = p \tilde{\nu} + \tilde{f}$$

where $\nu$ and $f$ represent the molar volume and molar Helmholtz free energy of the solute, respectively, and $\tilde{\sigma}_{ij}$ is the stress tensor in the viscous fluid.

Pressure solution creep is a coupled problem of diffusion and reaction (Dewers and Ortoleva, 1990). The chemical potentials derived in the nonequilibrium theory enable us to describe both diffusion- and reaction-limited kinetics. In this paper, I will formulate the kinetics of pressure solution using the chemical potentials $\mu^+$ and $\tilde{\mu}$.

2. Driving forces of pressure solution

In terms of nonhydrostatic and nonequilibrium thermodynamics, the driving force of pressure solution is the difference in chemical potentials $\mu^+$ and $\tilde{\mu}$ across solid–fluid boundaries (Shimizu, 1992a, p. 4592). According to Eqs. (1) and (5), the driving force for dissolution of a solid into an isotropic viscous fluid is:

$$X_{\text{dissolution}} = -\left( \tilde{\mu} - \mu^+ \right)$$

$$= -p (\nu - \tilde{\nu}) - \tilde{\tau} \nu + (f - \tilde{f})$$

where $\tilde{\tau}$ represents the effective component of $\tau$:

$$\tilde{\tau} \equiv \tau - (-p)$$

The first term in the right side of Eq. (6) represents the contribution of hydrostatic pressure (Thomson principle), and the second term represents that of effective stress (Poynting principle), and the effects of elastic strain energy (Rieke principle) is included in the last parentheses (Bathurst, 1971; Durney, 1978; Engelder et al., 1981). The hydrostatic pressure effect is dependent on the sign of $\nu - \tilde{\nu}$. The solubilities of most rock-forming minerals exhibit positive dependencies on hydrostatic pressure. As a rare case, the solubility of pyrite decreases with in-
Fig. 1. Elementary processes of pressure solution creep. At the compressive site of the solid surface (A) the stressed solid is dissolved into the intergranular water. The solutes are transported by diffusion through grain boundary and precipitated at the extensional site (B). See detailed discussions in the text.

Increasing hydrostatic pressure (Henley et al., 1986). Nevertheless, McClay and Ellis (1983, 1984) reported that framboidal pyrite dissolved in the shortening direction along cleavage seams. This fact strongly suggests that the main cause of pressure solution is not increase in hydrostatic pressure.

The dissolved materials will be deposited at less stressed portions of the rock. As illustrated in Fig. 1, the solid materials are (1) dissolved at grain-to-grain contacts oriented normal to the compressive direction (A), (2) transported by a diffusive mechanism through the intergranular fluid, and (3) precipitated at sites normal to the extensional direction (B). As a result, grains become flattened parallel to the compressive direction and elongated parallel to the extensional direction. The deformation mechanism causing this grain shape change is called “pressure solution creep” (Green, 1984). The driving forces of the elementary steps are written as:

\[ X_{\text{dissolution}} = - (\tilde{\mu}_A - \mu_+^A) \]  
\[ X_{\text{diffusion}} = - (\tilde{\mu}_B - \tilde{\mu}_A) \]  
\[ X_{\text{precipitation}} = - (\mu_+^B - \tilde{\mu}_B) \]

The driving force of the whole process is:

\[ X_{\text{all}} = - \Delta \mu^+; \quad \Delta \mu^+ = - \Delta (\tau v) + \Delta f \]  

where \( \Delta \) represents the difference between portions \( A \) and \( B \). Note that the driving force is the chemical potential gradient of the solid alone (Robin, 1978). Hydrostatic pressure does not affect the all-over process of dissolution–diffusion–precipitation; therefore it is excluded from possible causes of pressure solution creep. In this regard, the term “pressure solution” is misleading and some authors prefer to use “solution transfer” creep. The last term in Eq. (11) splits into two parts (Shimizu, 1992a):

\[ \Delta \mu^+ = - (\tau v) + \Delta f^{\text{elas}} + \Delta f^{\text{plas}} \]  

where \( f^{\text{elas}} \) is elastic strain energy due to instantaneous state of stress, and \( f^{\text{plas}} \) is plastic strain energy stored in dislocations, twin boundaries and point defects.

Let us evaluate these three terms in the hypothetical metamorphic condition described below: (1) differential stress \( \Delta \sigma \) is 100 MPa; (2) total strain by intracrystalline plasticity \( \varepsilon_{ij}^{\text{plas}} \) is about 100%.

The molar volume of quartz under atmospheric pressure is 22.688 cm\(^3\) (Robie et al., 1978) and its elastic compliance \( S_{ijkl} \) is about 10\(^{-5}\) MPa\(^{-1}\) (Clark, 1966). Using these values, the first term is estimated as:

\[ - (\tau v) = \Delta \sigma v = 2000 \text{ J mol}^{-1} \]  

This term reflects the anisotropy of the stress tensor, while the variations in strain energy terms reflect the heterogeneity in stress fields (Green, 1984). The range of variation in elastic strain energy is estimated as:

\[ \Delta f^{\text{elas}} < f^{\text{elas}} = \frac{1}{2} S_{ijkl} \sigma_{ij} \sigma_{kl} v = 1 \text{ J mol}^{-1} \]  

where \( \sigma_{ij} \) is the deviatoric stress of the solid defined as:

\[ \sigma_{ij} = \sigma_{ij} - \sigma; \quad \sigma = \sigma_{kk}/3 \]  

During plastic deformation, probably more than 90% of the external work will be dissipated. Hence the third term is estimated as:

\[ \Delta f^{\text{plas}} < f^{\text{plas}} = \sigma_{ij} \varepsilon_{ij}^{\text{plas}} v \times 0.1 \approx 200 \text{ J mol}^{-1} \]
Comparing Eqs. (13), (14) and (16), it is clear that $\Delta(\tau\nu)$ is dominant in Eq. (12). The calculation by Wintsch and Dunning (1985) also indicates that the increase in solubility due to plastic strain energy is small, even if the dislocation density of quartz is very high ($=10^{11}$ cm$^{-2}$).

Dissolution occurring at the solid surfaces facing pores and cracks is called “free-face dissolution” (Paterson, 1973; Engelder, 1982). Because of mechanical equilibria at a solid–fluid interface ($\tau = -p$), the effective stress term in Eq. (6) is diminished. Therefore the driving force of free-face dissolution is hydrostatic pressure or strain energy. Dissolution driven by strain energy, named “strain solution” (Wintsch and Dunning, 1985) or “strain-induced preferential dissolution” (Bosworth, 1981), may take place in the early stage of diagenesis, where point contacts of detrital grains may be load-supporting; hence stress and strain fields are very heterogeneous because of stress concentration (as is illustrated photoelastically by Gallagher et al., 1974). Some authors consider that pressure solution proceeds by free-face dissolution at the margin of grain-to-grain contacts causing “undercutting” or “necking” (Ostapenko, 1968; see also the explanation by Weyl, 1959). Ostapenko (1968, 1975) suggested the importance of crushing and plastic deformation in enhancing fluid percolation and increasing the solubility at the contact zones. Pharr and Ashby (1983) also emphasized the role of plastic deformation, and presented the “coupled plasticity-and-dissolution” model. A similar concept named “plastic deformation plus free-face pressure solution” was proposed by Tada and Siever (1986) in their dissolution experiments, based on the change in creep rate and the development of grooves and dislocation pits around the contact of a knife-edge silica and a halite plate. Behaviour of this type was recently reported by Spiers and Brzesowski (1993) in compaction experiments on wet NaCl aggregates. On the contrary, in the halite–halite dissolution experiment performed by Hickman and Evans (1991), “neck growth” (sintering) occurred, with no “necking” or “convergence”, whereas in their halite–silica experiment, convergence occurred with no neck growth. The experimental configuration is similar to that of Tada and Siever (1986), but differs in that they used smooth lenses of halite and silica. The contrast between these two experiments is probably due to the difference in the degrees of stress concentration and defect densities at the contact zones. Necked grain contacts have not been reported in compaction experiments on quartz, though crushing and cracking occurred in some low-temperature runs (Schutjens, 1991). According to Milliken (1994), such cataclasis at grain contacts is more prominent and widespread in natural sandstones than previously recognized. She showed by scanned cathodoluminescence imaging techniques that what often appears to be concavo–convex grain contacts produced by pressure solution is actually the result of local cracking and healing.

As a summary of this section, I distinguish two categories of pressure solution, namely “stress solution” at loaded faces and “strain solution” at free faces (Fig. 2). The latter is possibly coupled with plastic deformation and/or crushing at grain contacts. The stress solution is dominant in deformation of low-porosity rocks during metamorphism, where anisotropic dissolution occurs under a differential stress. The strain solution may occur in compaction of sediments during early diagenesis, where inhomogeneous dissolution is caused by stress concentration and subsequent deformation at the grain contacts. However, its ubiquitousness as a compaction mechanism has not been experimentally confirmed. A modified model of strain solution was proposed by Tada et
al. (1987). They considered that grain boundaries have an island structure (see next section for explanation) and that strain solution occurs on a smaller scale within the grain boundaries.

3. Rate-limiting step of pressure solution creep

3.1. The grain boundary structure

The kinetics of stress solution in low-porosity rocks will be greatly influenced by the structure and physical properties of grain boundaries. Two different models of “wet” grain boundaries have been proposed so far (Fig. 3). One is the “viscous film model”, in which contact between solid grains is sustained by intergranular films of structured water (Weyl, 1959; Rutter, 1976, 1983; Hickman and Evans, 1991). Full continuity of stress at the interface between a solid and a water film requires:

$$\bar{\sigma}_{ij} = \sigma_{ij}$$ for the viscous film model \hspace{1cm} (17)

though in general, continuity is required only for the normal and shear stress components, i.e., $$\bar{\sigma}_n = \sigma_n$$ and $$\bar{\sigma}_s = \sigma_s$$. The other is the “island structure model”, in which solid grains have rough surfaces and where contact is sustained by solid “islands” on the surfaces (Bathurst, 1971; Raj and Chyung, 1981; Lehner and Bataille, 1984; Tada et al., 1987; Spiers and Schutjens, 1990; Gratz, 1991). In this model, intergranular water is considered to be a low-viscous fluid unable to sustain shear stress:

$$\bar{\sigma}_{ij} = -p\delta_{ij}$$ for the island structure model \hspace{1cm} (18)

The “loading frame model” used by Paterson (1973) represents the same situation.

The shear stress measurement of aqueous solutions sandwiched by silica sheets (Horn et al., 1989) indicates that a water layer exceeding 2 nm in thickness behaves as a Newtonian fluid and its viscosity is close to that of bulk water. Consequently, the viscous film model is not applicable to water films over 2 nm thick.

3.2. The kinetics of quartz–water reactions under nonhydrostatic stress

Hereafter, we shall restrict our discussion to pressure solution in silica–water systems, but the theory developed in this paper can also be extended to other minerals with more complex reactions, e.g., incongruent pressure solution of Fry (1982). Reaction between quartz and water from 0 to 300°C can be approximated as:

$$\text{SiO}_2(s) + 2\text{H}_2\text{O}(l) \iff \text{H}_4\text{SiO}_4(aq) \hspace{1cm} (19)$$

Based on Eyring’s absolute rate theory, Rimstidt and Barnes (1980) expressed the rate equation of the above reaction in the following form:

$$\frac{d}{dt} a_{\text{H}_4\text{SiO}_4} = -\frac{A\rho_0}{\rho} \gamma_{\text{H}_4\text{SiO}_4} (k_+a_{\text{SiO}_2(aq)} a_{\text{H}_2\text{O}}^2 - k_- a_{\text{H}_4\text{SiO}_4}) \hspace{1cm} (20)$$

where $$a$$ is activity, $$\gamma$$ is activity coefficient, $$k_+$$ and $$k_-$$ are the rate constants for the forward and backward reaction respectively, $$\rho$$ is the fluid density, $$\rho_0$$ is a unit density, and

$$A = \frac{\Omega L_0}{W} \hspace{1cm} (21)$$

is a dimensionless constant representing the relative interfacial area, where $$\Omega$$ is the interfacial area between solid and fluid, $$L_0$$ is a unit length, and $$W$$ is volume of the fluid. For example, the
1. Grain boundary with the width of $w$ is expressed as:

$$ A = \frac{\beta}{w} \quad (22) $$

where $\beta$ is a shape factor representing the roughness of the interfaces ($\beta = 2$ for planar interfaces).

Let us consider the situation in which $p$ in the water equals the mean stress in the solid:

$$ p = -\bar{\sigma} \quad (23) $$

Taking the pure states under hydrostatic pressure $p$ and temperature $T$ as reference states denoted by $\star$, the activity of quartz under nonhydrostatic stress is written as:

$$ a_{SiO_2} = \exp \left( -\frac{\mu_{SiO_2}^+ + \mu_{SiO_2}^-}{RT} \right) \quad (24) $$

where $R$ is the gas constant. Hereafter we shall ignore the effect of tangential shear stress for simplicity, and use the Gibbs–Kamb Equation (3) instead of (1). Neglecting the second-order effects of strain energies, the above then becomes:

$$ a_{SiO_2} = \exp \left( -\frac{\hat{\sigma}_n v_{SiO_2}}{RT} \right) \quad (25) $$

where

$$ \hat{\sigma}_n = \sigma_n - ( -p ) \quad (26) $$

is the effective normal stress. Applying Eq. (5) for the aqueous phase, we have:

$$ a_{H_4SiO_4} = C \quad (27) $$

$$ a_{H_2O} = 1 \quad (28) $$

where $C$ is the molar fraction concentration of the solute. For dilute solutions, we may assume:

$$ \gamma_{H_4SiO_4} = 1 \quad (29) $$

Substituting Eqs. (25), (27) and (28) into Eq. (21), we obtain:

$$ \frac{\partial}{\partial t} C = A \left[ k_+ \exp \left( -\hat{\sigma}_n v_{SiO_2}/RT \right) - k_- C \right] \quad (30) $$

This equation represents the first-order kinetic law, corresponding to the adhesive growth mechanism in the theory of crystal growth (e.g., Sunagawa, 1981).

3.3. One-dimensional diffusion model

Now we shall roughly estimate the rate of the dissolution–diffusion–precipitation process at grain boundaries using a one-dimensional diffusion model as illustrated in Fig. 4. If the stress distribution is not uniform on the solid–water interface, dissolution and precipitation will take place at different locations on the interfaces. As a result initially planar surfaces will become undulated, and the stress distribution will be modified. Here we shall consider the beginning of the reaction–diffusion process when the change of surface morphology is infinitesimally small. The differential equation governing our problem is:

$$ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + F \quad (31) $$

where

$$ F(x,t) = A \left[ k_+ \exp \left( -\hat{\sigma}_n v_{SiO_2}/RT \right) - k_- C \right] \quad (32) $$

is the rate of production of the solute, and $D$ is the diffusion coefficient of the solute through the grain boundary region. For the island structure model, $D$ represents the averaged value of the diffusion coefficient through water channels ($D_w$) over the grain boundary. Phenomenologically $D$ is expressed as:

$$ D = \phi D_w; \quad 0 < \phi < 1 $$

![Fig. 4. The configuration of the one-dimensional diffusion model, and the distribution of normal stress ($\sigma_n$) assumed in Eq. (34). The thickness of the water film (hatched area) between the quartz surfaces is $w$. The distance from maximum to minimum compressive sites is $L$.](image)
Here \( \phi \) is a function of the island/channel ratio, connectivity, and tortuosity of fluid channels. Under the upper-crustal stress conditions of \( \sigma_n \leq 100 \) MPa (Zoback et al., 1993), we may use the approximation:

\[
\exp\left(-\frac{\hat{\sigma}_n\nu_{SiO_2}}{RT}\right) \approx 1 - \frac{\hat{\sigma}_n\nu_{SiO_2}}{RT}
\]

(33)

Giving a stress distribution

\[
\hat{\sigma}_n(x) = \sigma \cos \lambda x; \quad \sigma = \text{const.}, \quad \lambda = \pi/L
\]

(34)

and boundary conditions

\[
C(x,0) = 0
\]

(35)

\[
\frac{\partial}{\partial x}C(0,t) = \frac{\partial}{\partial x}C(L,t) = 0
\]

(36)

we obtain:

\[
C(x,t) = K \left(1 - e^{-Ak_-t}\right) \frac{Ak_+\nu_{SiO_2}\sigma}{(\lambda^2D + Ak_-)RT} \times \left[1 - e^{-\left(\lambda^2D + Ak_-\right)t}\right] \cos \lambda x
\]

(37)

where \( K = k_+/k_- \) is the equilibrium constant. The approximation (33) is used to derive this expression. The first term represents the hydrostatic concentration. The relaxation time \( t_0 \) of Eq. (37) is:

\[
t_0 = \max \left(\frac{1}{Ak_-}, \frac{1}{\lambda^2D + Ak_-}\right) = \frac{1}{Ak_-} = \frac{w}{bk_-}
\]

(38)

Since \( t_0 \) is a very short period (less than a day in hydrothermal conditions), we shall consider steady state diffusion (\( \partial C/\partial t = 0 \)) in the following discussion. The dissolution flux \( J \) on the grain boundary is written as:

\[
J(x,t) = \frac{F(x,t)w}{2v_{H_2O}}
\]

(39)

The growth rate of the quartz grain is thus written as:

\[
u(x,t) = J\nu_{SiO_2}
\]

(40)

Let us now estimate the rate of pressure solution creep using the above result. Considering a quartz grain with diameter \( d \), strain rate is defined as:

\[
\dot{\varepsilon} = \frac{2u}{d}
\]

(41)

The length of a diffusion path from compressive to extensional sites of the grain is about \( \pi d/4 \). Using Eqs. (37)-(41), and putting \( L = \pi d/4 \) and \( t = \infty \), the strain rate in the extensional direction \( (x = 0) \) for the quasi-steady state creep (not truly steady because we neglect the change in grain shape) is solved as:

\[
\dot{\varepsilon} = \left(\frac{\beta\nu_{SiO_2}k_+}{v_{H_2O}RTd}\right)\left(\frac{16Dw}{16Dw + \beta k_- d^2}\right)\sigma
\]

(42)

If the diffusion product \( Dw \) is small enough \( (Dw \ll \beta d^2k_-/16) \), the above reduces to:

\[
\dot{\varepsilon} = \frac{\alpha\nu_{SiO_2}KDw}{v_{H_2O}RTd^3}\sigma
\]

(43)

where \( \alpha = 16 \) is a factor depending on the grain shape and stress distribution. If \( Dw \) is large enough \( (Dw \gg \beta d^2k_-/16) \), it reduces to:

\[
\dot{\varepsilon} = \frac{\beta\nu_{SiO_2}k_+}{v_{H_2O}RTd}\sigma
\]

(44)

Here \( \beta = 2 \) for a grain boundary with smooth solid–water interfaces as assumed in the viscous film model, and \( \beta > 2 \) for rough interfaces as assumed in the island structure model.

3.4. A spherical grain under triaxial stress conditions

In the following, we shall derive the flow law of pressure solution creep under triaxial stress conditions more precisely. Consider a spherical quartz grain with diameter \( d = 2r_1 \) and grain boundary width which is \( w = r_2 - r_1 \) (Fig. 5). Diffusion of the solute in the grain boundary is expressed as:

\[
\frac{\partial C}{\partial t} = D\nabla^2C; \quad r_1 < r < r_2
\]

(45)
Using Eqs. (30), the boundary condition is given as:

$$\mathbf{D} \cdot \nabla \mathbf{C} + \left[ k_+ \exp \left( - \tilde{\sigma} v_{\text{SiO}_2} / RT \right) - k_- C \right] = 0;$$

$$r = r_1, r_2$$

(46)

where \( \mathbf{n} = (n_1, n_2, n_3) \). In this equation, the reaction kinetics are incorporated in the boundary condition rather than the production term. Using spherical coordinates \((r, \theta, \phi)\), the normal stress on the solid surface is given as:

$$\sigma_n = \sigma_1 \sin^2 \theta \cos^2 \phi + \sigma_2 \sin^2 \theta \sin^2 \phi + \sigma_3 \cos^2 \theta$$

(47)

where \( \sigma_1, \sigma_2, \) and \( \sigma_3 \) are the principal stresses.

Assuming a quasi-steady state deformation \((\partial C / \partial t = 0; \) not truly "steady" because we are ignoring the shape change of the grain) and applying the approximation (33), Eq. (45) is analytically solved. Neglecting \( \mathcal{O}(w/d) \ll 1 \), we obtain equations similar to Eqs. (43) and (44). When the diffusion product \( D_w \) is small enough \((D_w \ll \beta k_- d^2/8)\), the strain rate is written as:

$$\dot{\epsilon}(\theta, \phi) = \frac{\alpha' v_{\text{SiO}_2} K D_w}{v_{\text{H}_2\text{O}} RT d^3} \sigma(\theta, \phi)$$

(48)

where the shape factor \( \alpha \) is 48. When \( D_w \) is large enough \((D_w \gg \beta k_- d^2/8)\), it is written as:

$$\dot{\epsilon}(\theta, \phi) = \frac{\beta v_{\text{SiO}_2} k_+}{v_{\text{H}_2\text{O}} RT d} \sigma(\theta, \phi)$$

(49)

where the shape factor \( \beta \) is 2 for the smooth solid–water interface. The orientation-dependent function of stress in the above equations is defined as:

$$\sigma(\theta, \phi) = (\sigma_1 - \sigma_3) P_2^0(\cos \theta)$$

$$+ \frac{1}{2}(\sigma_2 - \sigma_3) P_2^2(\cos \theta) \cos 2\phi$$

(50)

where \( P_n^m(x) \) represents the Legendre functions:

$$P_2^0(x) = \frac{1}{4}(3x^2 - 1)$$

$$P_2^2(x) = \frac{3}{5}(1 - x^2)$$

Eq. (48) represents the flow law of pressure solution creep limited by the size of diffusion coefficient (diffusion-controlled pressure solution creep), whereas Eq. (49) represents that limited by reaction (reaction-controlled pressure solution creep). Noticing that the equilibrium constant \( K \) equals the equilibrium concentration \( C_0 \) under hydrostatic pressure \( p \), Eq. (48) is rewritten as:

$$\dot{\epsilon} = \frac{\alpha' v_{\text{SiO}_2} C_0 D_w}{RT d^3} \sigma$$

(51)

where \( \alpha' = \alpha v_{\text{SiO}_2} / v_{\text{H}_2\text{O}} \). This form of flow law is proposed by Stocker and Ashby (1973) and Rutter (1976). Equations comparable to Eq. (49) are proposed by Raj and Chyung (1981), and Raj (1982). Both Eqs. (48) and (49) represent a linear dependence of strain rate on differential stress. Some experimental works have demonstrated a linear dependence of volumetric strain rate \( \dot{\epsilon} \) on effective stress \( \sigma \) (Raj, 1982; Pharr and Ashby, 1983; Spiers and Schutjens, 1990; Spiers et al., 1990). Although the flow law of compaction creep derived from experimental works is not strictly comparable with this theory, \( \hat{\epsilon} \) and \( \dot{\epsilon} \) in compaction creep roughly correspond to \( \sigma \) and \( \dot{\epsilon} \) in deviatoric creep, respectively (Raj, 1982; Spiers and Schutjens, 1990). At higher stresses \((\sigma \gg 100 \text{ MPa})\) where the approximation (33) is broken, the creep rate depends on stress exponentially rather than linearly (Rutter, 1976; Durney, 1976). The \( d^{-3} \) dependence of strain rate corresponding to the diffusion-controlled creep was observed in compaction experiments by Spiers and Schutjens (1990) and Spiers et al. (1990), and a \( d^{-1} \) dependence corresponding to reaction-controlled creep was observed by Raj and Chyung (1981), and Raj (1982).

In this model, it is postulated that the strain rate of a single crystal grain is the same as that of...
macroscopic deformation. However, if grain boundary sliding is possible in a polycrystalline rock, the length of the diffusion path becomes much shorter, thus the macroscopic creep rate becomes much faster than that in non-slip cases. This point is very important in considering granular flow or superplastic flow accommodated by diffusional mass transfer (Raj and Ashby, 1971; Ashby and Verrall, 1973; Paterson, 1995).

4. Discussion

Under crustal conditions grain size varies from micrometres (e.g., meta-chert) to millimetres (e.g., gneiss), and differential stress varies from tens to hundreds of megapascals (Zoback et al., 1993). The fluid density depends on $P-T$ conditions and fluid compositions. Amongst these parameters, pressure solution creep is most sensitive to

Fig. 6. Strain rate in pressure solution creep of quartz calculated with the rate constants of quartz determined by Rimstidt and Barnes (1980): (a) 150°C; (b) 250°C; (c) 350°C. The horizontal parts of iso-diffusivity lines represent the reaction-controlled regimes, while the oblique parts represent the diffusion-controlled ones. The hatched areas represent the grain boundary diffusion coefficients ($D$) after Nakashima (1995) and the possible ranges of the grain boundary widths ($d = 2–25$ nm). See text for detailed discussion.
the grain size. In Fig. 6 the strain rate is calculated by Eq. (42), with typical grain size \((d = 100 \mu m)\), differential stress \((\sigma = 100 \text{ MPa})\), and fluid density \((\rho = 10^3 \text{ kg/m}^3)\) in high-\(P\) type metamorphism. Smooth grain surfaces \((\beta = 2)\) are postulated here. There remain the ambiguous parameters \(w\) and \(D\).

Crystals growing from aqueous solution have steps and kinks on their surfaces, so that the lower limit of \(w\) is twice the unit cell lengths of quartz (about 5 Å). The upper limit is given by direct observations of wet grain boundaries. Urai et al. (1986), Spiers and Schutjens (1990), and Spiers et al. (1990) found island–channel structures developed in grain-to-grain contact zones (the thickness is 100 nm order) after their compaction experiments of halite, and interpreted them as nonequilibrium grain boundary structures maintained in a stationary state during deformation. This interpretation was, however, questioned by Hickman and Evans (1991) in the point that the island–channel structures might be formed by crack healing. Such continuous fluid-channels were not optically observed in their in situ dissolution experiment, and the width of the wetted contact of halite/silica was measured to be less than 30 nm by the interference method.

Many authors have claimed that water in a narrow grain boundary space will be structured and thus diffusivity in the wet grain boundary will be much lower than the bulk diffusivity, about \(10^{-9} \text{ m}^2\text{s}^{-1}\) at room temperature (Balashov et al., 1983). But the water viscosity measured by Horn et al. (1989) suggests that the thickness of the structured water layer is only about 2 nm and that, without electroviscous effects, mobility in water films over 2 nm thick is not much different from the bulk value. Rutter (1976) estimated the electroviscous effects on diffusivity and obtained \(D \approx 10^{-14} \text{ m}^2\text{s}^{-1}\) at room temperature, postulating the water film thickness to be 2 nm. This value gives the upper limit of \(D\), since the effects of absorption will dominate over the electroviscosity at this thickness (Tada et al., 1987).

Based on recent experimental researches, Nakashima (1995) concluded that the diffusion coefficient of aqueous ions of silica and oxygen through wet grain boundaries is about \(D = 5 \times 10^{-14} \text{ m}^2\text{s}^{-1}\) at room temperature and atmospheric pressure, and that the activation energy of \(D\) is about 15–30 kJ/mol, hence smaller than the activation energy of quartz dissolution (67.4–76.6 kJ/mol) determined by Rimstidt and Barnes (1980). Comparing this diffusion coefficient with the value deduced above, the grain boundary width \(w\) is inferred to be larger than 2 nm. On the other hand, \(w\) is measured to be less than 25 nm by mercury porosimetry (Nakashima, 1995). The extrapolation of the grain boundary diffusion coefficient to higher temperature (see fig. 7 of Nakashima, 1995) indicates that the grain boundary diffusion coefficient is \(10^{-13} \text{–} 15\), \(10^{-12} \text{–} 14\), and \(10^{-11} \text{–} 14 \text{m}^2\text{s}^{-1}\) at 150, 250, and 350°C, respectively. These values are in fairly good agreement with the compaction experiment on quartz under high confining pressure (150 MPa) performed by Gratier and Guiguet (1986), where the diffusion product was determined as \(Dw = 2.5 \times 10^{-19} \text{–} 20 \text{m}^2\text{s}^{-1}\) at 360°C. Using these diffusivities and assuming \(w\) as 2–25 nm, strain rate is plotted in the ranges of \(10^{-9} \text{–} 13\), \(10^{-8} \text{–} 11\) and \(10^{-7} \text{–} 11 \text{s}^{-1}\) at 150, 250 and 350°C, respectively, around the transition from the diffusion- to reaction-controlled creep regimes in Fig. 6. Let us compare the theory with the long-time compaction experiment on quartz sand \((d = 80–100 \mu m)\) performed by Schutjens (1991). In his 350°C experiment, where clear microstructural evidence for pressure solution and overgrowth was observed, the volumetric strain rate was about \(10^{-8} \text{ s}^{-1}\) at the effective stress of 10 MPa. This strain rate is within the prediction of this theory \((10^{-8} \text{–} 12 \text{ s}^{-1})\).

It must be noted that diffusion experiments under atmospheric pressure may not realize the physical properties of grain boundaries at depth. In fact, the strain rates estimated here are very large on geological time scales. For example, the duration of regional metamorphism in each constituent nappe of the Sambagawa belt is about \(10^{15} \text{ s}\) (Takasu and Dallmeyer, 1990). Shimizu (1988a) found that radiolarian fossils in the low-grade part of the Sambagawa belt are 6–15% strained by pressure solution. It follows that the mean strain rate during the metamorphism is about \(10^{-16} \text{ s}^{-1}\). This apparent disagreement between the natural and theoretical creep rates...
suggests that the grain boundaries were fluid-free in most of the metamorphic period. In the field of metamorphic petrology, Thompson (1983) has also suggested the ubiquitousness of “fluid-absent metamorphism”, i.e., apart from a few absorbed monolayers, grain boundaries were not saturated with water and fluid flow was restricted in localized pores and cracks, except for early stages of metamorphism and short pulses of devolatilization events. Intergranular water involved in subducted materials might escape from the grain boundaries very quickly, presumably because wetting angles between silicates and aqueous fluids are non-zero (Watson and Breman, 1987; Horn et al., 1989).

5. Conclusions

(1) Two modes of pressure solution are distinguished. One is “stress solution” at loading-faces driven by differential stress, and the other is “strain solution” at free-faces driven by strain energy. Stress solution is dominant in metamorphic conditions.

(2) Using the chemical potentials defined in nonhydrostatic and nonequilibrium thermodynamics, coupling equations of diffusion and reaction in quartz-water systems under stress are solved to derive the flow laws of pressure solution creep, which are applicable to both the viscous film model and the island-structure model. If the diffusion coefficient in grain boundary water is small enough, the creep rate is proportional to $d^{-3}$ (diffusion-controlled pressure solution creep), whereas if it is large enough, the creep rate is proportional to $d^{-1}$ (reaction-controlled pressure solution creep).

(3) When grain boundaries are saturated with aqueous fluids, the rate of pressure solution creep in a typical metamorphic condition ($\rho = 10^3$ kg/m$^3$, $d = 100$ $\mu$m, $\sigma = 100$ MPa) is estimated as $10^{-9}$ to $10^{-13}$, $10^{-8}$ to $10^{-11}$ and $10^{-7}$ to $10^{-11}$ s$^{-1}$ at 150, 250 and 350°C, respectively. These high strain rates suggest rapid pressure solution and escape of grain boundary fluids in the early stage of metamorphism, followed by fluid-absent metamorphism.

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Appendix—Notation

$a$ activity
$a_i$ growth direction vector
$C$ molar fraction
$D$ grain-boundary diffusion coefficient (m$^2$/s)
$d$ diameter of a grain (m)
$e$ volumetric strain rate
$f$ molar Helmholtz free energy (J/mol)
$J$ dissolution flux (mol m$^{-2}$ s$^{-1}$)
$K$ equilibrium constant
$k_+$ the rate constant of dissolution (s$^{-1}$)
$k_-$ the rate constant of precipitation (s$^{-1}$)
$n_i$ outward unit normal vector
$P$ pressure (N/m$^2$)
$p$ hydrostatic pressure component in a viscous fluid (N/m$^2$)
$R$ the gas constant (J mol$^{-1}$ K$^{-1}$)
$r$ a spherical coordinate
$T$ absolute temperature (K)
$t$ time (s)
$u$ growth rate of a crystal (m/s)
$v$ molar volume (m$^3$/mol)
$W$ volume of fluid (m$^3$)
$w$ grain boundary width (m)
$X$ driving force
$a$ a shape factor
$\beta$ a shape factor representing the roughness of solid surface
$\gamma$ activity coefficient
$\delta_{ij}$ Kronecker’s delta
$\epsilon$ strain rate
$\theta$ a spherical coordinate
$\theta_{ij}$ orientation factor
$\mu^+$ chemical potential for phase transition under stress (J/mol)
$\tilde{\mu}$ chemical potential for diffusion of a solute (J/mol)
$\rho$ density of fluid (kg/m$^3$)
\( \sigma \) deviatoric stress of a solid (N/m\(^2\))
\( \bar{\sigma} \) mean stress of a solid (N/m\(^2\))
\( \sigma_{ij} \) stress tensor of a solid (N/m\(^2\))
\( \sigma_{kk} = \sigma_{11} + \sigma_{22} + \sigma_{33} \) (Einstein summation convention)
\( \bar{\sigma}_{ij} \) deviatoric stress tensor of a solid (N/m\(^2\))
\( \vec{\sigma}_{ij} \) stress tensor of a viscous fluid (N/m\(^2\))
\( \sigma_n \) normal stress on a solid surface (N/m\(^2\))
\( \sigma_s \) shear stress on a solid surface (N/m\(^2\))
\( \tau \) a stress function (N/m\(^2\))
\( \phi \) a spherical coordinate
\( \Omega \) interfacial area between solid and fluid (m\(^2\))

References


