Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 196 (2017) 271–288

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Evaluation of the effects of 3D diffusion, crystal geometry, and initial conditions on retrieved time-scales from Fe–Mg zoning in natural oriented orthopyroxene crystals

Daniel Krimer [a,b,*], Fidel Costa [a,b]

[a] *Earth Observatory of Singapore, Nanyang Technological University, Singapore 639798, Singapore*
[b] *Asian School of the Environment, Nanyang Technological University, Singapore 639798, Singapore*

Received 18 December 2015; accepted in revised form 27 September 2016; available online 3 October 2016

Abstract

Volcano petrologists and geochemists increasingly use time-scale determinations of magmatic processes from modeling the chemical zoning patterns in crystals. Most determinations are done using one-dimensional traverses across a two-dimensional crystal section. However, crystals are three-dimensional objects with complex shapes, and diffusion and re-equilibration occurs in multiple dimensions. Given that we can mainly study the crystals in two-dimensional petrographic thin sections, the determined time-scales could be in error if multiple dimensional and geometrical effects are not identified and accounted for. Here we report the results of a numerical study where we investigate the role of multiple dimensions, geometry, and initial conditions of Fe–Mg diffusion in an orthopyroxene crystal with the view towards proper determinations of time scales from modeling natural crystals.

We found that merging diffusion fronts (i.e. diffusion from multiple directions) causes 'additional' diffusion that has the greatest influence close to the crystal's corners (i.e. where two crystal faces meet), and with longer times the affected area widens. We also found that the one-dimensional traverses that can lead to the most accurate calculated time-scales from natural crystals are along the *b*- crystallographic axis on the *ab-plane* when model inputs (concentration and zoning geometry) are taken as measured (rather than inferred from other observations). More specifically, accurate time-scales are obtained if the compositional traverses are highly symmetrical and contain a concentration plateau measured through the crystal center. On the other hand, for two-dimensional models the *ab*- and *ac-planes* are better suited if the initial (pre-diffusion) concentration and zoning geometry inputs are known or can be estimated, although these are a priory unknown, and thus, may be difficult to use in practical terms.

We also found that under certain conditions, a combined one-dimensional and two-dimensional model performed on the *ab-section* can reveal the initial (pre-diffusional) concentration, and thus, offer a unique opportunity to recover lost petrologic information. The influence of three-dimensional diffusion on the one-dimensional two-dimensional model estimates is the combined result of the crystal shape, in particular the presence of facets, and somewhat of the aspect ratio. Our study focuses on Fe–Mg in orthopyroxene, but many of the effects we report are also applicable to other minerals and elements.

Keywords: Volcano; Eruption; Orthopyroxene; Diffusion; Modeling

1. INTRODUCTION

Diffusion in various geological materials has long been the interest of scientists (e.g. Bowen, 1921; Sutton, 1932;

* Corresponding author at: Earth Observatory of Singapore, Nanyang Technological University, Singapore 639798, Singapore.
E-mail address: daniel1@e.ntu.edu.sg (D. Krimer).

http://dx.doi.org/10.1016/j.gca.2016.09.037
0016-7037/

Li and Gregory, 1974). Petrologists and volcanologists have used chemical and thermal diffusion to understand a variety of processes such as crystal growth (e.g. Lasaga, 1982; Hammer, 2008) and dynamic magma mixing (e.g. Fourcade and Allegre, 1981; Morgavi et al., 2013). In the last decade, modeling chemical diffusion in minerals has helped to constrain the timing and duration of certain magmatic process recorded in the volcanic crystal cargo (e.g. Costa et al., 2008 and references therein). In particular, studies dealing with active volcanoes have used this technique as a tool interpreting monitoring signals, which can be potentially used for improved forecasting of volcanic behavior (e.g. Morgan et al., 2006; Kahl et al., 2011; Saunders et al., 2012; Martí et al., 2013; Kilgour et al., 2014).

Modeling the diffusion of concentrations gradients in minerals to retrieve the duration of magma mixing (e.g. Costa and Chakraborty, 2004; Costa et al., 2013), magma residence time (e.g. Allan et al., 2013; Fabbro, 2014), and the timing of other magmatic processes (e.g. Zellmer et al., 1999) is now routinely done. This is partially due to a better understanding of the variables [e.g. composition (C), temperature (T), pressure (P), and redox state (fO_2)] governing diffusion in solid crystalline materials (e.g. Zhang, 2010 and referenced therein), and also the many new experiments aimed at establishing the diffusion coefficients (D) of elements (e.g. Mg, Fe, Mg–Fe, Cr, Ni, REE, etc.) in a wide variety of minerals (e.g. olivine, pyroxenes, garnet, plagioclase, magnetite).

Elements may diffuse at differing rates along different crystallographic axes in many minerals, i.e. diffusion is anisotropic (e.g. Fe–Mg in olivine; Chakraborty, 2010). Several studies have shown that even though compositional traverses are taken along the same crystallographic orientation from crystals presumed to be from the same population, the estimated time-scales show a scatter of up to an order of magnitude (e.g. Kahl et al., 2011; Saunders et al., 2012; Fabbro, 2014). Moreover, many minerals have rather prismatic morphologies and are faceted, and thus, diffusion in three dimensions (3D) may have a significant impact that is difficult to recognize and which is not accounted for in one-dimensional (1D) diffusion models. Most studies have used 1D data, and apart from some preliminary studies on the effect of crystal shape on diffusion (e.g. Ganguly and Tirone, 1999; Watson et al., 2010), a comprehensive evaluation of the effect of 3D geometries is still lacking. Costa et al. (2003) and Costa and Chakraborty (2004) summarily investigated the 2D zoning patterns in plagioclase and diffusion anisotropy in Fe–Mg in olivine. Most recently, Shea et al. (2015) conducted simulations on Fe–Mg diffusion in olivine crystals with various shapes (from sphere to polyhedral) demonstrating that crystal shape (3D) affects the compositional patterns, and that 1D models cannot always retrieve the correct time-scales. Thus, part of the scatter in time-scales determinations from 1D diffusion modeling may be artifacts resulting from the simplification of the real situation of 3D diffusion (Shea et al., 2015).

In this contribution we focus on differences in between 1D and 2D models and how successfully they reproduce the 3D diffusional Fe–Mg pattern in orthopyroxene. We present first the simulation results conducted on the typical orthopyroxene polyhedral shape (i.e. Deer et al., 1992) in order to compare simulated 3D diffusion patterns of Fe–Mg under isotropic (i.e. Ganguly and Tazzoli, 1994) and anisotropic conditions (i.e. Schwandt et al., 1998; Ganguly et al., 2007; Dohmen et al., 2016). We highlight the importance of crystal zoning and shape, the location of modeled 1D traverses and 2D planes, and the advantages and disadvantages of 1D and 2D model applications.

2. COMMONLY USED TERMS AND DEFINITIONS

To avoid confusion we first define commonly used terms in our manuscript. Some of these terms are also illustrated in Figs. 1 and 2.

3D (three-dimensional) or 'real' data: composition distribution obtained by the 3D diffusion simulation. When we extracted 1D or 2D data from the 3D model we also called them 'real' data as we treat them as representing a natural case.

3D or 'real' time (t_{3D}): the duration of the 3D diffusion simulation.

1D (one -dimensional) model/estimate: data from 1D diffusion modeling.

2D (two-dimensional) model/estimate: data from 2D diffusion modeling.

Traverse (tr): array of concentrations in 1D.

Plane (section): a 2D array of concentrations.

Plateau: 1D of 2D array of **constant** concentration that is part of a traverse or plane (Fig. 1d).

Profile: part of a traverse or plane where there is a concentration gradient.

Zoning geometry: the initial configuration of the chemical zoning pattern of a crystal. Here we consider it as a step-function, i.e. the concentration changes instantly with no change in spatial attribute (Fig. 1c). This is the position of the initially highest chemical gradient.

'True Initial' (concentration or zoning geometry): relates to the 3D crystal **before** diffusion and is used for some 1D and 2D models as starting model input (Fig. 1c).

'Apparent initial' (concentration or zoning geometry): that of the 3D crystal **after** diffusion and used for some 1D and 2D models as starting model input. It would correspond to the observed values in natural crystals (Fig. 1c).

Time-scale: the estimated duration of 3D diffusion by 1D or 2D models (t_{1D} or t_{2D}).

Mismatch (ΔC): the difference between the *'real'* concentration dataset and the estimated 1D or 2D concentration dataset calculated at every corresponding data point [$\Delta C = C_{3D} - (C_{1D\ or\ 2D})$].

3. METHODS AND SET UP OF THE MODELS

In this contribution we focus on understanding diffusion profiles along the crystallographic axes of oriented crystals. For a discussion of randomly oriented cuts, see Shea et al. (2015). Below we first describe all models (1D, 2D, and 3D) and the variables such as the crystal shape and size, zoning patterns, diffusing elements and diffusion coefficients, and numerical methods.