Apparent activation energy and rate-limiting process estimation from natural shale deformed by pressure solution in shallow subduction zone

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ABSTRACT

Pressure solution is one of the main deformation mechanisms for lithify and stress release in the rocks from shallow subduction zones. We observed temperature-dependent pressure solution development in naturally deformed shale in Shimanto accretionary complex in southwest Japan. The pressure solution develops with shear-dominated or co-axial-dominated deformation. We evaluated apparent activation energy by applying the constitutive equation of pressure solution creep to the temperature-dependent relations. The activation energy of each deformation type was estimated as 18 kJ mol⁻¹ for shear-dominated and 45 kJ mol⁻¹ for co-axial-dominated shale. The energies enable us to speculate rate-limiting processes of pressure solution i.e. dissolution, diffusion and precipitation, by comparing the energies obtained in this study with energies had been measured by experiments. The lower activation energy estimated here was similar with that of diffusion. The similarity indicates that possible rate-limiting process of shale deformation in shallow subduction zone would be diffusion. The difference of energy between deformation types can be explained by distinctive grain boundary structure.

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1. Introduction

While accumulated elastic strain energy in rocks is mainly released by seismic slip, a significant part of the convergence in accretionary prisms of subduction zones is accommodated by aseismic slip. One of the most important mechanisms for aseismic slip is ductile deformation by pressure solution (e.g. Rutter and Mainprice, 1979; Rutter, 1983; Gratier et al., 2003; Tanaka et al., 2007). Pressure solution deformation can be decomposed in three successive basic processes: dissolution, mass transfer and precipitation (Rutter, 1976; Spiers et al., 1990; Shimizu, 1995). As these processes operate sequentially, the total strain rate is controlled by the slowest of these processes, called “rate-limiting process”.

Most flow laws derived from experiments can be expressed, independently of the precise deformation process involved, as \( \text{de/dt} = a \cdot \exp(-H/RT) \), where \( e \) is the strain, \( t \) is the duration, \( a \) is a constant, \( H \) is an activation energy, \( R \) is the gas constant and \( T \) is the temperature (K). Deformation by pressure solution includes the temperature-dependent flow law and activation energies have been reported from experiments (Rutter, 1983; Gratier and Jenatton, 1984; Schutjents, 1991; Dewers and Hajash, 1995; Niemeijer et al., 2002; Tenthorey and Cox, 2006). The activation energy enables us to estimate rate-limiting process through deformation by comparing with energies, which had been measured by experiments of dissolution, diffusion and precipitation.

Temperature-dependent development of pressure solution has also been suggested in natural rock deformation by investigating the relationship between deformation of sedimentary rock and its burial depth (Tada and Siever, 1989). Recently, we quantitatively evaluated it from natural shales of the Shimanto accretionary complex (Kawabata et al., 2007). We quantified intensity of the deformation using pressure solution seams (PSS) and obtained a positive correlation between the intensity and paleotemperature measured by vitrinite reflectance. After Kawabata et al. (2007), we considered the temperature and duration of PSS development to estimate its corresponding activation energy. Accretion and thermal history of Shimanto accretionary complex have been well studied and was proposed to be a simple thermal structure, which was made mainly by a heating event rather than by the accretion history of sediments (e.g. Sakaguchi, 1999). The simple thermal history allows us to understand the timing and duration of PSS developed in the Shimanto accretionary complex. In this paper we performed an extending study of Kawabata et al. (2007) by compiling the thermal structure and to apply creep law to PSS development for the estimation of activation energies in natural...
shale. Finally, we interpret the phenomenological laws in terms of microscopic mechanisms and discuss the possible rate-limiting process of pressure solution creep.

2. Geologic outline and sampling

The Shimanto belt is an ancient accretionary complex distributed on the Pacific side of southwest Japan, subparallel to the modern Nankai Trough and the Ryukyu Trench (Fig. 1). The belt is divided into two subbelts by the Aki Tectonic Line (ATL), a major thrust separating cretaceous sedimentary rocks in the northern subbelt from tertiary ones in the southern subbelt (Fig. 1) (Taira et al., 1980). The sedimentary sequence within the subbelts trend generally ENE–WSW and dip steeply to the north. The subbelts include coherent, tectonic mélange units and slope-basin deposits. The coherent units consist of trench turbidite and the mélange units consist of a mixture of trench turbidite, hemipelagic, pelagic sediments and basalt.

All of the samples used here are composed of shales collected in the eastern coastal area of Shikoku (Fig. 1). In this study, we used two distinct kinds of shale samples, characterized by very different deformation modes: either highly sheared samples from mélange rocks or samples from co-axial-dominated coherent units. In the following the deformation modes are referred as type S for shear-dominated samples from the tectonic mélange and as type C for co-axial dominated samples from the slope-basin deposits.

3. Microstructural observation and analysis of the shales

Microstructural observations indicate that shales are composed of quartz and feldspar grains, clay minerals and small amount of opaque minerals (Fig. 2a and b). In shale of type S larger grains show asymmetric fringes, on the other hand, fringes in type C shales are more symmetrically developed (Fig. 2a and b), suggesting that deformation types are different also at the microstructural scale. However, such large fringes are rather infrequent in both kinds of samples.

PSS are well developed in shale of both types (Fig. 2a and b). PSS are black seams generated as residue during pressure solution deformation (Fig. 2c). PSS density ($\gamma_{PSS}$), which we defined as the ratio of PSS-occupied area over the total area in a thin section photograph, can be used as indicator of pressure solution intensity (Kawabata et al., 2007). PSS density is up to 50% for type S and 30% for type C.

Grain size distributions within PSS of two types are shown in Fig. 3. A fractal distribution of grain size is apparent for both types with $N = 0.995d^{-1.89}$, where $N$ is the number of grains and $d$ is the diameter of grain, suggesting fracturing during lithification and/or pressure solution deformation in shales.

Pressure solution mechanism is also known to promote under presence of clay minerals in nature and experiments (e.g. Weyl, 1959; Renard et al., 1997). We carried out X-ray diffraction analysis to determine the composition of clay mineral. The analysis was carried out for shale samples under CuKα at 40 kV and 20 mA (Rigaku RINT2100).

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**Fig. 1.** Geological maps of the Shimanto Belt, southeast Shikoku, Japan. Shimanto belt is divided into northern and southern belts by Aki Tectonic Line.
The samples were measured in fixed time (FT) scan mode (0.02° step) at a counting time of 1 s, which were mounted by gentle press on a standard glass sample holder. As clearly shown in Fig. 4, all of the clay mineral peaks (illite and chlorite) are almost the same for all of the samples. Thus, it is clear that mineral compositions are identical for both type S and type C. From these observations we infer that the main difference between type S and type C is only the mode of deformation.

4. Duration of pressure solution and heating in Shimanto accretionary complex

Vitrinite reflectance, which is an indicator of thermal diagenesis, has been extensively used to analyze the geothermal structure of the Shimanto Belt (Underwood, 1992; Sakaguchi, 1996; Mori and Taguchi, 1988; Kitamura et al., 2005). Temperature is empirically determined by mean vitrinite reflectance (Barker and Pawlewicz, 1994). All of previous studies using vitrinite reflectance support the idea that sedimentary rocks of both the northern and the southern Shimanto subbelts have experienced high geothermal gradients (45–90 °C/km) (Ditullio and Byrne, 1990; Sakaguchi, 1996; Ohmori et al., 1997). The distinctive geothermal structure and the high geothermal gradient of the Shimanto belt have been explained by the subduction of the spreading ridge of the Shikoku basin (Hibbard and Karig, 1990). Sakaguchi (1996, 1999) suggested that a heating event overprinted through Shimanto northern subbelt during Tertiary accretion based on vitrinite reflectance data. Ditullio and Byrne (1990) suggested high heating of tertiary sediments by subduction of young and hot crust and interpreted that pressure solution cleavages in shale of Tertiary age would develop in periods of the heating event.

In our study area, PSS density is well correlated with vitrinite reflectance (Fig. 5a and b). In contrast, there is seemingly no correlation between sedimentary age estimated by microfossils (Taira et al., 1980) and PSS density (Fig. 5b). The correlations indicate that pressure solution deformation is enhanced by the temperature rather than age. Consequently, we can assume that pressure solution deformation in shales was generated within the high temperature period and durations of pressure solution deformation would be almost the same among the shale samples. The heating periods of accretionary complex by ridge subduction were estimated as 7–10 million years (Delong et al., 1979). In Section 6, we use 10 my as duration (t) for both types to make Arrhenius type diagram.

5. Equation of pressure solution deformation

Pressure solution is a deformation mechanism involving first the dissolution, then the transport and finally the precipitation of minerals. Various attempts have been made to examine rheology and constitutive laws of pressure solution by experimental and theoretical methods (e.g., Coble, 1963; Rutter, 1976; Spiers et al., 1990; Shimizu, 1995). These studies yielded constitutive equations relating...
the creep rate of pressure solution (%/dt) to several physical and chemical parameters as

\[
de/dt = A \cdot \sigma \cdot V \cdot k \cdot R \cdot T \cdot d^{-1}
\]

for reaction (dissolution or precipitation) limiting creep, and as

\[
de/dt = A \cdot \sigma \cdot V \cdot w \cdot D \cdot S \cdot R \cdot T \cdot d^{-1}
\]

for diffusion limiting creep, where \(de/dt\) represents volumetric strain here (s\(^{-1}\)), \(\sigma\) is the differential stress (in Pa), \(w\) is the width of grain boundary film (in m), \(k\) is the reaction rate constant of dissolution or precipitation on mineral surface, \(D\) is a diffusion coefficient in the film (m\(^2\)s\(^{-1}\)), \(S\) is the solid’s solubility in the grain boundary film, \(V\) is the solid’s molar volume (m\(^3\)mol\(^{-1}\)), \(R\) is the gas constant (JK\(^{-1}\)mol\(^{-1}\)), \(T\) is the temperature (K) and \(d\) is the grain diameter (in m) and \(A\) is a dimensionless numerical coefficient.

In Eqs. (1.1) and (1.2), reaction rate constant \(k\), diffusion coefficient \(D\) and solubility of minerals for water \(S\) depend on temperature as

\[
k = k_0 \cdot \exp \left( \frac{H_k}{RT} \right),
\]

\[
D = D_0 \cdot \exp \left( -\frac{H_D}{RT} \right)
\]

and

\[
S = S_0 \cdot \exp \left( \frac{H_S}{RT} \right),
\]

where \(k_0\), \(D_0\) and \(S_0\) are reference values for \(1/T \to 0\) and \(H_k\), \(H_D\) and \(H_S\) show activation energies of \(k\), \(D\) and \(S\), respectively (e.g. Rimstidt and Barnes, 1980). Thus, for Eq. (1.2), product \((D \cdot S)\) can also be expected to exhibit an Arrhenius dependence on temperature (Spiers et al., 1990) as

\[
D \cdot S = D_0 \cdot S_0 \cdot \exp \left( -\frac{H_D}{RT} \right).
\]

Then, reaction rate-limiting strain rate is written as

\[
de/dt = A \cdot \sigma \cdot V \cdot k_0 \cdot \frac{\exp(-H_k/RT)}{R \cdot d \cdot T}, \tag{2.1}
\]
and diffusion control strain rate is described as
\[
\frac{de}{dt} = \frac{A \cdot \sigma \cdot w \cdot V \cdot D_0 \cdot S_0 \cdot R \cdot d^4}{R \cdot d^4} \cdot \exp\left(-\frac{H_{\text{DS}}}{RT}\right).
\]

(2.2)

6. Pressure solution development rate and its activation energy

Quartz grains in the samples appear to be transformed to elliptic shape during development of pressure solution by dissolution with the forming of PSS (Fig. 2c), which suggests that PSS density (\(\gamma_{\text{PSS}}\)) reflects to existence and shape change of quartz grains. In other words, PSS development and the size, shape and/or amount of quartz are indicators of pressure solution dissolution. From bulk chemical analysis, Kawabata et al. (2007) had shown that the increase of \(\gamma_{\text{PSS}}\) linearly corresponded to the volume decrease of shales and also to the decrease of quartz amount, suggesting that development of \(\gamma_{\text{PSS}}\) directly showed volume decrease and was controlled mainly by the decrease of quartz. These independently derived results from the observation under microscope and from the bulk chemical analysis reach to consequence of that \(\gamma_{\text{PSS}}\) appears to be associated with the amount of quartz grains in both scale of microstructure and bulk sample. On the other hand, \(\gamma_{\text{PSS}}\) developed depending on temperature (Fig. 5), suggesting that the development of \(\gamma_{\text{PSS}}\) could be presented by a thermal activation term such as general creep law (Eqs. (2.1) and (2.2)). These results allow us to make assumptions to apply a creep law of pressure solution as the following.

(i) the \(\gamma_{\text{PSS}}\) is linearly correlated with the total strain (\(e_{\text{total}}\)) of the rock, \(\gamma_{\text{PSS}} = c_0 e_{\text{total}}\) and (ii) the duration of the deformation (\(t\)) is similar in all samples, \(e_{\text{total}} = (de/dt)\). Assuming as above, \(\gamma_{\text{PSS}}\) is represented as,
\[
\frac{\gamma_{\text{PSS}}}{t} = B \cdot \exp\left(-\frac{H}{RT}\right) \frac{1}{T}.
\]

(3)

where \(H = H_k\) for reaction limiting (Eq. (2.1)) and \(H = H_{\text{DS}}\) for diffusion limiting (Eq. (2.2)). B includes respective constants in Eqs. (2.1) and (2.2). Here we assume constant strain rate described as \(\langle\gamma_{\text{PSS}}/t\rangle\), although it is difficult to prove that \(\gamma_{\text{PSS}}\) was incrementally and homogeneously developed in the duration from natural samples.

The Arrhenius type plot of PSS density and paleotemperature of type S and C samples using \(t = 10\) my (Fig. 6) shows a good consistency with Eq. (3). By fitting Eq. (3) to the data, we obtained apparent \(H\) as \(H = 18\) kJ mol\(^{-1}\) for type S, and \(H = 45\) kJ mol\(^{-1}\) for type C. In the next section, we discuss microscopic interpretation of these values of activation energies.

7. Discussion

7.1. Rate-controlling process

Determining the rate-limiting process out of dissolution, diffusion and precipitation, experimentalists use a large range of pressure, strain rate and temperature conditions to assess the correlation between these various parameters and the constitutive flow laws of
the elementary processes. This approach is not possible with natural samples, but we can nevertheless compare the activation energies we derived with literature data.

We summarized in Table 1 previously reported activation energies of quartz dissolution, precipitation as well as diffusion coefficient of oxygen and some ionic species in fluid. We additionally present previously published activation energies of pressure solution deformation estimated by compaction or shear experiment using mainly fluid saturated quartz aggregate under variable conditions (Table 1).

7.1.1. Activity energy of elementary process of pressure solution

Using Eq. (2.1), Eq. (2.2) and the data of Table 1, we can estimate the activation energies of the elementary processes involved in pressure solution. Activation energies \( H_k \) (Eq. (2.1)) for silica reactions in water or alkali solution (dissolution and precipitation) have been directly estimated to be in the range of 60–88 kJ mol\(^{-1}\) (Rimstidt and Barnes, 1980; Criscenti et al., 2006) and 50 kJ mol\(^{-1}\) (Rimstidt and Barnes, 1980), respectively. In the case of diffusion control \( H_{DS} \) (Eq. (2.2)), the activation energy of the diffusion coefficient \( H_d \) must be added to the activation energy of the equilibrium solubility constant \( H_s \). Activation energies for diffusion of ionic species in aqueous solutions and of grain boundary films are reported as approximately to be 15 kJ mol\(^{-1}\) (Nakashima, 1995). Activation energy of quartz solubility was estimated to be approximately 20 kJ mol\(^{-1}\) (Rimstidt and Barnes, 1980). Applying these experimental results to pressure solution constitutive law (Eq. (2.2)), an activation energy \( H_{DS} \) was obtained to be approximately equal to 35 kJ mol\(^{-1}\), which is significantly lower than activation energy for silica reaction (dissolution or precipitation).

7.1.2. Rate-controlling process of experimental and natural pressure solution

Several experimental studies about pressure solution deformation have yielded to the estimation of activation energies (Table 1). From the comparison of their estimated activation energy and theoretical activation energies \( (H_k \text{ and } H_{DG}) \) computed above, these studies inferred the limiting process of pressure solution deformation. Schutjens (1991), Dewers and Hajash (1995) and Niemeijer et al. (2002) showed similar activation energies (60–85 kJ mol\(^{-1}\)), which were done by compaction experiments of fluid saturated quartz sand. Gratier and Jenatten (1984) obtained about 70 kJ mol\(^{-1}\) of activation energy for fluid inclusions deformation by compaction experiment of quartz. Tenthorey and Cox (2006) reported about 70 kJ mol\(^{-1}\) of activation energy for sandstone shearing experiment. These values were similar with the activation energy values of quartz dissolution \( H_k \) (60–88 kJ mol\(^{-1}\)) (Rimstidt and Barnes, 1980), so these pressure solution experiments led to the conclusion that the limiting processes of pressure solution is the quartz dissolution.

In contrast to these experiments yielding high activation energy values, the apparent activation energies we estimated here are much lower, of the order of 18 kJ mol\(^{-1}\) for shear-dominated shale (type S) and 45 kJ mol\(^{-1}\) for compaction-dominated shale (type C). These low values, similar to the energy \( H_{DS} \) approximately equal to 35 kJ mol\(^{-1}\) derived above, suggest that the rate-limiting process of pressure solution in our samples was diffusion. Pressure solution of diffusion rate-limiting had been studied by indenter experiments (e.g. Rutter, 1976; Gratier et al., 2009). Gratier et al. (2009) point out that in many cases, experiments using porous aggregate show dissolution controlled deformation and that using a solid sample resulted in diffusion controlled. From these examples, they proposed that the difference of kinetics of pressure solution in experiments would be related to sample condition such as solid/fluid ratio. Considering PSS in our sample would develop after solidification (non-porous condition), the idea of Gratier et al. (2009) supports the results obtained in this study showing pressure solution of diffusion rate-limiting.

7.2. Shear and compaction pressure solution deformation

While apparent activation energies of two types of shales are both relatively low with respect to experimental values, the activation energy in type S is much lower than that in type C. Observations show any significant mineralogical difference between the two kinds of rocks (Figs. 2.3 and 4). The main microstructural difference between two types lies only within the deformation type. Farver and Yund

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**Table 1**

Activation energies of dissolution, diffusion and pressure solution creep estimated by experiments in previous published papers.

<table>
<thead>
<tr>
<th>Reaction of silica in fluid</th>
<th>Activation energy (kJ/mol)</th>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>Experimental mode</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_k ) (dissolution)</td>
<td>67–88</td>
<td>Quartz</td>
<td>(Some conditions in respective summarized paper)</td>
<td>Dissolution</td>
<td>Criscenti et al. (2006)</td>
<td></td>
</tr>
<tr>
<td>( H_k ) (dissolution)</td>
<td>60–76</td>
<td>Quartz, cristobalite, cristobalite, amorphous silica</td>
<td>0–300</td>
<td>Dissolution</td>
<td>Rimstidt and Barnes (1980)</td>
<td></td>
</tr>
<tr>
<td>( H_k ) (dissolution)</td>
<td>50</td>
<td>Quartz, cristobalite, cristobalite, amorphous silica</td>
<td>0–300</td>
<td>Dissolution</td>
<td>Rimstidt and Barnes (1980)</td>
<td></td>
</tr>
<tr>
<td>( H_k ) (equilibrium constant)</td>
<td>20</td>
<td>Quartz, cristobalite, amorphous silica</td>
<td>0–300</td>
<td>Dissolution</td>
<td>Rimstidt and Barnes (1980)</td>
<td></td>
</tr>
<tr>
<td>Diffusion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( H_d )</td>
<td>113</td>
<td>Quartz aggregate</td>
<td>450–800</td>
<td>100(a)</td>
<td>Oxygen diffusion through grain boundary</td>
<td>Farver and Yund (1991)</td>
</tr>
<tr>
<td>( H_d )</td>
<td>15</td>
<td>Quartz aggregate</td>
<td>450–800</td>
<td>100(a)</td>
<td>Oxygen diffusion through grain boundary</td>
<td>Farver and Yund (1992)</td>
</tr>
<tr>
<td>Pressure solution</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( H_{DS} ) (dissolution)</td>
<td>15–30</td>
<td>(Some materials and conditions in respective reviewed paper)</td>
<td></td>
<td></td>
<td>Diffusion of ionic species in rock</td>
<td>Nakashima (1995)</td>
</tr>
<tr>
<td>( H_{DS} ) (dissolution)</td>
<td>60–75</td>
<td>Quartz sand</td>
<td>150–350, 150–200</td>
<td>20–30(a), 20.7(b)</td>
<td>Compaction creep</td>
<td>Schutjens (1991)</td>
</tr>
<tr>
<td>( H_{DS} ) (dissolution)</td>
<td>73</td>
<td>Quartz sand</td>
<td>400–600, 227–427</td>
<td>300(a), 150–250(b)</td>
<td>Compaction creep</td>
<td>Dewers and Hajash (1995)</td>
</tr>
<tr>
<td>( H_{DS} ) (dissolution)</td>
<td>65–85</td>
<td>Quartz sand</td>
<td>700–900</td>
<td>200(b)</td>
<td>Shearing creep</td>
<td>Niemeijer et al. (2002)</td>
</tr>
<tr>
<td>( H_{DS} ) (dissolution)</td>
<td>70</td>
<td>Sandstone</td>
<td>20–90</td>
<td>0.5–2.2(a)</td>
<td>Compaction creep</td>
<td>Gratier and Jenatten (1984)</td>
</tr>
<tr>
<td>( H_{DS} ) (dissolution)</td>
<td>24</td>
<td>NaCl powder</td>
<td></td>
<td></td>
<td></td>
<td>Tenthorey and Cox (2006)</td>
</tr>
<tr>
<td>(*) Speculated limiting process by comparing previous reported ( H_k ), ( H_d ), and ( H_{DS} ).</td>
<td></td>
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<tr>
<td>(a) Confining pressure.</td>
<td></td>
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<tr>
<td>(b) Pure water pressure.</td>
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</tbody>
</table>
(1992) and Nakashima (1995) indicated that activation energy of grain boundary diffusion coefficient was strongly dependent on grain boundary structure. According to their studies, activation energy of quartz aggregate with non-wetted grain boundary (non-connected grain pores) displayed 113 kJ mol\(^{-1}\) and that with wetted grain boundary (connected grain pores and boundary) was 15 kJ mol\(^{-1}\) under the same pressure–temperature conditions (450–800 °C, 100 MPa). Similarly with Nakashima (1995), the difference we observed here between S- and C-type shales, deformed by shear and co-axial compaction, respectively, could be related to a difference in grain boundary structure. The microstructures in clay-rich natural samples are difficult to document connectivity of pores even under electron microscopic image. Thus it is not so simple as quartz sand used in experiments mentioned above. However, shear deformation could contribute to increase connectivity by asymmetrically deformed grains. Our results suggest that shear deformation generates microstructures where diffusion is enhanced (i.e. smaller activation energy) with respect to co-axial compaction-dominated deformation, due to the development of an extensive network of wetted (connected) grain boundary.

8. Conclusions

Correlating the empirical estimate of pressure solution density to paleotemperatures, we obtained very low apparent activation energies in naturally deformed shale. We propose accordingly that pressure solution is rate-limited rather by the diffusion elementary process than by dissolution or precipitation, in contrast with previous experimental results.

The difference in activation energy between samples deformed by shear (type S: 18 kJ mol\(^{-1}\)) and co-axial compaction (type C: 45 kJ mol\(^{-1}\)) is probably related to differences in the microstructure of the grain boundary developed during deformation. Further study on microscopic processes such as shear deformation promoting grain boundary diffusion is needed to clarify the next question that how complicated natural examples differ from experimental simpler situation and which process contributes to it. These results will be an important milestone for understanding stress releasing processes within active accretionary prism, where pressure solution would be meaningfully responsible for aseismic deformation in subduction zones.

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