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A coupled model for intragranular deformation and chemical diffusion

Xin Zhong [a,*], Johannes Vrijmoed [a,b], Evangelos Moulas [a], Lucie Tajčmanová [a]

[a] *Department of Earth Sciences, ETH Zürich, Switzerland*
[b] *Institute für Geologische Wissenschaften, Freie Universität Berlin, Malteserstr. 74-100, 12249 Berlin, Germany*

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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.

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

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[*] Corresponding author at: NO E 53.1. Sonneggstrasse 5, Zürich, Switzerland.
E-mail address: xinzhong0708@gmail.com (X. Zhong).

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was investigated. They found that pressure variations can drive chemical diffusion, and maintain 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 the classical diffusion model 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, 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 study 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 approximation of metamorphic microstructures of a host-inclusion environment. Temperature is considered as spatially constant which is a reasonable assumption for grain-scale distances (<mm) over geological time. The model considers isotropic elastic moduli, viscosity and diffusion coefficients.

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 acceleration. Derivations for the following equations can be found in the Appendix.

$$\frac{d\rho}{dt} + \rho\frac{\partial \vec{v}_k}{\partial x_k} = 0 \tag{1}$$

$$\rho\frac{dc}{dt} + \frac{\partial \vec{q}_k}{\partial x_k} = 0 \tag{2}$$

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0 \tag{3}$$

where ρ is the density ($\frac{\text{kg}}{\text{m}^3}$), c is the concentration (mass fraction) of component A in a binary mixture (from 0 to 1), $\vec{v}_k$ is the velocity vector ($\frac{\text{m}}{\text{s}}$), t is time in (s), $\vec{q}_k$ is the chemical diffusion flux vector ($\frac{\text{kg}}{\text{m}^2\,\text{s}}$), and σ_{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 $\vec{q}_i$ is defined as (see Tajčmanová et al., 2015):

$$\vec{q}_i = -\frac{\rho}{RT} D\tilde{c}(1-\tilde{c})\frac{M_A M_B}{\tilde{c}M_A + (1-\tilde{c})M_B}\frac{\partial \xi}{\partial x_i} \tag{4}$$

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

$$\xi = \mu_\text{A} - \mu_B \tag{5}$$

which has the unit of ($\frac{\text{J}}{\text{kg}}$). 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.

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

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

$$\dot{\varepsilon}'_{ij} = \dot{\varepsilon}_{ij} - \dot{\varepsilon}_{kk}\frac{\delta_{ij}}{3} \tag{7}$$

where $\dot{\varepsilon}_{ij}$ is the total strain rate tensor. The strain rate is concisely expressed using the gradient of velocity as:

$$\dot{\varepsilon}_{ij} = \frac{1}{2}\left(\frac{\partial \vec{v}_i}{\partial x_j} + \frac{\partial \vec{v}_j}{\partial x_i}\right) \tag{8}$$

Inserting Eq. (7), (8) into Eq. (6), the momentum balance equation can be derived in a form containing velocity and pressure:

$$\eta\left[\frac{\partial}{\partial x_j}\left(\frac{\partial \vec{v}_i}{\partial x_j}\right) + \frac{1}{3}\frac{\partial}{\partial x_i}\left(\frac{\partial \vec{v}_k}{\partial x_k}\right)\right] - \frac{\partial P}{\partial x_i} = 0 \tag{9}$$

No viscous volumetric strain rate is considered in our model. The model can be compressible (for $\frac{\partial \vec{v}_k}{\partial x_k} \neq 0$), 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:

$$dg = \text{v}dP + \mu_A dc + \mu_B d(1-c) = \text{v}dP + \xi dc \tag{10}$$

where g is the specific Gibbs energy in ($\frac{\text{J}}{\text{kg}}$), v is the specific volume ($\frac{\text{m}^3}{\text{kg}}$). Legendre transformation is performed to construct the Korzhinskii's potential Ω (Korzhinskii, 1959):

$$\Omega = g - \xi c \tag{11}$$

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

$$d\Omega = \text{v}dP - cd\xi \tag{12}$$

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