A coupled model for intragranular deformation and chemical diffusion

Xin Zhong\textsuperscript{a}; Johannes Vrijmoed\textsuperscript{ab}; Evangelos Moulas\textsuperscript{a}; Lucie Tajčmanová\textsuperscript{a}

\textsuperscript{a} Department of Earth Sciences, ETH Zürich, Switzerland

\textsuperscript{b} Institute für Geologische Wissenschaften, Freie Universität Berlin, Malteserstr. 74-100, 12249 Berlin, Germany

Corresponding author: Xin Zhong (xinzhong0708@gmail.com)

Address: NO E 53.1. Sonneggstrasse 5, Zürich, Switzerland
ABSTRACT

A coupled model for chemical diffusion and mechanical deformation is developed in analogy to the studies of poroelasticity and thermoelasticity. Nondimensionalization of the governing equations yields a controlling dimensionless parameter, the Deborah number, given by the ratio of the characteristic time for pressure relaxation and concentration homogenization. Using the Deborah number two types of plausible chemical zonation are distinguished, i.e. diffusion controlled, and mechanically controlled. The transition between these two types of chemical zonation is determined at the conditions where the Deborah number equals one.

We apply our model to a chemically zoned plagioclase rim in a spherical coordinate frame assuming homogeneous initial pressure. Using thermodynamic data, an experimentally derived diffusion coefficient and a viscous flow law for plagioclase, our numerical simulations show that up to ~0.6 GPa grain-scale pressure variation is generated during the diffusion-deformation process. Due to the mechanical-chemical coupling, the pressure variations maintain the chemical zonation longer than predicted by the classical diffusion model. The fully coupled mechanical-chemical model provides an alternative explanation for the preservation of chemically zoned minerals, and may contribute to a better understanding of metamorphic processes in the deep Earth interior.

Keywords: Chemical diffusion; mechanical deformation; grain-scale pressure variation; feldspar chemical zonation

1. INTRODUCTION

Chemically zoned minerals are important witnesses of the pressure, temperature, time, and deformation (P-T-t-D) history of a rock. Numerical simulations of chemical diffusion processes in chemically zoned minerals have been proven useful in quantifying the duration of metamorphic processes (e.g. Ague and Baxter, 2007). During metamorphism, chemical diffusion and mechanical deformation can occur simultaneously, and in several recent studies are considered as coupled (e.g. Milke et al. 2009; Schmid et al. 2009; Scheidl et al. 2014; Tajčmanová et al. 2015). Assuming a spatially homogeneous pressure, inter or intra-granular chemical diffusion can be conveniently modeled as a single process (Joesten, 1977; Lasaga, 1998). Such classical diffusion models are appropriate if the pressure heterogeneities are dissipated significantly fast by mechanical deformation.
Non-lithostatic pressure arises in rocks that experience external shear deformation (Moulas et al., 2014; Schmalholz and Podladchikov, 2013; Schmid and Podladchikov, 2003) or elastic interactions among different mineral phases (Gillet et al., 1984; Rosenfeld and Chase, 1961; Zhang, 1998; Angel et al., 2015). In fact, kilobar (kbar)-level residual pressure of mineral inclusions in many (ultra)-high-pressure rocks has been measured using laser Raman spectroscopy (e.g. Sobolev et al. 2000; Enami et al. 2007; Korsakov et al. 2009; Ashley et al. 2014). These studies document the preservation of grain-scale pressure variations at geological time scales owing to a slow viscous relaxation rate (Dabrowski et al., 2015). Ignoring such pressure variations in a quantitative analysis of a microstructure can lead to errors in depth estimates that are comparable to the typical thickness of the continental crust. The magnitude of this error then influences our understanding of geodynamic processes. Since the chemical and mechanical processes in rocks are coupled, it is important to have a rigorous quantification approach to understand the interplay between the two processes.

Systematic petrological investigations have documented that there is a strong correlation between grain-scale pressure variations and the chemical, mineralogical, or textural signature (Moulas et al., 2015; Tajčmanová et al., 2014, 2015; Vrijmoed and Podladchikov, 2015; Zhong et al., 2017). In this contribution, we focus on the effect of grain-scale pressure variations on the chemical zonation by extending the work of Tajčmanová et al., (2014, 2015). In their study, the effect of an existing pressure gradient on the distribution of chemical components in a binary system was investigated. They found that pressure variations can drive chemical diffusion, and maintains the compositional zoning under chemical equilibrium. Tajčmanová et al., (2014, 2015) used this model to explain how chemical zoning in a plagioclase rim can be maintained by a spatial variation in pressure at high temperature above 800°C, while classical diffusion predicts complete chemical homogenization within short amount of time (i.e. thousands of years). Their study focused on the consequence of a given heterogeneity in pressure on chemical redistribution but did not consider the potential opposite effect of chemical diffusion on mechanical deformation.

Here, we develop a system of equations that fully couple these two processes – chemical diffusion and mechanical deformation. The approach is analogous to the classical theories of poroelasticity or thermoelasticity, which focus on the coupling of fluid flow to solid deformation, and heat conduction to solid deformation, respectively. Both of them require the mass, momentum, and energy conservation, and constitutive relations to relate different physical state variables (Biot, 1956; Rice and Cleary, 1976; Wang, 2000). We apply the
coupled chemo-mechanical model to the plagioclase case in Tajčmanová et al. (2014, 2015).

We show that during chemical diffusion in a plagioclase grain, a gradient of pressure can be triggered due to the coupling effect and is maintained at geological time scale. This pressure gradient maintains the chemical zonation longer than expected using the classical diffusion model. It emphasizes the significance of mechanical deformation and provides an alternative explanation to the preservation of chemical zoning in metamorphic or magmatic minerals at high temperatures.

2. METHODS

The modeled material is treated as one continuum phase containing two components A and B. The following derivations in a Cartesian coordinate frame are aimed at providing a general strategy. The coordinate frame is subsequently modified to spherical to study the solutions of the coupled system in one-dimensional (radial) profiles. This simplification allows to approximate metamorphic microstructures of a host-inclusion environment. Temperature is considered as spatially constant which is a reasonable assumption for a grain-scale (<mm) over geological time. The model considers isotropic elastic moduli, viscosity and diffusion coefficient.

2.1 Conservation of mass, concentration and momentum

The conservation of the total mass, concentration, and momentum are presented using substantial (material) time derivatives and neglecting the acceleration. Derivations for the following equations can be found in the Appendix.

\[
\frac{dp}{dt} + \rho \frac{\partial \tilde{v}_k}{\partial x_k} = 0 \quad (1)
\]

\[
\rho \frac{dc}{dt} + \frac{\partial \tilde{q}_k}{\partial x_k} = 0 \quad (2)
\]

\[
\frac{\partial \sigma_{ij}}{\partial x_j} = 0 \quad (3)
\]

where \( \rho \) is the density \( \frac{kg}{m^3} \), \( c \) is the concentration (mass fraction) of component A in a binary mixture (from 0 to 1), \( \tilde{v}_k \) is the velocity vector \( \frac{m}{s} \), \( t \) is time in (s), \( \tilde{q}_k \) is the chemical diffusion flux vector \( \frac{kg}{m^3s} \), and \( \sigma_{ij} \) is the Cauchy stress tensor. The notations \( i, j, k \) denote the coordinate indices. The Einstein summation is applied here, i.e. repeated indices imply summation. The diffusion flux \( \tilde{q}_i \) is defined as (see Tajčmanová et al. 2015):
\[
\tilde{q}_i = -\frac{D}{R} D \tilde{c} (1 - \tilde{c}) \frac{M_A M_B}{c_{M_A + (1 - \tilde{c}) M_B}} \partial x_i
\]  
\tag{4}

where \(\tilde{c}\) is the molar fraction, \(D\) is the inter-diffusion coefficient of the binary system \(\frac{m^2}{s}\), \(M_A, M_B\) are the molar masses of the two components A and B \(\frac{kg}{mol}\), \(R\) is the gas constant \(\frac{J}{Kmol}\), and \(T\) is the absolute temperature in Kelvin. The notation \(\xi\) is introduced as the difference between the chemical potential \(\mu\) of the two diffusing components:

\[
\xi = \mu_A - \mu_B
\]  
\tag{5}

which has the unit of \(\frac{J}{kg}\). The driving force for diffusion is given by the gradient of the chemical potential difference \(\frac{\partial \xi}{\partial x_i}\) (Hillert, 2007, page 64; Tajčmanová et al., 2015).

2.2 Momentum balance and viscous rheology

The Stokes equation is formulated below using the force balance (Eq. 3) and applying a linear viscous rheology for shear deformation (e.g. Ranalli 1995). A spatially constant shear viscosity is considered in the model.

\[
\frac{\partial \sigma_{ij}}{\partial x_j} = \frac{\partial \tau_{ij}}{\partial x_j} - \frac{\partial P}{\partial x_i} = 2\eta \frac{\partial \varepsilon'_{ij}}{\partial x_i} - \frac{\partial P}{\partial x_i} = 0
\]  
\tag{6}

where the total stress \(\sigma_{ij}\) is composed of the deviatoric stress tensor \(\tau_{ij}\) and pressure \(P\), which is positive in compression \((\sigma_{ij} = \tau_{ij} - P \delta_{ij})\). The Kronecker delta is denoted as \(\delta_{ij}\). The shear viscosity is \(\eta\) in \((Pa \cdot s)\), and \(\varepsilon'_{ij}\) is the deviatoric strain rate tensor in \((s^{-1})\), which is by definition:

\[
\varepsilon'_{ij} = \varepsilon_{ij} - \varepsilon_{kk} \delta_{ij} \frac{1}{3}
\]  
\tag{7}

where \(\varepsilon_{ij}\) is the total strain rate tensor. The strain rate is concisely expressed using the gradient of velocity as:

\[
\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial \tilde{u}_i}{\partial x_j} + \frac{\partial \tilde{u}_j}{\partial x_i} \right)
\]  
\tag{8}

Inserting Eq. 7, 8 into Eq. 6, the momentum balance equation can be derived in a form containing velocity and pressure:
No viscous volumetric strain rate is considered in our model. The model can be compressible (for $\frac{\partial \bar{v}_k}{\partial x_k} \neq 0$), and the compressibility is introduced in the next section.

2.3 Constitutive relations: Chemical and mechanical coupling

The specific Gibbs energy for a binary system can be expressed using intensive variables (Callen, 1985). Assuming isothermal conditions and using Eq. 5, we get:

$$dg = v dP + \mu_A d c + \mu_B d (1 - c) = v dP + \xi d c$$

(10)

where $g$ is the specific Gibbs energy in ($\frac{1}{kg}$). Legendre transformation is performed to construct the Korzhinskii’s potential $\Omega$ (Korzhinskii 1959):

$$\Omega = g - \xi c$$

(11)

Subsequently, taking the total differential of $\Omega$ and combing $d\Omega$ with Eq. 10 gives:

$$d\Omega = v dP - c d\xi$$

(12)

The Korzhinskii’s potential allows us to use $P$ and $\xi$ as independent state variables to describe the system. From Eq. 12, both $v$ and $c$ are functions of $P$ and $\xi$. Therefore, the total differentials of $v$ and $c$ can be expressed as:

$$dv = \left(\frac{\partial v}{\partial P}\right)_\xi dP + \left(\frac{\partial v}{\partial \xi}\right)_P d\xi$$

(13)

$$dc = \left(\frac{\partial c}{\partial P}\right)_\xi dP + \left(\frac{\partial c}{\partial \xi}\right)_P d\xi$$

(14)

Applying the time derivative and replacing $v$ with $1/\rho$, we get:

$$\frac{1}{\rho} \frac{dP}{dt} = \frac{1}{\rho} \left(\frac{\partial P}{\partial P}\right)_\xi \frac{dP}{dt} + \frac{1}{\rho} \left(\frac{\partial P}{\partial \xi}\right)_P \frac{d\xi}{dt}$$

(15)

$$\rho \frac{dc}{dt} = \rho \left(\frac{\partial c}{\partial P}\right)_\xi \frac{dP}{dt} + \rho \left(\frac{\partial c}{\partial \xi}\right)_P \frac{d\xi}{dt}$$

(16)

Since the order of the differentiation for the energy function $\Omega$ with respect to $P$ and $\xi$ is irrelevant in eq. 12 (exact differential), we can derive the following Maxwell relation for the constitutive coefficients:
In Eq. 17, it is clear that the cross coefficients in Eq. 15, 16 are equal: $\rho \left( \frac{\partial c}{\partial p} \right)_{\xi} = \frac{1}{\rho} \left( \frac{\partial p}{\partial \xi} \right)_{p}$. This equality derived from the construction of Korzhinskii’s potential $\Omega$ provides a symmetry in the matrix of constitutive coefficients in this chemo-mechanical model, which is analogous to the classical thermoelastic and poroelastic theories (Wang, 2000 chapter 1). Combining Eq. 15, 16 with the conservation of mass and concentration Eq. 1, 2, we end up with the following relations:

\[
\begin{align*}
- \frac{\partial \bar{v}_k}{\partial x} &= a_{11} \frac{dp}{dt} + a_{12} \frac{d\xi}{dt} \\
- \frac{\partial \bar{a}_k}{\partial x} &= a_{21} \frac{dp}{dt} + a_{22} \frac{d\xi}{dt}
\end{align*}
\]

The constitutive coefficients $a_{mn}$ are used in replacement of the partial derivatives in Eq. 15, 16.

\[
\begin{align*}
a_{11} &= \frac{1}{\rho} \left( \frac{\partial p}{\partial \xi} \right)_{p} \\
a_{22} &= \rho \left( \frac{\partial c}{\partial \xi} \right)_{p} \\
a_{12} &= \frac{1}{\rho} \left( \frac{\partial \xi}{\partial \xi} \right)_{p} \\
a_{21} &= \rho \left( \frac{\partial c}{\partial p} \right)_{\xi}
\end{align*}
\]

The first coefficient $a_{11}$ is the compressibility, which relates volumetric strain rate with pressure change. The last coefficient $a_{22}$ relates the diffusion flux to the change of chemical potential difference. The cross-coefficient $a_{12}$ (or equally $a_{21}$) couples the changes of pressure and chemical potential difference to the diffusion flux and mechanical volumetric strain rate, respectively. The magnitude of the coupling effect is sensitive to the magnitude of the cross coefficient. The parameter $\left( \frac{\partial p}{\partial \xi} \right)_{p} = \rho \left( \frac{\partial c}{\partial \xi} \right)_{p}$ couples the pressure and the concentration change under fixed chemical potential difference buffered by the surrounding environment. The value of $\left( \frac{\partial p}{\partial c} \right)_{\xi}$ for common metamorphic minerals are plotted in Fig. 1. Depending on the mineral, the absolute value of $\left( \frac{\partial p}{\partial c} \right)_{\xi}$ ranges from 0 to 70 GPa which
indicates that the coupling effect may be significant in common metamorphic minerals. A rough estimate can be made using calculated \( \left( \frac{\partial P}{\partial c} \right)_\xi \) values in Fig. 1: e.g. 0.01 concentration change in a mineral with the property \( \left( \frac{\partial P}{\partial c} \right)_\xi = 50 \text{GPa} \) (orthopyroxene) would correspond to a 0.5 GPa pressure change.

### 2.4 Model formulation in a spherical coordinate frame

The two constitutive relations Eq. 18, 19, and momentum balance Eq. 9 form a system of five equations containing five unknowns \( \xi, P, \) and \( \bar{v}_r \) in 3D. In order to investigate the coupling effect in a simplified form, we transform the governing equations to a 1D spherical coordinate system (see Appendix for details).

This leads to a system of three equations and three unknowns \( \xi, P, \) and \( v_r \):

\[
\frac{4}{3} \eta \left( \frac{\partial^2 v_r}{\partial r^2} + \frac{2 \partial v_r}{r \partial r} - 2 \frac{v_r}{r^2} \right) - \frac{\partial P}{\partial r} = 0
\]  

\[
a_{11} \frac{dp}{dt} + a_{12} \frac{d\xi}{dt} = -1 \frac{\partial^2 v_r}{\partial r^2}
\]  

\[
a_{21} \frac{dp}{dt} + a_{22} \frac{d\xi}{dt} = \frac{D}{R r^2} \frac{\partial}{\partial r} \left[ \rho r^2 \bar{v} (1-\bar{c}) M_A M_B \partial \xi \right]
\]

where the definition of diffusive flux Eq. 4 is used in one of the constitutive relations (Eq. 19), \( r \) is the radial coordinate, and \( v_r \) is the radial velocity. The \( a \) coefficients, \( \bar{c} \) (similarly \( \bar{\xi} \)) and \( \rho \) are obtained from equilibrium thermodynamic calculations based on the independent variables \( \xi \) and \( P \).

### 2.5 Nondimensionalization: Relaxation time for diffusion and deformation

Nondimensionalization is performed by choosing the scales as follows: the model length \( L_r \), reference bulk modulus \( K_0 \), reference density \( \rho_0 \), mean diffusion coefficient \( D_0 \), mean viscosity \( \eta_0 \), and energetic term \( \frac{RT}{M_A} \). The physical variables are used as below:

\[
r = \bar{r} L_r
\]

\[
P = \bar{P} K_0
\]
\( t = \frac{t^L}{D_0}; \)

\( \rho = \tilde{\rho}\rho_0; \)

\( D = \tilde{D}D_0 \)

\( \eta = \tilde{\eta}\eta_0 \)

\( \nu_r = \frac{\tilde{\nu}_r D_0}{L_r}; \)

\( \xi = \frac{\tilde{\xi}RT}{M_A} \)

\[ a_{11} = \frac{a_{11}}{K_0} \]

\[ a_{12} = \frac{a_{12} M_A}{RT} \]

\[ a_{21} = \frac{a_{21}}{K_0} \]

\[ a_{22} = \frac{a_{22}}{K_0} \]

where the macrons indicate dimensionless properties. Inserting the above scales into the system of Eq. 24, 25, 26, collecting the dimensionless parameters on one side, we end up with the final dimensionless equations:

\[ De \cdot \frac{4}{3} \tilde{\eta} \left( \frac{\partial^2 \tilde{\nu}_r}{\partial \tilde{r}^2} + \frac{2 \partial \tilde{\nu}_r}{\partial \tilde{r}} \right) - \frac{\partial \tilde{\rho}}{\partial \tilde{r}} = 0 \]

\[ \frac{a_{11}}{K_0} \frac{d \tilde{P}}{d \tilde{t}} + \frac{a_{12}}{RT} \frac{d \tilde{\xi}}{d \tilde{t}} = - \frac{1}{\tilde{r}^2} \frac{\partial \tilde{r}^2 \tilde{\nu}_r}{\partial \tilde{r}} \]

\[ \frac{a_{21}}{K_0} \frac{d \tilde{P}}{d \tilde{t}} + \frac{a_{22}}{RT} \frac{d \tilde{\xi}}{d \tilde{t}} = \frac{\tilde{D}}{\tilde{r}^2} \frac{\partial}{\partial \tilde{r}} \left[ \frac{\tilde{\rho}\tilde{r}^2(1-\tilde{c})}{\tilde{\rho}\tilde{r}^2(1-\tilde{c})} \frac{\partial \tilde{\xi}}{\partial \tilde{r}} \right] \]

where \( De \) is the Deborah number in a coupled diffusion-deformation system. Its original definition is the Maxwell viscoelastic relaxation time (\( \tau_{Max} \)) divided by the observation time (Reiner, 1964). In our coupled model, we choose the characteristic time of diffusion (\( \tau_{Diff} \)) as the observation time:

\[ De = \frac{\tau_{Max}}{\tau_{Diff}} = \frac{\eta_0/K_0}{Lr^2/D_0} = \frac{\eta_0D_0}{Lr^2K_0} \]

In minerals, viscosity and diffusion coefficient have the largest variations and can span orders of magnitude. A mineral with high viscosity and diffusion coefficient implies that the mechanical deformation is slow and chemical diffusion is fast. In this case, a large \( De \) value
is derived because of a longer time needed to mechanically relax a pressure perturbation with respect to a concentration perturbation. Furthermore, a shorter diffusion length (smaller $L_D$) reflects a shorter characteristic diffusion time scale which also yields a larger $De$ value. A more compressible mineral (smaller $K_0$) corresponds to a longer characteristic viscoelastic relaxation time based on $\tau_{Max} = \eta_0/K_0$, and leads to a larger $De$ value.

3. THE NUMERICAL APPROACH

The system of equations 28, 29, 30 is numerically solved using a finite difference code developed in MATLAB®. Three unknowns $\nu_r$, $P$ and $\xi$ are solved for and used to update the other unknowns $c$, $\bar{c}$, $\rho$, $a_{11}$, $a_{12}$, $a_{21}$ and $a_{22}$ by interpolating with the state variables $\xi$ and $P$ from the tabulated thermodynamic properties. As the system of equations is non-linear, we solve for the three unknowns $\nu_r$, $P$ and $\xi$ using a Picard iteration. In a grain-scale model with viscosity corresponding to natural samples, the velocity in a mineral is relatively small and material advection is not treated in the numerical model. The above steps are repeated until the numerical computation completes to a given amount of time.

For demonstration, the physical properties $c$, $\rho$, $a_{11}$, $a_{12}$, $a_{21}$ and $a_{22}$ of a plagioclase solid solution at 800°C are computed as functions of $\xi$ and $P$ in Fig. 2. The physical properties are presented as tabulated values calculated with thermodynamic computational package Perple_X (Connolly, 2009), thermodynamic database from Holland and Powell (2011), and the feldspar solid solution after Newton et al. (1980).

4. RESULTS

4.1 Effect of Deborah number on preserved chemical zoning

As an example, we apply the coupled model to a chemically zoned plagioclase grain. The model simulates a simple case where a plagioclase grain is initially zoned while having a spatially homogeneous pressure. The initial model setup is illustrated as open circles in Fig. 3. The chemical potential difference will consequently vary in space (right panel; Fig. 3). For clearer visualization, the state variables are re-scaled between 0 and 1.

The results of the two end member cases: 1) small $De$, and 2) large $De$, are shown in Fig. 3. The upper panel corresponds to the results computed with a small $De$ number.
Concentration, pressure and chemical potential difference are all flat, indicating the completion of both chemical diffusion and mechanical deformation (Fig. 3). The reason for the pressure profile being flat is that with small De number, the pressure relaxes faster than the chemical zoning. This case corresponds to a commonly considered scenario in metamorphic geology assuming weak minerals (rocks) in which a small perturbation of pressure is rapidly dissipated.

The lower panel in Fig. 3 provides the opposite case with large De number. The result shows that both pressure and concentration vary. The scale for pressure perturbation here is ~0.5GPa. However, the chemical potential difference is flat, indicating that chemical equilibrium is reached before the pressure variation relaxes. Consequently, the chemical variation will be maintained even after the characteristic time of chemical diffusion, and will only be flattened after the characteristic time of pressure relaxation. In this mechanically controlled case relaxation of stress is the dominating process.

A systematic investigation is performed by varying the Deborah number and the dimensionless time of a run scaled by the same characteristic time of diffusion (Fig. 4). The normalized variations of concentration and pressure are color shaded as function of the Deborah number and dimensionless time. The boundary at De=1 separates the behavior of the system into two regimes named here as: diffusion-controlled regime and mechanically-controlled regime.

1) The **diffusion-controlled regime** prevails when De number is smaller than 1, where pressure relaxation is fast and the preserved chemical zonation is controlled by chemical diffusion. In this case, chemical zonation can only be preserved by slow-diffusion kinetics and chemical potential gradients remain, as is commonly assumed for zoned metamorphic minerals. The speed of diffusion is controlled by the diffusion coefficient and the pressure influence is negligible. In this regime, the classical diffusion model is a good approximation to simulate the preserved chemical zonation.

2) The **mechanically-controlled regime** dominates at higher De number, where the pressure variation is slowly relaxing while chemical diffusion is fast, i.e. the chemical potential $\xi$ homogenizes fast. This means that the chemical zoning is maintained by pressure variations at chemical equilibrium (in Tajčmanová et al., 2014, 2015; Vrijmoed and Podladchikov 2015). In this regime, diffusion is not only driven by the concentration gradient,
and the coupling effect needs to be considered. Larger $De$ values will lead to slower relaxation of pressure variations (Fig. 4).

The Deborah number characterizes the competition of the two processes of mechanical deformation and chemical diffusion. Given a mineral with known viscosity and diffusion coefficient, the $De$ number can be easily computed and will allow estimating whether mineral zoning is mechanically or chemically controlled.

### 4.2 An application to plagioclase

As shown in Eq. 31, the Deborah number is a function of viscosity, diffusion coefficient, model length, and bulk modulus. The latter two values can be obtained from observed chemical zoning and equilibrium thermodynamics. The viscosity and diffusion coefficient need to be obtained from experiments and may vary orders of magnitude.

It has been experimentally confirmed that the NaSi-CaAl (albite-anorthite) inter-diffusion coefficient is a strong function of temperature, surrounding fluid pressure (approximated to solid confining pressure in most experiments) and plagioclase composition (Korolyuk and Lepezin, 2009). The viscosity is a strong function of temperature, grain size (diffusion creep), strain rate or stress (dislocation creep), and the amount of water content present in the sample (Bürgmann and Dresen, 2008). We first investigate the effect of the temperature, fluid content, and pressure by fixing other parameters.

We focus on the plagioclase example provided in Tajčmanová et al., (2014) with length ~100 $\mu$m. The strain rate is set to $10^{-15}$ s$^{-1}$, and the anorthite mole fraction is 0.3. An elastic bulk modulus of 60 GPa is calculated from equilibrium thermodynamics for the measured plagioclase composition. Using the experimentally calibrated flow law in Rybacki and Dresen (2000) and the diffusion coefficient data in Korolyuk and Lepezin (2009), we compute the Deborah number for dry/wet feldspar at various confining pressures as shown in Fig. 5. In order to find out the most relevant $De$ number in Fig. 5, the water content and the confining pressure has to be constrained. The water content in feldspar can very largely, ranging between 0.01 wt% to 0.5 wt%, as constrained by high resolution Fourier transform infrared (FTIR) measurements (Johnson et al., 2002; Rybacki and Dresen, 2004; Seaman et al., 2006). The water content generally plays an important role in reducing the effective viscosity of a material (Bürgmann and Dresen, 2008; Karato, 2012). It has been observed that the plagioclase rim is a single crystal with a uniform crystallographic orientation and is
lacking fluid infiltration features or fluid inclusions (Tajčmanová et al. 2011). Therefore, the
dry feldspar rheology is more favorable compared to the wet feldspar rheology. Given the
flow law for dry plagioclase, Newtonian viscosity that is independent of stress and strain rate
is applied in the model. As our modeled plagioclase has a peak pressure of 1.8 GPa, the
estimated $D_e$ number is c. 20 at 800°C as shown by the solid blue curve in Fig. 5. This
suggests that slow relaxation of pressure variation is responsible for the preservation of the
measured plagioclase zoning at the aforementioned physical conditions, in accordance with
the hypothesis proposed by Tajčmanová et al. (2014).

To illustrate the coupling effect, a 1-D numerical calculation is performed using the
previously determined physical parameters (Fig. 6), and starting from a homogeneous
pressure. Similar to the previous model in Fig. 3, the initial setup of this model represents a
chemically zoned plagioclase with anorthite concentration higher on the left, and lower on the
right. The decoupled diffusion is separately computed as comparison by considering only the
concentration gradient as the driving force neglecting the pressure effect (Fig. 6b). The
chemical potential difference has an initial spatial variation that triggers chemical diffusion.
Due to the ongoing diffusion, a pressure variation builds up quickly to $\sim$0.5 GPa at 0.01 kyr
(the blue curve in Fig. 6c). At 0.1 kyr, the concentration of the coupled model remains zoned
with a peak pressure variation up to 0.6 GPa (the red curve in Fig. 6a). On the contrary, the
decoupled model shows a flat profile (the green curve in Fig. 6b). This is because the
pressure variation that is built up at 0.01 kyr due to diffusion helps maintaining the chemical
equilibrium in the coupled model. In other words, the chemical potential difference in the
coupled model is flattened (see green curve in Fig. 6d) while maintaining the pressure
variation and chemical zoning. Such pressure variation only relaxes at the time scale of
mechanical viscoelastic relaxation shown by the yellow and purple curves in Fig. 6c. Finally
at 50 kyr, both chemical diffusion and mechanical deformation cease (the green curve in Fig.
6).

5. DISCUSSION AND IMPLICATION.

5.1 Building up a pressure variation via chemical diffusion

The results of the coupled plagioclase model shown in Fig. 6 support the conclusion in
Tajčmanová et al. (2014, 2015) that the observed chemical zoning in some microstructures
can be alternatively explained by slow mechanical relaxation. In this case, the chemical
zonation is mechanically preserved at the kyr scale, and this time scale will be extended with higher viscosity. Similarly, if an initial pressure gradient is prescribed (with initial homogeneous concentration distribution), a chemical zonation can be generated and preserved as in the shown model. This is due to the coupling of chemical diffusion and mechanical deformation, which have a feedback effect on each other (see also Tajčmanová et al. 2015).

The relaxation time of pressure variation is an important aspect that determines the preservation of chemical zoning if diffusion is fast. Recently, the time scale of pressure relaxation has been studied from a pure mechanical perspective, e.g. in an inclusion-host system. The analytical model of Dabrowski et al. (2015) documents that the host matrix can sustain a pressure gradient over geological time if the inclusion is initially pressurized and the matrix has a non-linear viscosity. The estimated preservation time of the pressure variation may be even longer when the confining pressure and temperature are changed during exhumation or burial that leads to differential expansion or contraction between the inclusion and the host (Angel et al., 2015; Enami et al., 2007b; Zhang, 1998). In a system under general shear, a pressure jump develops across the inclusion-matrix interface with a viscosity contrast (Moulas et al., 2014; Schmid and Podladchikov, 2003). The localized high pressure and shear stress around the inclusion can vary orders of magnitude depending on the applied boundary conditions, inclusion’s geometry and the viscosity contrast. This pressure jump between the inclusion-host interface, and the pressure variation within the surrounding matrix will not relax as long as the boundary conditions are applied. These models suggest a possibility of long-term-maintained pressure variation which could potentially leave their fingerprint on the preserved petrological observations. Recent studies support the fast diffusion rates by constraining the time scale of metamorphic reactions from tens to thousands of years based on geochronological dating or chemical diffusion modeling (Ague and Baxter, 2007; Camacho et al., 2005). Under fast chemical diffusion and reaction, the Deborah number will be elevated, increasing the chance that mechanical deformation has an effect on preserved metamorphic textures. Therefore, it is justified to consider grain-scale pressure variations as an alternative explanation to the classical, fast viscous relaxation, view of the petrology microstructures.
5.2 The effect of grain size and diffusion length

The time scale for chemical diffusion $\tau_{\text{diff}} = L_r^2 / D_0$ depends on the characteristic diffusion length $L_r$, whereas the time scale for Maxwell viscoelastic relaxation $\tau_{\text{Maxwell}} = \eta / K_0$ is mainly controlled by viscosity, which is a function of the mineral grain size in diffusion creep regime. It has been experimentally confirmed that an increase of grain size commonly leads to an increase of viscosity for diffusion creep (Bürgmann and Dresen, 2008). In the plagioclase case study, the applied flow law is experimentally calibrated for a plagioclase aggregate (Rybacki and Dresen, 2000). It needs to be noted that a difference between the viscosity of a single crystal and monocrystalline aggregates may exist. Apart from the viscosity difference, chemical diffusion may not necessarily take place in the entire mineral crystal (e.g. restricted diffusion halo next to an inclusion-host interface). In this case, diffusion length is smaller than the grain size. Bearing these considerations in mind, a plot of the computed chemical and mechanical relaxation time is shown in Fig. 7 at 800°C for a dry feldspar. The relaxation time for chemical diffusion increases monotonically as diffusion length increases. The viscosity increases with increasing grain size up to 100μm, leading to a longer viscoelastic relaxation time. Above 100μm, dislocation creep starts to be dominant and it results in grain-size insensitive viscoelastic relaxation time. The two curves intercept at a critical value of 600μm. A grain size smaller than this critical value indicates a longer viscoelastic relaxation time than diffusion time (mechanically controlled). A grain size larger than this critical value generally correspond to a diffusion-controlled chemical zonation. However, this larger grain size cannot rule out the possibility of a mechanically-controlled chemical zonation because if the diffusion length is significantly smaller than the grain size, it is still possible to reduce the diffusion time lower than the viscoelastic relaxation time. In general, both grain size and diffusion length have to be carefully chosen based on actual observations to correctly investigate if the chemical zonation is mechanically controlled, or diffusion controlled. We used a simple function $\tau_{\text{Maxwell}} = \eta / K_0$ to compute the viscoelastic relaxation time. For a non-Newtonian material in an inclusion-host environment, a more rigorous formulation of the relaxation time derived in Dabrowski et al., (2015) (Eq. 23) should be considered.
5.3 Concluding remarks

Our model consistently couples chemical diffusion and mechanical deformation based on conservation laws and local equilibrium thermodynamics. The major outcome of this study is that the relative dominance of these two processes can be quantified with the Deborah number. A practical example in chemically zoned plagioclase demonstrates that with a large $De$ number, a gradient of pressure can be generated by chemical diffusion and is maintained due to slow mechanical relaxation. Consequently, this pressure gradient holds the chemical zonation longer than predicted from the classical diffusion model. A major implication of this work is that it provides a framework to couple chemical diffusion and mechanical deformation for future studies on the chemo-mechanical processes in metamorphic rocks. This model can be extended to other systems involving more mineral phases (e.g. olivine, garnet, amphibole), model geometry (e.g. cylindrical, or irregular shape), and material’s rheology (e.g. non-Newtonian viscous, or elastoplastic). The current model considers isotropic elastic moduli, and natural crystals are often elastically anisotropic that may cause anisotropic stress under heterogeneous chemical concentration distribution (e.g. Scheidl et al., 2014). Due to the large variation in the magnitude of experimentally derived viscosity and diffusion coefficient of different mineral phases at various physical conditions (e.g. temperature, water fugacity, stress state), the dominant mechanism for the preservation of chemical zonation may potentially vary as characterized by the Deborah number (Eq. 31). This offers more possibilities in modelling chemical diffusion of metamorphic minerals, and more importantly appeals careful considerations on the mechanical environment based on observed microstructures and theoretical modelling of rock deformation.

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Fig. 1. The material property \( \frac{\partial p}{\partial c} \) plotted as a function of composition in binary systems for common metamorphic minerals. The composition 0 in the x coordinate corresponds to the left end member in the legend and composition 1 corresponds to the right end member in the legend. Magnesium and iron (Mg-Fe) end members are chosen for most of the minerals except for the Na-Ca end member for feldspar. The pressure and temperature are set at 1 GPa and 600°C. The solid solutions are: olivine (Sack and Ghiors, 1989); pyroxene (Holland and Powell, 1998); garnet (Holland and Powell, 1998); biotite (Tajčmanová et al., 2009); amphibole (Dale et al., 2005); feldspar (Newton et al., 1980). Computation is performed using the thermodynamic database from Holland and Powell (2011) and thermodynamic software package Perple_X (Connolly, 2009). The end member names are: fosterite (fo); fayalite (fa); ferrosilite (fs); enstatite (en); pyrope (py); almandine (alm); phlogopite (phl); annite (ann); magnesium tremolite (mgtr); iron tremolite (fetr); anorthite (an); albite (ab).
Fig. 2. Coefficients $\rho, c, a_{11}, a_{12}, a_{21}$ and $a_{22}$ computed using Perple_X (Connolly, 2009) by coordinate interpolation with the thermodynamic database of Holland and Powell (2011). Calculation was performed at 800°C using the feldspar solid solution after Newton et al. (1980) involving anorthite (an) and albite (ab) end members. These properties can be scaled as shown in the main text. The unit of $a_{11} = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial P} \right)_\xi$ is in $\left( \frac{1}{\rho_a} \right)$, $a_{12} = a_{21} = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial \xi} \right)_P = \rho \left( \frac{\partial c}{\partial P} \right)_\xi$ are in $\left( \frac{k,a}{T} \right)$, and $a_{22} = \rho \left( \frac{\partial c}{\partial \xi} \right)_P$ is in $\left( \frac{k,a^2}{m^2} \right)$. 
Fig. 3. The profiles of anorthite concentration ($c$), pressure ($\bar{P}$) and chemical potential difference ($\bar{\xi}$) in the plagioclase example for two different regimes (low and high $De$ respectively). The initial conditions are characterized by open circle symbols. (a) With low $De$ number, mechanical deformation occurs rapidly. Both the concentration and pressure are flattened. (b) With large $De$ number, the pressure and concentration gradient relax slower due to the coupling. Only the flat chemical potential difference ($\bar{\xi}$) is achieved. The calculation is performed using the thermodynamic database of Holland and Powell (2011) and the feldspar solid solution model of Newton et al. (1980).
Fig. 4. The preserved dimensionless (a) chemical concentration variation $c$ and (b) pressure variation $\bar{P}$ as function of dimensionless time scaled by characteristic diffusion time and $De$ number. The *mechanically-controlled* and *diffusion-controlled* regimes are separated by the boundary of $De=1$ (thick dashed line), which implies that the characteristic time of Maxwell viscoelastic and diffusive relaxation time are equal. A gradual transition zone occurs around $De=1$. The calculation is performed using plagioclase from the thermodynamic database of Holland and Powell (2011), and the feldspar solid solution model of Newton et al. (1980).
Fig. 5. Computed Deborah number using dry (solid curve) and wet (dashed curve) feldspar at fluid pressure of 1.8 GPa (blue), 0.8 GPa (green), and 0.3 GPa (red). Both dislocation and diffusion creep data is applied in the viscous flow law (Rybacki and Dresen, 2000). The color shading is separated by $De=1$, which is the boundary between the diffusion-controlled (light grey), and the mechanically-controlled (dark grey) regime. The dry feldspar remains mostly within the mechanically-controlled regime except at high temperature $> 850^\circ C$ with 0.3 GPa fluid pressure. This figure is computed using a strain rate of $10^{-15} s^{-1}$, anorthite mole fraction of $0.3$, and grain size of 100 $\mu m$. 
Fig. 6. Computed chemical profiles for a spherical geometry for (a) the coupled concentration, (b) decoupled concentration (classical diffusion without pressure effect), (c) pressure, and (d) chemical potential difference at different time scales. The open circles are the initial conditions at 0 kyr. The concentration profiles at 0.01 kyr (blue) between the coupled and decoupled (classical diffusion) are similar, implying the pressure effect is minimal at this point.
Fig. 7. Dry feldspar chemical and mechanical relaxation time computed as function of grain size (influencing mechanical relaxation time in blue) and diffusion length (influencing chemical relaxation time in red). The diffusion length scale has been chosen to be equal to the grain size. The mechanical relaxation time first increases up to the diffusion-dislocation transition at around 100 µm, and then shows a steady plateau due to the dominant dislocation creep, which is grain size insensitive. The strain rate is $10^{-15} \text{s}^{-1}$ and the temperature is at 800°C.
Appendix

A. Conservation equations

The complete formulations of mass, concentration and momentum balance are:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 \tag{A1}
\]

\[
\frac{\partial \rho c}{\partial t} + \nabla \cdot (\rho c \vec{v}) + \nabla \cdot (\vec{q}) = 0 \tag{A2}
\]

\[
\frac{\partial \rho \vec{v}}{\partial t} + \nabla \cdot (\rho \vec{v} \vec{v}) + \nabla \cdot (\sigma) = 0 \tag{A3}
\]

Expanding the divergence operator to get:

\[
\frac{\partial \rho}{\partial t} + \rho \nabla \cdot \vec{v} + \vec{v} \cdot \nabla \rho = 0 \tag{A4}
\]

\[
\rho \frac{\partial c}{\partial t} + c \frac{\partial \rho}{\partial t} + \rho c \nabla \cdot \vec{v} + \rho \vec{v} \cdot \nabla c + c \vec{v} \cdot \nabla \rho + \nabla \cdot (\vec{q}) = 0 \tag{A5}
\]

\[
\rho \frac{\partial \vec{v}}{\partial t} + \vec{v} \frac{\partial \rho}{\partial t} + 2 \rho \vec{v} \cdot \nabla \vec{v} + \vec{v} \cdot \nabla \rho + \nabla \cdot (\sigma) = 0 \tag{A6}
\]

Regrouping the equations:

\[
\left[ \frac{\partial \rho}{\partial t} + \vec{v} \cdot \nabla \rho \right] + \rho \nabla \cdot \vec{v} = 0 \tag{A7}
\]

\[
\rho \left[ \frac{\partial c}{\partial t} + \vec{v} \cdot \nabla c \right] + c \left[ \frac{\partial \rho}{\partial t} + \vec{v} \cdot \nabla \rho + \rho \nabla \cdot \vec{v} \right] + \nabla \cdot (\vec{q}) = 0 \tag{A8}
\]

\[
\rho \left[ \frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v} \right] + \vec{v} \left[ \frac{\partial \rho}{\partial t} + \vec{v} \cdot \nabla \rho + \rho \cdot \nabla \vec{v} \right] + \nabla \cdot (\sigma) = 0 \tag{A9}
\]

Replacing the partial time derivative with material time derivative, neglect the acceleration and applying the mass conservation to get the final formulations.

\[
\frac{\partial \rho}{\partial t} + \rho \nabla \cdot \vec{v} = 0 \tag{A10}
\]

\[
\rho \frac{\partial c}{\partial t} + \nabla \cdot (\vec{q}) = 0 \tag{A11}
\]

\[
\nabla \cdot (\sigma) = 0 \tag{A12}
\]

B. Spherical coordinate

In radially symmetric spherical coordinates, the divergence and gradient are expressed as:

\[
\nabla \cdot \vec{v} = \frac{1}{r^2} \frac{\partial^2 v_r}{\partial r^2} \tag{A13}
\]
Applying the expression of $\tilde{q}$ from Eq. 4 to get:

$$\nabla \cdot \tilde{q} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ \frac{\partial \rho r^2 c (1-c) M_A M_B}{\partial \xi} \right]$$  \hspace{1cm} (A15)

The momentum balance equation is obtained by first writing the force balance equation of the radial direction in a radially symmetric coordinate frame:

$$\frac{\partial \tau_{rr}}{\partial r} + \frac{3 \tau_{rr}}{r} - \frac{\partial p}{\partial r} = 0$$  \hspace{1cm} (A16)

Then we apply a Newtonian shear viscosity to express the stress deviator to get:

$$\tau_{rr} = 2\eta \varepsilon_{rr}' = 2\eta \left( \varepsilon_{rr} - \frac{1}{3} \nabla \cdot \tilde{v} \right) = 2\eta \left( \frac{\partial \nu_r}{\partial r} - \frac{1}{3} \nabla \cdot \tilde{v} \right) = \frac{4}{3} \eta \left( \frac{\partial \nu_r}{\partial r} - \frac{\nu_r}{r} \right)$$  \hspace{1cm} (A17)

Combining the above equations to write the force balance equation A18 identical to Eq. 24 in the main text:

$$\frac{4}{3} \eta \left( \frac{\partial^2 \nu_r}{\partial r^2} + \frac{2 \partial \nu_r}{r} - \frac{2 \nu_r}{r^2} \right) - \frac{\partial p}{\partial r} = 0$$  \hspace{1cm} (A18)