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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

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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 priori 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;...
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 processes 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; Marti 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 ([O₂])) 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 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 (t3D): the duration of the 3D diffusion simulation.

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

2D (two-dimensional) model: estimates: 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 (t1D or t2D).

Mismatch (ΔC): the difference between the ‘real’ concentration dataset and the estimated 1D or 2D concentration dataset calculated at every corresponding data point [ΔC = C3D – (C1D 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.
3.1. Model variables

For all models we used a temperature of 1000 °C, a pressure of 10^5 Pa, and oxygen fugacity (\(f_{O_2}\)) at nickel-nickel oxide reaction buffer. These conditions are representative for a magmatic environment where orthopyroxene is common, except for pressure, which has a negligible effect on the diffusion coefficient for crustal pressures due to the small activation volume (e.g. Chakraborty, 2010).

3.1.1. Diffusion coefficients

Diffusion coefficients (\(D\)) in orthopyroxene for Fe–Mg (Ganguly and Tazzoli, 1994) and Mg\(^{2+}\) (Schwandt et al., 1998), and for several trace elements (Cr, La, Nd, Eu, Gd, and Yb Cherniak and Liang, 2007; Ganguly et al., 2007; Sano et al., 2011) have been experimentally determined and their dependence on composition (C) and other variables (T, P, and \(f_{O_2}\)) has also been studied. Ganguly and Tazzoli (1994) proposed virtually isotropic \(D\) for Mg–Fe along the \(b\)-, and \(c\)-axes (e.g. \(D_c = D_b\)), but somewhat lower \(D\) for the \(a\)-axis, whereas Schwandt et al. (1998) found clear anisotropy \(D_b\) being the fastest, and \(D_a > D_b > D_c\). Trace elements also show diffusion anisotropy, with \(D_c\) is the fastest (e.g. Ganguly et al., 2007; Sano et al., 2011). Anisotropic \(D\) has been also proposed based on natural observations (e.g. Tomiya and...
Fig. 2. Flow chart and protocol we use to compare the 2D sections and 1D traverses derived from the 3D simulations with the purely 2D and 1D models. We first construct a 3D crystal with a given initial configuration of zoning geometry and composition (Fig. 1b) and make it diffuse for a given amount of time. Then we select 2D sections and 1D traverses from this 3D crystal (‘real’ data). After, we perform the 2D and 1D models with two main configurations according to the initial concentration and geometries: in the upper panel we use the same initial concentration as in the pre-diffusion 3D crystal (‘true initial’), and in the lower panel we use the values from the 3D crystal after the diffusion (‘apparent initial’) (Fig. 1c). We do quantitative comparisons of concentration using RMSD and the absolute mismatch between the ‘real’ 2D and 1D datasets and the modeled 2D and 1D datasets to determine which models are acceptable or not (see text for more details).
In our models we have also tested the effect of Fe–Mg anisotropy assuming that of Cr as a proxy and the results of Ganguly et al. (2007): \( \frac{D^{\text{Fe–Mg}}_a}{D^{\text{Fe–Mg}}_b} = \frac{t^{\text{Fe–Mg}}_a}{t^{\text{Fe–Mg}}_b} \). This anisotropy matches the recently determined one for Fe–Mg interdiffusion by Dohmen et al. (2016). For \( D^{\text{Fe–Mg}} \) we have used the formulation by Allan et al. (2013) (corrected for self-consistent units):

\[
D^{\text{Fe–Mg}} = \exp \left( -5.44 + 2.6 \times (1 - \text{Mg#}) - \frac{12530}{T} \right) \times \left( \frac{f_{\text{O}_2}(\text{NNO}, T)}{f_{\text{O}_2}(\text{IW}, T)} \right)^{0.5}.
\]  

where \( D^{\text{Fe–Mg}} \) in m\(^2\) s\(^{-1}\) \( T \) is temperature (K). Mg# = Mg/(Mg + Fe) in moles. The \( f_{\text{O}_2} \) at 1000 °C and NNO = 10\(^{-19}\) Pa, and at IW (Iron-wustite reaction buffer) = 10\(^{-15}\) Pa, following Frost (1991). Dohmen et al. (2016) reported a new calibration Fe–Mg diffusion in orthopyroxene (Mg# = 0.91) that is:

\[
D^{\text{Fe–Mg}} = 1.12 \times 10^{-6} \times \exp \left( -\frac{308}{RT} \right) \times \left( f_{\text{O}_2} \right)^{0.05}.
\]  

The diffusion coefficient calculated from Eq. (2) overlaps with that of Allan et al. (2013) for the \( T/f_{\text{O}_2} \) conditions we have used, although they are quite different for lower temperatures and \( f_{\text{O}_2} \).

### 3.1.2. Crystal shape and aspect ratio

Shea et al. (2015) showed that the shape of olivine has a great influence on the details of the equilibration of the Fe–Mg chemical zoning, and leads to differences of a factor of 0.1–25 between the 3D and the calculated 1D time-scales. Orthopyroxene habit depends on the environment and conditions that it forms (e.g. Grégoire et al., 2001; Durant and Fowler, 2002). Deer et al. (1992) identified three different polymorphic types of orthopyroxene: two out of these show orthorhombic symmetry (protoprosthenite and orthoorthosthenite) and one is monoclinic (clinoenstatite). Protoprosthenite is unknown in nature and clinoenstatite occurs below the temperature range typical of volcanic systems (i.e. 850–1200 °C). Orthoorthosthenite is stable below about 1300 °C both in magmatic and metamorphic environments, therefore we adopt the crystallographic and morphological parameters of the orthoorthosthenite. The most common shape in magmatic environment has well developed crystal facets of {100}, {010}, {101}, and {210}, and with an approximate unit cell ratio of 1:1.7:3.5 (a-axis: b-axis: c-axis) (Deer et al., 1992).

The principle crystallographic axes of our model crystal have a length of 103 × 173 × 355 voxels (along x, y, z coordinates, corresponding to the a, b, and c crystallographic axes, respectively), and orthorhombic symmetry where the crystallographic axes meet at acute angles (\( x = \beta = \gamma = 90^\circ \); Fig. 1a). In our model crystals, each voxel is assigned to a 2 × 2 × 2 μm\(^3\) cube. We define the crystal aspect ratio based on the unit cell parameters because polyhedral crystals usually take characteristic forms controlled by the symmetry elements of the crystal and the form and size of the unit cell (Sunagawa, 2005).

### 3.1.3. Investigated zoning patterns

We investigated two different reverse zoning patterns (e.g. higher Mg/Fe in the rim than in the core), with (Pattern A) and without (Pattern B) overgrowth rims (Fig. 1). The initial Fe–Mg concentrations and thus the magnesium number [Mg# = Mg/(Mg + Fe) in moles] for the core–melt or core-overgrowth rim values are 0.60 and 0.75. We used an open boundary condition at the crystal-melt interface (e.g. Costa et al., 2008), and thus the concentration was fixed at the crystal rim considered to be in equilibrium with an infinite melt reservoir.

### 3.1.4. Investigated orientation of traverses and planes

We compared 1D and 2D diffusion models to ‘real’ 3D data along two main types of sections (Fig. 1a & c): (1) through the center of the crystal and parallel to the crystallographic axes (i.e. a, b, and c, parallel to x, y, and z respectively), and these are called the along-axis and on-center sections, and (2) parallel to the crystallographic axes but not slicing through the center and these are called the along-axis and off-center sections. There are endless configurations or possible cuts for this later condition. We sampled the along-axis off-center sections every 6 μm (every third grid step) parallel to the axis in question and on the two 2D sections (Fig. 3). We did not investigate the effect of random sections, as this has been studied in detail by Shea et al. (2015) for olivine. Our purpose was to identify what are the best 1D and 2D orientations so that they can be selectively chosen from a natural dataset.

### 3.2. Numerical methods and diffusion equation

Fick’s 2nd law of diffusion in 3 dimensions takes the form (e.g. Crank, 1975):

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left( D_z \frac{\partial C}{\partial z} \right)
\]  

(3)

where \( C \) is the concentration of element \( i \), and \( D_x, D_y, \) and \( D_z \) are the diffusion coefficients along \( a, b, \) and \( c \) axes, and here we chose the crystallographic axes to be parallel to the spatial directions \( x, y \) and \( z \). The second derivative of the spatial part of the above equation (Eq. (3)), using central approximation of the Taylor Series, for the \( x \) coordinate writes as (e.g. Crank, 1975):

\[
\frac{\partial^2 C}{\partial x^2} = \frac{C_{i+1,j,k} - 2C_{i,j,k} + C_{i-1,j,k}}{\Delta x^2}
\]  

(4.a)

Similarly, the time derivative part is written as:

\[
\frac{\partial C}{\partial t} = \frac{C_{i+1,j,k} - C_{i-1,j,k}}{\Delta t}
\]  

(4.b)

where \( \Delta x \) is the spatial step (here it is 2 μm); \( C \) is the concentration; \( t \) is the temporal matrix coordinate; \( \Delta t \) is the time step, and \( x, y, \) and \( z \) are the numerical matrix coordinates. Combining Eqs. (4.a) and (4.b) and incorporating
the concentration dependence of the diffusion coefficient, the following one-dimensional numerical formulation is obtained regarding the $x$-direction (e.g. Costa et al., 2008):

$$D(x) = \frac{D_{0}}{1 + \left(\frac{x}{x_0}\right)^n}$$
$$C_{t+1}^i = C_{t+1}^i + \Delta t \left( \frac{D_{x+1}^i - D_j^i}{\Delta x} \right) \left( C_{t+1}^i - C_i^t \right)$$
$$+ D_j^i \Delta t \left( C_{t+1}^j - C_i^t \right) + C_i^{t-1}$$

(5)

3.3. Simulation protocol and preparation of the 1D & 2D models

3.3.1. Protocol for obtaining 3D (‘real’) and 1D & 2D models

We used two types of initial zoning patterns in the 3D crystal (Fig. 2) calculated the diffusion models for 14,600 days (i.e. 40 years) with daily time-steps (\( \Delta t = 1 \) day). The time-step was chosen to fulfill the stability criterion (e.g. Press et al., 2007; Costa et al., 2008). Simulations were done at the computing facility at the Earth Observatory of Singapore (NTU). A full simulation of the 3D crystal with the above-parameters took over 3 weeks and resulted in a dataset of approximately 9 GB.

The 3D results are used as ground-truth (‘real’) data. We sliced both the initial (pre-diffusion) and diffused 3D concentration matrix in the desired orientations in 1D (traverse) and 2D (plane). For the 1D and 2D models we used two types of initial concentrations: (1) same as those of the pre-diffusion 3D (‘true initial’), and (2) the highest or lowest concentrations values of the traverse or section after the diffusion in 3D (‘apparent initial’). This was done to account for cases where diffusion has reached the crystal center (see below) and in relation to how times are calculated from natural datasets. In some situations (e.g. short diffusion time or a special geometrical configuration) the ‘apparent initial’ concentration distributions are the same as the ‘true initial’ in the 3D matrix, but they are typically not. After we ran the 1D or 2D diffusion models we compared the concentrations with the 3D simulation for the same times. For zoning geometry in 1D and 2D models we mostly use the ‘true initial’ conditions, except for those models in Section 5.1.2.

3.3.2. 1D and 2D model settings and relation to strategies when modeling natural crystals

The ‘true initial’ concentration can be difficult to constrain in natural samples because of the unknown amount of diffusion that might have occurred. It is common to use the measured maximum and minimum concentrations as a proxy for the initial conditions (e.g. Costa and Chakraborty, 2004; Tomiya and Takahashi, 2005; Morgan et al., 2006; Costa et al., 2008; Kahl et al., 2011; Druitt et al., 2012; Allan et al., 2013). Such concentrations might correspond to the ‘true’ initial or to the ‘apparent’ initial, depending on whether diffusion has reached the crystal core. Insights into the ‘initial’ concentrations may be also estimated using concentrations of a slower diffusing element (e.g. Ca, Al, or REE) than the one we want to model.

The zoning geometry, i.e. the position of the initially largest chemical gradient is also important, because we have an initial step-like concentration distribution that creates the gradient for diffusion to occur. For long diffusion times the inferred ‘apparent initial’ zoning geometry might be different to the ‘true initial’ one. Due to the complex shape of orthopyroxene crystal this occurs in 1D traverses parallel to the c-axis that are on the principal ac-plane into the prism of \{101\} and \{101\} facets (Fig. 1a). Any such traverse shows the ‘apparent initial’ boundary locations that are different from the ‘true initial’ due to the effect of 3D diffusion. Thus, the results of modeling critically depend on the boundary location in the 1D (and 2D) models. For this special case, we also investigated two scenarios: (1) using the ‘true initial’, and (2) using the ‘apparent initial’ zoning geometry (see Section 5.1.2.). This is a significant issue when one models diffusion in natural orthopyroxene, since a slowly diffusing element (e.g. Al or Ca) may indicate the position of the initial zoning geometry (‘true initial’), whereas the fast diffusing Fe–Mg indicates it to be somewhere else (‘apparent initial’ zoning geometry) (e.g. Allan et al., 2013; Saunders et al., 2014).

3.3.3. Comparison of 1D & 2D model results to 3D (‘real’) model data

Comparison of ‘real’ and modeled data can be done using the differences in time-scales and/or in concentration distributions (i.e. profile shapes). Time comparisons are very useful and provide immediate understanding of the multidimensional effects on time-scales (Shea et al., 2015). However, they are only meaningful when the time obtained from modeling in 1D or 2D the datasets extract from the 3D model can be achieved with low overall errors, so that they can be considered good fits. This was not the case for many of our simulations and thus we decided to report the differences between the 3D and 1D and 2D models using two parameters. The first one is to compare the concentration distributions between different models (see Appendix 1 for details) using the root-mean square deviation (RMSD; e.g. Girona and Costa, 2013; Shea et al., 2015):

$$\text{RMSD}_{1D} = \sqrt{\frac{\sum_M (C_{1D}^i - C_{1D}^m)^2}{M}}$$

(6)

$$\text{RMSD}_{2D} = \sqrt{\frac{\sum_M \sum_{j} (C_{2D}^i - C_{2D}^m)^2}{M \times N}}$$

(7)

for 1D traverses [Eq. (6)] and 2D planes [Eq. (7)]; where \( M \) and \( N \) are the number of total cells in the x and y direction respectively, \( i \) and \( j \) are the spatial coordinates of the traverse or plane, \( C_{1D} \) is the ‘real’ concentration obtained from the 3D simulation, and \( C_{1D} \) or \( C_{2D} \) is the concentration obtained by the 1D or 2D model. The RMSD represents the sample standard deviation of the differences between predicted values and observed values over the entire population and gives a measure of how different the 3D versus the 1D or 2D concentration distributions. RMSD is always a positive real number that is \( \geq 1 \), and thus it only carries aggregated information on the measure of the overall deviation, but not on its direction, i.e. whether the model under- or overestimates the actual observation (here the ‘real’ time-scale). To decide if the model under- or overestimates the
actual concentration profile a visual comparison of the ‘real’ and modeled profiles is necessary. An underestimation of the concentration profile, i.e. the model has not reached the ‘real’ values (n. h. $t_{1D/2D} = t_{3D}$) means that the given model would overestimate the time-scale, since to reach (or acceptably approach) the ‘real’ concentration distribution more time is needed than the actual time (i.e. $t_{1D/2D} > t_{3D}$). Consequently, an overestimation of the concentration profile means underestimation of the actual time-scale (see also Appendix 1).

The second parameter we used to give a measure of the goodness of the fits was an arbitrary (but practical) acceptable error of 1% (relative) of the concentration of mismatch, which extends over at least 3 data points (i.e. 6 μm). These conditions are representative of the typical analytical and spatial resolution precision for quantitative electron microprobe analysis of natural crystals. When the residuals ($C_{3D} - C_{1D}$ or 2D) of at least 6 data points (we use 6 data points because of symmetry of rim-to-rim traverses) are larger than the analytical error (1%) we consider the model unacceptable. This is a fairly strict criterion, but since we are not dealing with natural data we consider it reasonable. A perfect model estimate compared to ‘real’ data would result an overall close-to-zero mismatch ($\Delta C \cong 0$; depending on the precision of the numerical model, and assuming no analytical error). The RMSD and mismatch of the concentrations do not necessarily go together: some traverses have a low RMSD, but the model estimate is not acceptable because there are too many data points outside the acceptable error bounds (Fig. 3). On the other hand, an estimate can be acceptable even if the overall RMSD is relatively high, but all the data points are within error.

4. RESULTS

We describe the results of the simulations according to section orientation and number of dimensions. The exact values of the results (i.e. $t_{3D}$, RMSD, $\Delta C$) are valid only for the models with the above-described parameters (i.e. most importantly $T$, $C$, aspect ratio, size, and shape of the crystal). Models were performed with ‘apparent initial’ concentration and ‘true initial’ concentration, and for the zoning geometry we have used ‘true initial’ in all cases. Most of our results are based on a detailed investigation of crystals with reverse zoning (patterns A and B); simulations on normal zoning patterns (C and D) are not discussed here, because the effects are similar (see also more details in Shea et al., 2015 for olivine).

4.1. 1D models along-axes and on-center traverses

These traverses are along the central symmetry axes of the crystal which corresponds to the three main crystallographic axes: $a$, $b$ and $c$ (Fig. 4). We find that using pattern A (e.g. homogenous crystal) and ‘apparent initial’
concentration, models along the b-axis show the best results and the smallest overall RMSD values, followed by models long a-axis (Fig. 4a). Models along the c-axis perform poorly overall, with high RMSD and a large mismatch. With these conditions diffusion anisotropy does not have a major effect. With increasing time the mismatch tends to increase in all cases, although it might still give acceptable fits (Fig. 4a). Using a ‘true initial’ condition gives the same overall results except that the mismatch occurs earlier in time. When we use pattern B (step function of concentration) we find the same results (Fig. 4b): models along b-axis produces better overall matches than those along a-axis, and those along c-axis are the worst. However, the time range for acceptable estimates is about 50% shorter for both a- and b-axis models. The effect of the step-zoning initial pattern crucially depends on the size of the core relatively to the entire crystal, the larger relative size of the core, the smaller the effect. Thus, models along b-axis perform overall better when using apparent initial’ conditions, and the mismatches are much smaller if the crystal is not initially zoned to start with.

Another important observation is that when the concentration plateau is affected by diffusion from another axis (i.e. diffusion reaches the crystal core along another axis) all 1D data are quite different in shape from the 3D ones (e.g. Fig. A1). This is reflected in a significant increase of the RMSD (Fig. 4). At the point of plateau loss, the RMSD still increases and models become unacceptable even along b- or a-axis.

The poor results along the c-axis are due to the effect of the merging diffusion fronts, at the prism [101] & [101] and [101] & [101] facets. This agrees with Shea et al. (2015) for olivine and shows that crystal shape and aspect ratio have a substantial influence on the diffusion patterns along the individual axes. We discuss this issue in detail in Section 5.1.2.

4.2. 1D models along-axes and off-center traverses

There are infinite possible traverses in this category. We have organized our analysis by choosing traverses contained within the principal planes defined by two principal crystallographic axes (Fig. 5). Traverses along the (e.g. parallel to) a-axis on ab- and ac-sections, show similar results: short diffusion times give acceptable fits until the traverse approaches the crystal facet corner, after which RMSD and overall mismatch become much larger (Fig 5a). The exact time where models become unacceptable depends on the distance between the crystal center and the facet corner. Traverses along the b-axis on ab- and bc-sections also show much worse fits when the traverse approaches a crystal corner (Fig. 5b). In general, these traverses perform better than those along a-axis, with acceptable estimates for all investigated times. However, the good performance of b-axis traverses on the bc-section is partly an artifact (indicated by stars on the lines in Fig. 5b) of complete re-equilibration of concentration due to the large amount of diffusion that occurs along the prism of the c-axis approaching the crystal center with time (see Section 5.1.1). This ‘additional’ diffusion results in very low (or zero) concentration gradients and thus virtually no mismatch. We found that the worst performance was for traverses along c-axis on ac- and bc-sections (Fig. 5c). The model fits are not acceptable for virtually all times and all locations investigated. There are some acceptable estimates at intermediate locations that are not straightforward to explain. In summary, the best results are obtained for traverses close to the crystal center and along b-axis on ab-section. The acceptable models are variably restricted to the vicinity of the crystal with increasing diffusion duration, i.e. with increasing diffusion duration (τ_{dp}), the area of acceptable estimates is more restricted to the crystal center area. This is the result of the complex relationship between crystal shape and aspect ratio.

4.3. 2D models along-axis and on-center sections

There are three principal planes that cut through the core of the crystal: the ab-, bc-, and ac-planes (Fig. 6). Here we show results obtained with two initial zoning patterns (A and B), and using the ‘true initial’ and ‘apparent initial’ concentration. The 2D diffusion modeling results are very similar to those of the 1D model, but RMSD values are about an order of magnitude lower due to the effect of the zoning geometry (see Section 5.1.2.).

We find that in crystal pattern A using apparent initial concentration model along the ac-section shows the best results and the smallest overall RMSD values; models on the ab-section also give acceptable estimates with slightly larger RMSD (Fig. 6a). With increasing time the RMSD increases, but acceptable models can be obtained up to 12,000 days (Fig. 6a). Models on the bc-section gave the largest RMSD values and did not yield acceptable estimates; with mismatch exceeding 1% error at multiple points. As for the 1D on-center model, diffusion anisotropy does not play a significant role, and 3D diffusion affects the zoning pattern in a similar fashion (Fig. 6). Using true initial concentration both ac- and ab-section models perform better with overall lower RMSD for the entire investigated diffusion duration (Fig. 6). Employing crystal pattern B we find the same results (Fig. 6b): models on the ac-section perform better than those on the ab-section, and again the ones on the bc-section are the worst. However, the time range for acceptable estimates is somewhat shorter (Fig. 6b). This shows, again, that the effect of the initial zoning geometry depends on the relative sizes of the core and the overall crystal. In summary, these 2D models perform best both on ac- and ab-sections when using true initial concentration (Fig. 6).

4.4. 2D along-axis and off-center sections

These 2D models were performed using both the apparent initial and true initial concentration. Models on ab-sections show similar results when using apparent initial and true initial concentration; for short diffusion times acceptable estimates can be obtained up to the point where facets meet, after which the RMSD strongly increases and the mismatch is beyond acceptable limits (Fig. 7a). The exact time where models become unacceptable depends
on the interaction between the crystal shape and diffusion time. Models with ‘true initial’ concentration yield acceptable estimates up to about 50% of the crystal volume around the center at the longest investigated time (14,000 days). Models on ac-sections also yield acceptable estimates for longer times when ‘true initial’ concentration, and the location of the crystal facet corner limits the area of acceptable estimates (Fig. 7b). The worst performance was again for sections on bc-plane although under certain configurations of parameters are still valid (Fig. 7c). To sum up, the best results are obtained for sections close to the crystal center and on ab- and ac-sections when ‘true initial’ concentration is used. The acceptable models are for sections located between the crystal center and the intersections of the prism and the pyramid for the shorter diffusion times.
5. DISCUSSION

A very important effect of the interacting diffusion fronts in 3D is that the interaction becomes more complex with time, and with more complex crystal shape (e.g. larger number of facets). Thus, the longer the diffusion duration and the smaller and more complex geometry the crystal has, the more likely that one will calculate unreliable time-scales. Here we rationalize some of our findings and discuss the issues that need to be taken into account to obtain reliable time-scales. All the effects we report occur with or without diffusion anisotropy, but the number of acceptable estimates is smaller and more limited to the crystal center when anisotropy is present.

5.1. 1D or 2D models – what is more applicable in different cases?

5.1.1. The role of the initial concentration – ‘apparent initial’ or ‘true initial’?

The 1D models return good estimates if the diffusion is mainly controlled by the modeled direction in the 3D crystal, i.e. as long as the modeled direction is not influenced by diffusion from other directions. However, we also found that if there is a concentration plateau, even if small, using the ‘apparent initial’ concentration the model yield acceptable estimates. This is true even for traverses with a concentration plateau that is different from the initial concentration (‘true initial’). This is because diffusion parallel to the modeled direction controls the shape of the traverse and thus yields correct time estimates. On the other hand, if ‘true initial’ concentration is used in the 1D model then there is an ‘extra’ amount of flux to be removed from the plateau, the model overestimates the actual diffusion duration (e.g. Costa et al., 2008; Shea et al., 2015). If there is no plateau (i.e. diffusion has reached the crystal center along the axis in question) the 1D models perform poorly using any initial condition.

The 2D models yield better estimates when ‘true initial’ concentration input is used (Fig. 6) because they account for two out of the three dimensions, and give realistic estimates as long as diffusion along the third (non-modeled) dimension does not play a significant role. For instance, 2D models of ac-sections (with both apparent and true initial concentration) yield estimates as reliable as 1D at short durations (Fig. 8). After diffusion has reached the crystal core parallel to the a-axis, however, models with ‘initial apparent’ concentration are not reliable, but models using the ‘true initial’ concentration are still good (Fig. 8b). After diffusion parallel to the b-axis becomes effective in the modeled section, 2D model cannot account for the ‘extra’ diffusion from the third direction and give poor estimates (Fig. 8c). The effect of diffusion from the third direction occurs the latest with the on-center ab-plane because the c-axis is the longest (even if it experiences additional diffusion because of the prism facets). Thus, 2D models performed on ab-sections yield acceptable estimates for the longest time (t3D) when the ‘true initial’ concentration model input is used (Figs. 6 and 7). When diffusion from the c-axis reaches the modeled

Fig. 6. Plot of t3D versus RMSD for 2D models in various configurations of parameters along the principal planes. (a) Homogenous crystal (pattern A) (b) reverse zoning with overgrowth rim (pattern B). See text for more discussion.
ab-section, \( t_{3D} \) is progressively overestimated depending on the amount of diffusion and the position of the ab-plane along the c-axis. In summary, 1D models give generally better results when the 'apparent initial' concentration is used, whereas 2D models yield better overall estimates with the 'true initial' concentration.

5.1.2. The role of the zoning geometry and model input – 'apparent initial' or 'true initial'?

The initial zoning geometry plays a significant role in the determination of time-scales and it is not always possible to unambiguously assess it in natural crystal (e.g. Costa et al., 2008; Saunders et al., 2014). It may appear shifted towards the crystal center with increasing time (\( t_{3D} \)) due to multiple-dimensional effects at the prisms (Fig. 9a). Thus, the diffusion profile may suggest a different zoning geometry from the 'true initial' (c.f. Fig. 1d) to the extent that an initially homogenous crystal (pattern A) may develop a zoning pattern with time that would suggest an initial step-function, or an initially zoned crystal (pattern B) would imply a different zoning geometry from the initial one (Fig. 9). It is merely a geometric effect, and thus, it should also occur in other minerals (and elements) where facets meet in an angle.

Simulations using the 'apparent initial' zoning geometry (i.e. step-function as may be inferred from the 'real' data) show that 1D models give satisfactory estimates with low errors (<1%), thus, correct time-scales can be obtained employing 1D models on the c-axis with 'apparent initial' concentration and zoning geometry configurations (Fig. 9b & e). In contrast, if we use the 'true initial' zoning geometry and the 1D models are run for the same time as

Fig. 7. RMSD plotted against location of the 2D sections (distance from crystal center) for homogenous zoning settings (pattern A) using 'apparent initial' C and 'true initial' zoning geometry. Scale of Y-axis of each plot corresponds to maximum observed RMSD at any \( t_{3D} \). Gray dashed lines (and arrows) denote positions of joining facets. See text for more discussion.
Fig. 8. Comparison of 1D and 2D model estimates to 3D results along the a-axis and ac-plane using isotropic D. Three scenarios are considered: (a) at short $t_{3D}$, before diffusion reaches the crystal center from any of the three directions; (b) at an intermediate $t_{3D}$, after diffusion penetrated through the entire crystal but only along a-axis (the shortest one); and (c) at relatively long $t_{3D}$, where diffusion reached the center from the two short axes (a- and b-axis), but not from the longest (c-axis). Both ‘apparent initial’ (solid line) and ‘true initial’ (dashed line) C model inputs are considered using ‘true initial’ zoning geometry. Note that for the 2D models only the c-axis is plotted instead of the entire ac-section for simplicity and to facilitate direct comparison between the two model results. In (a) both 1D and 2D models give acceptable estimates of concentration distribution along the modeled traverse and plane. In (b) 1D model using ‘apparent initial’ C returns good estimate, whereas 2D model performs well when ‘true initial’ C is used. In (c) 1D model cannot return acceptable estimate, but 2D model is still accurate if ‘initial true’ C model input is used. This suggests that it is possible to combine 1D and 2D models using different initial configurations and obtain a unique answer for the time and initial concentration distribution. Arrows and shaded areas illustrate the contribution of the diffusion flux from the different directions. See text for more discussion.
Fig. 9. Schematic illustration of compositional traverses and mismatch to exemplify the effect of using different zoning geometries. (a) the ac-plane shows a longer penetration distance along the c-axis due solely to ‘additional’ diffusion from the merging diffusion fronts from the facets; comparison of the ‘real’ 1D traverse and 1D model conducted with ‘apparent initial’ zoning geometry condition for $t = t_{3D}$ (b) is for an homogenous crystal (pattern A) and (e) is for the initially zoned crystal (pattern B). The match between the model and the ‘real’ traverse is acceptable using this ‘apparent initial’ zoning geometry in both cases. In contrast in both the pattern A crystal (c) and the pattern B crystal (f) using the ‘true initial’ zoning geometry there is a significant mismatch between the models and ‘real’ concentration distribution. (d) and (g) It is difficult to reproduce the ‘real’ 1D profile within acceptable error using the ‘true initial’ zoning geometry configuration, and it would require significantly longer time ($t_{1D}$) and comparison between drastically differently shaped traverses and a quite subjective judgment of the fit. Note the differences in scale of mismatch. See text for more discussion.
the 3D simulations \( t_{1D} = t_{3D} \), then the models cannot be fitted to the ‘real’ traverse; there is a large misfit \( (\Delta C \approx 0.06; \sim 10\% \text{, Fig. 9c & f}) \). In fact, if the 1D model runs for longer time it is not possible to obtain a best-fit concentration distribution with acceptable mismatch. For example, a 1D model estimate of the initially homogenous crystal is obtained at \( t_{1D}^* = 3000 \text{ days} \) (which is about \( \times 3 \) the ‘real’ time; * refers to the best-fit time), where the absolute mismatch is about \( 4 \) times larger than the acceptable threshold (Fig. 9d; solid lines). In comparison, when the 1D model runs for even longer time \( t_{1D} = 6000 \text{ days} \) the absolute mismatch is significantly reduced (by a factor of two), the mismatch profile is more symmetric, but the number of outlier data points is significantly larger than the acceptable 3 points (Fig. 9d; dashed lines). Similarly, there is no acceptable 1D model if the initial zoning geometry is used in the case of crystal pattern B (Fig. 9g). To model natural crystals (where \( t_{3D} \) is unknown) a subjective judgment needs to be made if ‘true initial’ zoning geometry is used, and the calculated time-scale may be overestimated by several times or even an order of magnitude depending on the ‘real’ time \( t_{3D} \). Thus, using slowly diffusing elements (e.g. Al or Ca) in natural Opx crystals to determine the position of the boundary in Fe–Mg profiles suggesting step-like initial zoning geometry is not a good strategy if the traverse is along the c-axis on the principal bc-plane.

In 2D models the choice of zoning geometry is complex since it involves many points along the entire section. Although we did not do 2D models with ‘apparent initial’ zoning geometry, we anticipate they would retrieve appropriate concentrations in the plateau, but the size (area) of the plateau would be smaller, and thus, the overall mismatch (and RMSD) would be higher (over a more extensive area) than the acceptable error. Using the ‘true initial’ zoning geometry and concentration this effect does not occur and one obtains acceptable 2D model estimates. In sections where the c-axis is not involved (ab-plane), the ‘true initial’ zoning geometry gives better results, whereas in sections containing the c-axis the choice of zoning geometry is not obvious.

5.2. A unique opportunity to assess absolute (pre-diffusion) magmatic conditions by diffusion modeling

We have discussed the relationship between 1D and 2D and 3D models for a variety of starting model inputs of concentration and zoning geometry. However, it is challenging to decide whether the analyzed concentration and zoning geometry are ‘apparent initial’ or ‘true initial’ when it comes to natural samples. The ab-sections of orthopyroxene close to the crystal center, however, hold a unique opportunity to not only calculates the proper time-scales of diffusion but also to gain insights into initial concentrations. As long as there is a concentration plateau along the b-axis a 1D model can yield an appropriate time-scale \( t_{1D}^* \) using the measured (‘apparent initial’) concentration and zoning geometry. If the c-axis lacks a concentration plateau then the crystal center is affected by diffusion, and thus, the measured concentration at the plateau along the b-axis is not the ‘true initial’ concentration. In such a case, conducting a 2D model using the previously calculated \( t_{1D}^* \) would allow determination of the true initial concentration. This means that information on the original geochemical characteristics can be estimated even if they are not longer recorded in the crystal. This piece of information can be used for other petrological aspects, for instance, to calculate the real concentration of melt in equilibrium with the crystal in question, or to improve thermometric calculations.

5.3. Influence of crystal morphology on concentration distributions

Previous studies (e.g. Ganguly and Tirone, 1999; Watson et al., 2010) have also found that different shapes (e.g. cylinder, sphere, etc.) yield different results when other parameters are identical. Most recently Shea et al. (2015) performed a series of numerical simulations on polyhedral olivine crystals and have shown that crystal morphology has a significant influence on modifying diffusion gradients through converging diffusion fronts at convex junctions of crystal facets. Our results confirm such an effect. We also found that as diffusion progresses, larger areas around the convex facet-intersections (i.e. the crystal edges) get involved. 1D models cannot account for this effect, and therefore the calculated time-scales are likely to be incorrect. Furthermore, 2D models can only keep up with the effect of merging diffusion fronts if only two crystal facets intersect (e.g. ab-sections for merging \{210\} with \{100\} or \{010\}; and ac-sections for converging \{101\} with \{100\}).

The same situation occurs in an initially zoned crystal (overgrown rim) at the core-rim interface. However, in this case, the shape of the core, not that of the entire crystal, is what controls the morphological effect on the diffusion pattern. A core with the same shape as the crystal itself has the same influence as described above with the exception of the absolute position of the intersections of facets with respect to the crystal (Fig 6). Therefore, for an initially zoned crystal, the morphology of the core and its impact has to be taken into account when modeling diffusion.

This study and Shea et al. (2015) demonstrate that crystal morphology substantially influences the diffusional penetration around the convexly converging crystal facets. This effect is present in various shapes (e.g. sphere, parallelepiped, different polyhedral habits) and it results mostly in overestimation of actual diffusion durations estimated by 1D (or 2D) models. Even if diffusion is isotropic like for example in garnet, Ganguly et al. (2000) note that profiles selected for modeling should be perpendicular to the 3D concentration gradient otherwise ambiguous time-scales may be calculated. Thus, the morphological effect plays an important role in diffusional penetration distance in garnet, as well. The magnitude of differences between estimated and ‘real’ time, however, depends on the location within the crystal, i.e. where the modeled profile was taken with respect to intersectiong facets and diffusion duration. For instance, diffusion modeled on a 1D profile from a simple spherical crystal almost always yields overestimation of the real time by a minimum of 30% (Shea et al., 2015). Therefore, in accord with our findings, if diffusion is mod-
eled in spherical (e.g. Ducea et al., 2003) or complexly shaped (e.g. Ganguly et al., 2000) garnet crystals, it may potentially yield misleading results, unless attention is paid to morphological effects.

5.4. Suggested strategy for modeling Fe–Mg diffusion in orthopyroxene

The results and discussion above can be used to derive some guidelines for choosing the best 2D sections and 1D profiles to determine the time scales from Fe–Mg of natural orthopyroxene, which we summarize below:

- **The orientation** of the 2D section needs to be determined either by a micro-analytical technique (e.g. electron backscattered diffraction; EBSD) or optical microscopy observations, since this is critical for appropriate section selection and also helpful to account for diffusion anisotropy.
- **Avoid euhedral and symmetric sections with obviously asymmetric concentration patterns.** These sections may be too close to converging facets.
- **Aim for ab-sections** and **ac-sections**. Ignore bc-sections because they are the toughest to evaluate for their absolute location within the crystal, and if oblique they were most presumably affected by diffusion along a-axis.
- **Use grains with a concentration plateau and compositional symmetry** (e.g. use the gray-scale of a BSE image as proxy for Fe–Mg; e.g. Allan et al., 2013).
- **Traverses should be taken away from crystal corners** in order to avoid the influence of additional diffusion from other dimensions.
- **1D models** should target traverses **parallel to the b-axis** on the **ab-plane** and use ‘apparent initial’ model input (concentration and zoning geometry).
- **1D models** performed on the **c-axis** along the prisms should use the ‘true initial’ zoning geometry and the ‘apparent initial’ concentration and not simply use a slow diffusing element (e.g. Al or Ca) as a proxy for the initial zoning geometry. Although properly correcting for the effects along c-axis might not be as straightforward, it has the advantage of profiles being much longer, and thus better analytical precision can be achieved (e.g. Saunders et al., 2014).
- **2D models** should aim for **ab-sections**, if possible. Note that 2D models perform best if ‘true initial’ concentration and zoning geometry is employed; check for the initial boundary position and zoning in slow diffusing element(s).

The guidelines above should lead to better time estimations, but one cannot be sure whether the selected section cuts through the center of the crystal or not. The largest and most symmetric crystal sections are more likely to come closest to the center.

6. CONCLUSIONS

We have conducted 3D, 2D and 1D diffusion numerical simulations of Fe–Mg in orthopyroxene and showed the relationship between crystal shape, initial conditions (concentration and zoning geometry inputs), and anisotropy of diffusion. A key finding is that interacting diffusion fronts at crystal facets can significantly modify the diffusion and the concentration pattern. This effect can only be accounted for in certain 1D and 2D models and depends mainly on the crystal shape and aspect ratio, and thus it should occur in other minerals and elements. 1D models are most likely to give acceptable estimates if the ‘apparent initial’ concentration and zoning geometry are used as can be inferred from the measured natural data. In contrast 2D models perform better with ‘true initial’ (pre-diffusion) concentration and zoning geometry, but this might be difficult to know. For 1D models, concentrations along the a- and b-axis, and for 2D models the ab- and ac-sections should be preferred; these orientations most likely yield appropriate estimates of concentration distribution and thus calculated time-scales. Results also indicate that once diffusion has penetrated the crystal core and modified significantly the initial concentration, calculating proper time-scale by performing 1D or 2D diffusion models is unlikely. However, for ab-sections close to the crystal center can be used to obtained unique information about the initial pre-diffusion concentration by combining 1D and 2D modeling.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2016.09.037.

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