Neodymium diffusion in orthopyroxene: Experimental studies and applications to geological and planetary problems

Jennifer Sano a,b, Jibamitra Ganguly a,⇑, Richard Hervig c, Ralf Dohmen d, Xiaoyu Zhang a

a Department of Geosciences, University of Arizona, Tucson, AZ 85721, USA
b Chemostrat Inc., 5850 San Felipe, St. Houston, TX 77057, USA
c School of Earth and Space Sciences, Arizona State University, Tempe, AZ 85287, USA
d Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität, Bochum D-44780, Germany

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Abstract

We have determined the Nd³⁺ diffusion kinetics in natural enstatite crystals as a function of temperature, f(O₂) and crystallographic direction at 1 bar pressure and applied these data to several terrestrial and planetary problems. The diffusion is found to be anisotropic with the diffusion parallel to the c-axial direction being significantly greater than that parallel to a- and b-axis. Also, D(∥a) is likely to be somewhat greater than D(∥b). Diffusion experiments parallel to the b-axial direction as a function of f(O₂) do not show a significant dependence of D(Nd³⁺) on f(O₂) within the range defined by the IW buffer and 1.5 log unit above the WM buffer. The observed diffusion anisotropy and weak f(O₂) effect on D(Nd³⁺) may be understood by considering the crystal structure of enstatite and the likely diffusion pathways. Using the experimental data for D(Nd³⁺), we calculated the closure temperature of the Sm–Nd geochronological system in enstatite during cooling as a function of cooling rate, grain size and geometry, initial (peak) temperature and diffusion direction. We have also evaluated the approximate domain of validity of closure temperatures calculated on the basis of an infinite plane sheet model for finite plane sheets showing anisotropic diffusion. These results provide a quantitative framework for the interpretation of Sm–Nd mineral ages of orthopyroxene in planetary samples. We discuss the implications of our experimental data to the problems of melting and subsolidus cooling of mantle rocks, and the resetting of Sm–Nd mineral ages in mesosiderites. It is found that a cooling model proposed earlier [Ganguly J., Yang H., Ghose S., 1994. Thermal history of mesosiderites: Quantitative constraints from compositional zoning and Fe–Mg ordering in orthopyroxene. Geochim. Cosmochim. Acta 58, 2711–2723] could lead to the observed ~90 Ma difference between the U–Pb age and Sm–Nd mineral age for mesosiderites, thus obviating the need for a model of resetting of the Sm–Nd mineral age by an “impulsive disturbance” [Prinzhofer A, Papanastassiou D.A, Wasserburg G.J., 1992. Samarium–neodymium evolution of meteorites. Geochim. Cosmochim. Acta 56, 797–815].

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1. INTRODUCTION

The relative abundance of the trivalent rare earth elements (REE) in basaltic rocks provides important constraints on the extent of partial melting of their mantle source regions in the Earth and other planetary bodies. The REE patterns in magmas depend on the equilibrium distribution coefficient of these elements between the solids and melt, their diffusivities in solids, and the rates of melting and melt extraction (e.g. Qin, 1992; Tirone et al., 2005; Cherniak and Liang, 2007). Garnet and clinopyroxene are the primary hosts of REE in the terrestrial mantle and have conspicuous ionic radius dependent mineral-melt distribution coefficients. Consequently, these minerals essentially
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govern the REE patterns of the extracted basaltic magmas. However, it is the mineral-melt partitioning and diffusion property of orthopyroxene, along with clinopyroxene, that govern the REE patterns of basaltic magmas in the relatively smaller planetary bodies, such as the Earth’s moon and asteroids, in which garnet is absent as a mineral phase. Coexisting clinopyroxene and orthopyroxene in spinel lherzolite and harzburgites could also develop diffusion induced compositional zoning during subsolidus cooling that may be modeled to retrieve the cooling rate of the host rocks if the necessary data for equilibrium fractionation and volume diffusion kinetics of the species are available. On the basis of results of numerical modeling, Cherniak and Liang (2007) have suggested that REE patterns in residual orthopyroxenes in rocks subjected to partial melting may provide important constraints on the time scales of partial melting and melt migration.

In addition to its importance in constraining the nature of the source region of partial melts, the dynamics of melting processes and rates of subsolidus cooling, the diffusion kinetic data of two trivalent rare earth ions, namely Sm and Nd, in the host minerals are essential for the proper interpretation of the Sm–Nd mineral ages of terrestrial and planetary samples. While in terrestrial rocks, the mineral of primary interest for the determination of Sm–Nd mineral ages is garnet (as it most strongly fractionates the parent nuclide, Sm$^{3+}$), for other planetary samples the minerals of interest are clino- and ortho-pyroxenes, as garnets are absent in these samples.

In recent years, several authors have determined the diffusion coefficients of selected REEs in garnet (Van Orman et al., 2002; Tirone et al., 2005), clinopyroxene (Van Orman et al., 2001) and orthopyroxene (Ganguly and Tirone, 2001; Cherniak and Liang, 2007). Ganguly and Tirone (2001) reported Nd diffusion data parallel to the c-axis of a natural enstatite crystal at 1 bar, 827 °C and f(O$_2$) defined by a flowing CO/CO$_2$ mixture to that corresponding to IW buffer condition. Cherniak and Liang (2007) carried out diffusion kinetic studies of the trivalent Gd, Yb and Eu as function of temperature between 1000 and 1250 °C at f(O$_2$) defined by solid IW buffer and atmospheric conditions. Except for four experiments for Eu diffusion normal to (0 0 1) at 1000–1200 °C, all experiments for Gd, Yb and Eu$^{3+}$ (a total of 28) were carried out to determine the diffusion coefficients normal to (2 1 0). The data of Cherniak and Liang (2007) do not show any systematic dependence of the diffusivities of trivalent rare earths on ionic radius, whereas both orthopyroxene and clinopyroxene are known to exhibit significant diffusion anisotropy of divalent cations (Schwandt et al., 1998; Zhang et al., 2010). Also, diffusion of Cr$^{3+}$ in enstatite has been found to be anisotropic (Ganguly et al., 2007). On the other hand, Cherniak (2001) did not find any significant anisotropy for Pb$^{2+}$ diffusion in Cr-diopside.

Even though the limited data of Cherniak and Liang (2007) for Eu$^{3+}$ diffusion at 1100 and 1200 °C normal to (0 0 1) and (2 1 0) planes do not show any anisotropic effect, it is premature to accept that the REE$^{3+}$ diffusion in orthopyroxene is isotropic at all temperatures of geological and planetary interest, especially in view of the evidence of anisotropic diffusion in pyroxene discussed above. We note specifically that anisotropy of diffusion may diminish with increasing temperature (Zhang et al., 2010) so that it might have become undetectable in the experiments of Cherniak and Liang (2007) at 1100 °C for diffusion normal to (0 0 1) and (2 1 0) planes. Furthermore, the insensitivity of D(REE$^{3+}$) to large change of f(O$_2$) condition, as found by these authors, suggests that the diffusion of a trivalent rare earth ion is not significantly affected by the point defect concentrations in the lattice sites. This is not impossible, but rather surprising and counterintuitive.

For the reasons discussed above, we have investigated the Nd diffusion kinetics in orthopyroxene, for which very little direct experimental data are available, as a function of temperature between 975 and 1200 °C, crystallographic orientation and f(O$_2$). The results of these experimental studies and their potential implications for geological and planetary problems are presented and discussed in this paper.

2. EXPERIMENTAL STUDIES

2.1. Starting materials and sample preparation

We have used gem quality natural Mg-rich orthopyroxene crystals from Sri Lanka. Complete microprobe analyses of typical grains yielded an average composition of (Mg$_{0.90}$Fe$_{0.02}$Al$_{0.02}$)(Si$_{0.97}$Al$_{0.03}$)O$_3$, and showed the grains to be homogeneous in composition within the resolution of microprobe data. Diffusion in orthopyroxene is expected to be anisotropic (Ganguly and Tazzoli, 1994; Schwandt et al., 1998), with the three principal diffusion axes being parallel to the three crystallographic axes. Therefore, the orthopyroxene crystals were oriented in a single crystal diffractometer (Bruker Apex X8) and cut normal to the a, b and c axial directions. The cut surfaces were ground and polished stepwise downwards from 1 to 0.25 μm diamond powder and finally finished to a mirror-polish by a combination of chemical and mechanical polishing using silica suspension on OP-chem cloth from Struers. The last step was intended to remove a very thin disturbed layer that usually develops close to a crystal surface after the mechanical polishing.

Each sample was pre-annealed at or close to the chosen experimental temperature and oxygen fugacity for 24–36 h in order to equilibrate the point defect concentrations to
the experimental conditions and to heal any near-surface damage that might have been caused by the mechanical polishing during sample preparation. A thin layer of Nd was then deposited on the polished surface of a pre-annealed crystal. Except for one sample, labeled as R-NdEn-c, the Nd layer was deposited by thermal evaporation of Nd$_2$O$_3$, which was achieved by spreading powdered oxide on a W-filament and resistive heating of the filament under high vacuum condition. For R-NdEn-c, the Nd layer was deposited from plasma that was created by Laser ablation of Nd$_2$O$_3$ target (Dohmen et al., 2002). The diffusion experiment for this sample was carried out at the Ruhr-University (R-U), Bochum, Germany while those for all others were carried out at the University of Arizona, USA.

2.2. Tracer-diffusion experiments and measurements of diffusion profiles

All experiments were carried out under controlled oxygen fugacity ($f$(O$_2$)) conditions in vertical gas-mixing furnaces. The experimental conditions are summarized in Table 1 along with the calculated diffusion coefficient for each experiment. Some of the experiments, which were in the range of 1100–1200 °C, might have been in the field of proto-enstatite or high-clinopyroxene (C2/c) (Yang and Prewitt (2000)). We have, thus, examined a sample annealed at 1200 °C for 41 h (run # NdEn06) by single crystal X-ray diffraction, but did not find any evidence of polymorphic change. The diffraction pattern shows the presence of only orthopyroxene. Thus, either the stability of orthopyroxene extends at least up to 1200 °C at 1 bar pressure for the composition used in our study or the conversion was kinetically inhibited.

The $f$(O$_2$) was controlled by a flowing mixture of CO and CO$_2$ and cross checked by a zirconia sensor. The furnace was pre-conditioned to the desired temperature and $f$(O$_2$) condition of an experiment, keeping the ends of the vertical tube furnace closed. The sample, with a thin layer of diffusing material, was quickly inserted from the top to the hot spot of the furnace, and the two ends of the ceramic tube were completely sealed thereafter. At the end of an experiment, the sample was quenched quickly by pulling it out of the furnace and cooling in air.

The $f$(O$_2$) conditions of the experiments were controlled primarily to correspond to those defined by the wüstite-magnetite (WM) buffer. A limited number of experiments were carried out at 1095 °C at 1.5 log units higher $f$(O$_2$) (WM + 1.5) and that corresponding to the iron-wüstite (IW) buffer condition to study the effect of $f$(O$_2$) on the Nd diffusion coefficient in orthopyroxene. Time series experiments were carried out at 1065 °C for 96, 168 and 240 h and $f$(O$_2$) corresponding to the WM buffer condition to check if there is any time dependence of the retrieved diffusion coefficients that would be indicative of the effects of non-diffusive process on the development of the concentration profiles. In both sets of experiments, the diffusion direction was chosen to be parallel to the $b$-axis since the $(010)$ surface of orthopyroxene is much easier to polish than the $(100)$ and $(001)$ faces. The results of the $f$(O$_2$) effect and time series experiments are discussed later.

The experimentally induced Nd diffusion profiles of all samples, except R-NdEn-c, were determined by depth profiling of $^{14}$Nd with Cameca ims-3f/6f SIMS, using a primary ion beam of $^{16}$O$^+_+$ rastered over areas of ~125 × 125 to 175 × 175 μm$^2$. An aperture was inserted into the paths of the ions to allow only those originating from around a 16 μm diameter circular area in the center of the crater into the mass spectrometer. The sample surface was coated with Au in order to dissipate electrostatic charging of the sample by the primary ion beam. At the end of a depth profiling,

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$T$ (°C)</th>
<th>Time (h)</th>
<th>$D$(1σ) (cm$^2$/s)</th>
<th>log$_{10}$($D$(1σ)) (cm$^2$/s)</th>
<th>$f$(O$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdEn-a-05</td>
<td>975</td>
<td>622.5</td>
<td>5.49(1.27)E-18</td>
<td>-17.26(0.10)</td>
<td>WM</td>
</tr>
<tr>
<td>NdEn-a-01</td>
<td>1025</td>
<td>241</td>
<td>9.38(2.59)E-18</td>
<td>-17.03(0.12)</td>
<td>WM</td>
</tr>
<tr>
<td>NdEn-a-03</td>
<td>1095</td>
<td>98.5</td>
<td>2.01(0.60)E-17</td>
<td>-16.70(0.13)</td>
<td>WM</td>
</tr>
<tr>
<td>NdEn-a-04</td>
<td>1150</td>
<td>48</td>
<td>6.44(1.19)E-17</td>
<td>-16.19(0.08)</td>
<td>WM</td>
</tr>
<tr>
<td>NdEn-a-06</td>
<td>1200</td>
<td>41</td>
<td>1.59(0.47)E-16</td>
<td>-15.80(0.13)</td>
<td>WM</td>
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<tr>
<td>NdEn-b-05</td>
<td>975</td>
<td>622.5</td>
<td>3.63(1.25)E-18</td>
<td>-17.44(0.15)</td>
<td>WM</td>
</tr>
<tr>
<td>NdEn-b-01</td>
<td>1025</td>
<td>241</td>
<td>3.21(1.03)E-18</td>
<td>-17.49(0.14)</td>
<td>WM</td>
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<tr>
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<td>96</td>
<td>1.05(0.29)E-17</td>
<td>-16.98(0.12)</td>
<td>WM</td>
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<tr>
<td>NdEn-b02.2</td>
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<td>168</td>
<td>8.87(0.32)E-18</td>
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<td>WM</td>
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<tr>
<td>NdEn-b02.3</td>
<td>1063</td>
<td>240</td>
<td>8.30(1.82)E-18</td>
<td>-17.08(0.08)</td>
<td>WM</td>
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<tr>
<td>NdEn-b-09</td>
<td>1095</td>
<td>120</td>
<td>1.37(0.32)E-17</td>
<td>-16.84(0.10)</td>
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<tr>
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<td>1095</td>
<td>98.5</td>
<td>2.05(0.47)E-17</td>
<td>-16.86(0.10)</td>
<td>WM</td>
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<tr>
<td>NdEn-b-07</td>
<td>1095</td>
<td>98.5</td>
<td>1.03(0.21)E-17</td>
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<tr>
<td>NdEn-b-08</td>
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<td>1.81(0.42)E-17</td>
<td>-16.74(0.10)</td>
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<td>NdEn-b-04</td>
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<td>48</td>
<td>5.10(1.06)E-17</td>
<td>-16.29(0.09)</td>
<td>WM</td>
</tr>
<tr>
<td>NdEn-c-05</td>
<td>975</td>
<td>622.5</td>
<td>4.17(1.15)E-18</td>
<td>-17.38(0.12)</td>
<td>WM</td>
</tr>
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<td>NdEn-c-01</td>
<td>1025</td>
<td>241</td>
<td>3.02(0.69)E-17</td>
<td>-16.52(0.10)</td>
<td>WM</td>
</tr>
<tr>
<td>NdEn-c-03</td>
<td>1095</td>
<td>98.5</td>
<td>8.35(0.96)E-17</td>
<td>-16.08(0.05)</td>
<td>WM</td>
</tr>
<tr>
<td>NdEn-c-04</td>
<td>1150</td>
<td>48</td>
<td>1.01(0.16)E-16</td>
<td>-16.00(0.05)</td>
<td>WM</td>
</tr>
<tr>
<td>R-NdEn-c</td>
<td>1100</td>
<td>48</td>
<td>2.15(0.64)E-17</td>
<td>-16.66(0.13)</td>
<td>WM</td>
</tr>
</tbody>
</table>
the crater depth within a sample was measured by a Dektak surface profilometer that was calibrated against known standards. An average step size was initially estimated by dividing the crater depth by the total number of steps, and was used to generate ion intensity vs. depth data (and plots) for different isotopes monitored during depth profiling. Since the sputtering rate in an Au-coating is much faster than that in a silicate matrix, the actual step size in the silicate matrix is somewhat smaller than the average step size. This problem has been addressed in the next section. The crater depths range between 4100 and 12,800 Å, with an average error of ~3%. The error in a crater depth measurement was estimated on the basis of a few measurements along profilometer lines that were normal to each other, and was treated as 1σ value. Further details about the SIMS measurement procedures may be found in earlier publications from our group on tracer-diffusion studies (e.g. Zhang et al. 2010; Ganguly et al., 2007).

The count rates for $^{30}\text{Si}$, $^{44}\text{Ca}$, $^{26}\text{Mg}$, $^{197}\text{Au}$ were also measured along with those of $^{144}\text{Nd}$ during depth profiling in order to help determine the location of the thin film and crystal surfaces and to monitor the stability of the analysis, as discussed below. The secondary ion intensities of the species were obtained in peak switching mode, with each measurement cycle requiring 18–25 s depending on the count time selected for each isotope, and whether or not a charge-compensation check was applied. A total of 150–220 measurement cycles were typically obtained in each profile analysis. A typical set of analytical data for a sample (annealed at 1025 °C, $f_\text{O}_2$ = WM buffer) are illustrated in Fig. 1.

The smearing of $^{197}\text{Au}$ counts was due to ion beam mixing during depth profiling. Because of the energetic interaction of the primary beam (impact energy of ~17–20 keV) and the resulting change in the chemistry of the sample surface, a few cycles are required to reach a steady state. Thus, the data for these initial cycles have to be neglected in constructing the diffusion profile, resulting in the loss of data at the near-surface region. As in earlier studies (Ganguly et al. 2007; Zhang et al., 2010), it was assumed that the crystal surface was located at approximately the initial peak of $^{30}\text{Si}$. This criterion for locating the crystal surface is based on the work of Ganguly et al. (1998) in which the diffusing species was deposited on the crystal surface from a dilute HCl solution. It was found that a sharp drop of Cl counts to almost zero, which should coincide with or be very close to the crystal surface, was always associated with an initial peak of $^{30}\text{Si}$ counts before these settled down to a plateau value with minor oscillations in a stable analysis (Fig. 1). We also show in Fig. 1 the profile for $^{44}\text{Ca}$ that appears to be a non-diffusing species in our experiments.

The Nd-profile for R-NdEn-c was analyzed by Rutherford backscattering spectroscopy (RBS) at the Dynamitron tandem accelerator facility at the Ruhr University, Bochum, Germany, using a 20 nA, 2 MeV beam of $^6\text{He}^+$ (alpha) particles. This RBS analysis was carried out primarily to cross-check the results from the SIMS analyses of the diffusion profiles of the other samples. The RBS spectrum was simulated using the software RBX (Kotai, 1994) that permits the user to vary the sample composition as a function of depth. Initially a spectrum was calculated on the basis of the microprobe analysis of the samples and compared with the measured spectra. The difference between the calculated and measured spectra for a sample was then minimized by introducing depth variation of composition. The RBS data do not indicate formation of any new phase at or near the crystal surface by reaction between the layer of thin film and the crystal substrate.

The Nd diffusion coefficient determined from RBS data is ~0.5 log unit smaller than that predicted by the least squares fit to the SIMS data at the same condition (Fig. 3, lower left panel). We have also noticed similar discrepancy between the D values retrieved from SIMS and RBS data in an earlier study (Tirone et al., 2005). The reason for these discrepancies is not clear, but may lie partly with the calculation of stopping power in the RBS analysis (Ziegler et al., 1988). Additionally, SIMS is more sensitive than RBS for the analysis of trace elements so that when the concentration of the diffusing species becomes very diffuse in the tail ends of the profiles that we have measured so far, RBS analysis may show a somewhat shorter diffu-
sion profile than measured by a SIMS. On the other hand, SIMS analysis may tend to stretch a diffusion profile somewhat due to mixing effects. However, the approximate constancy of $D$ values in a time series study, as discussed below, argues against a significant mixing effect in the SIMS analysis.

3. RESULTS AND DISCUSSION

3.1. Modeling of the diffusion profiles

The modeling of the experimentally induced $^{144}$Nd diffusion profiles in orthopyroxene follows the procedure described in several of our earlier publications on tracer-diffusion studies (e.g. Ganguly et al. 2007; Zhang et al., 2010). The best fits to the profiles were obtained by using the 1-dimensional solution of diffusion equation for diffusion into a semi-infinite medium with homogeneous initial composition and fixed surface concentration of the diffusing species (Crank, 1975):

$$C_s - C(x, t) = C_s - C_\infty = \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$

where $x$ is the normal distance from the surface that is coated with a layer of the diffusing species, (serving as an effectively infinite reservoir), $D$ is the diffusion coefficient, $t$ is the time, $C_s$ is the surface concentration and $C_\infty$ is the initial concentration within the substrate that is preserved at sufficiently large distance from the surface after a diffusion anneal. As the secondary ion signals are typically unstable for the first 4-5 analytical cycles, the data for these initial cycles always had to be neglected (Fig. 1), thereby requiring an indirect estimation of $C_s$ that is needed for the calculation of the diffusion profile. Thus, the solution to the diffusion equation was interfaced with an optimization program, MINUIT (James and Ross, 1975), in order to find the combination of $D$ and $C_s$ such that a calculated diffusion profile has the best fit (using least squares method) to the measured concentration vs. depth data, as illustrated in Fig. 1. Besides the fact that the above equation yields a better match between the model and measured profiles than the solution of the diffusion equation with a depleting source at the surface, Zhang et al. (2010) have discussed the experimental evidence that shows that the thin surface layer of the diffusing species, as in our experimental studies, preserves the property of a homogeneous semi-infinite reservoir.

Initially all diffusion profiles (ion intensity vs. distance) were generated on the basis of the average step size in SIMS depth profiling. In a related study in our laboratory, we have recently measured the sputtering rates in Au and almandine garnet and also measured the thickness of the Au-layer on the garnet by RBS. It is found that the sputtering rate in Au is $\sim$9 times faster than in garnet. On the basis of these data and SIMS depth profiling data on a garnet sample that was Au-coated in the same session and under identical condition as the one analyzed by RBS, we concluded that the base of the Au-layer lies at around $80\%$ of the maximum intensity of the Au-profile. Making the reasonable assumption that the sputtering rates in garnet and enstatite are similar, since Al has a mass in between Mg and Si, we determined the step size in enstatite in SIMS depth profiling of a sample on the basis of the total number of steps ($S_T$), the estimated number of steps in the Au-layer (on the average $\sim$2% of $S_T$) and the crater depth. These calculations show that, on average, the step size in enstatite ($\Delta_{enst}$) is $\sim$$78\%$ of the average step size ($\Delta_{aver}$) that is obtained by dividing the crater depth by the total number of steps, and used in the modeling of diffusion profiles to retrieve the $D$ values. Since, according to Eq. (1), $D \propto (X_T)^2$

where $X_T$ is the total length of a diffusion profile, each $D$ value was finally reduced by the factor ($\Delta_{enst}/\Delta_{aver}$)$^2$. These refined $D(Nd)$ and log $D(Nd)$ values from the different experimental profiles, along with their respective standard deviations, are summarized in Table 1. Except for three experiments (Run Nos. NdEnb01, NdEnb02.1, R-OpxNd1), the profile lengths for all runs are between $\sim$1170 and 2500 Å (the total diffusion length, $X_T$, of any experimental profile can be calculated from the associated $D$ and $t$ values (Table 1) according to $X_T \propto 4\sqrt{(Dt)}$ that follows from Eq. (1)).

The results of time series experiments at 1 bar, 1063 °C and $f(O_2)$ corresponding to that of the WM buffer are illustrated in Fig. 2. The diffusion direction is parallel to the $b$-axis of enstatite. Unfortunately, Au-profile was not measured in the shortest duration experiment (Run No. NdEn-b-2.1) in the time series. Thus, we illustrate two diffusion coefficients for this experiment, one based on the average step size through Au and enstatite, and the other on the reduction of $D$ by a factor that is given by the average value of ($\Delta_{enst}/\Delta_{aver}$)$^2$ for all other samples. The retrieved diffusion coefficients do not show any noticeable dependence on time. Thus, there is no evidence for the interference by any non-diffusive process that might have affected the retrieval the retrieved $D$ values from the measured concentration profiles of $^{144}$Nd.

3.2. Statistical error propagation

The statistical errors for the tabulated values of diffusion coefficients (Table 1) derived from the SIMS data have been
calculated as follows, taking into account the scatter of the depth profiling data (Fig. 1), errors in the measurement of crater depths (∼3%) and location of the crystal surfaces (50–125 Å). Combination of the last two errors causes a stretching or contraction of the distance scale without significantly affecting the scatter of the data around the best-fit model fit to the C vs. X data according to the solution of the diffusion equation (Eq. 1). Thus, the net variance of a D value, \( \sigma_{D}^{2} \), may be approximated as:

\[
\sigma_{D}^{2} \approx \sigma_{D(s)}^{2} + \sigma_{D(X)}^{2}
\]

where \( \sigma_{D(s)}^{2} \) and \( \sigma_{D(X)}^{2} \) are, respectively, the variance of D arising from the scatter of the data and stretching/contraction of the distance scale. The first of the two variances on the right has been calculated according to Tirone et al. (2005), whereas the second one is assumed to be approximately equal to the square of the change of the D value, \( \Delta D \), due to the stretching/contraction of the distance scale.

It can be easily shown from Eq. (1) that

\[
\Delta D \approx D \left[ \left( \frac{X_{T} + \Delta X_{T}}{X_{T}} \right)^{2} - 1 \right]
\]

where \( X_{T} \) is the best estimate of total diffusion distance (based on the best estimate of the crater depth and position of crystal surface) and \( \Delta X_{T} \) is the estimated error of \( X_{T} \). For the sample R-NdEn-c that was analyzed by RBS, the standard error of D was estimated from the range of visually acceptable fits to the Nd-spectra.

### 3.3. Arrhenius relations and diffusion anisotropy

The Arrhenius relations of the experimentally determined diffusion coefficients parallel to the \( a, b \) and \( c \) axial directions of orthopyroxene are illustrated in Fig. 3. The Arrhenius relation is given by \( D = D_{o}\exp(-E/RT) \) where \( D_{o} \) is a constant and \( E \) is the activation energy of diffusion. The vertical error bars on the data points represent \( \pm 1\sigma \) values, estimated according to the procedure discussed above. We show two least squares fits for each data set, one (solid line) being a weighted fit calculated by taking into account the errors of the log D values, and another (dashed line) in which these errors are ignored. Except for diffusion parallel to the \( c \) axial direction, the weighted and unweighted (unw) fits to the data are effectively the same. The Arrhenius parameters for diffusion parallel to the three crystallographic directions, which are derived from the regression parameters of the weighted least squares fits for diffusion data parallel to \( a \) and \( b \) directions, and both weighted and unweighted fits to the data parallel to the \( c \) direction, are summarized below. The parenthetical numbers indicate one standard deviation (1σ) of the retrieved Arrhenius parameters.

<table>
<thead>
<tr>
<th>( Q ) (kJ/mol)</th>
<th>( D_{o} ) (cm²/s)</th>
<th>( \log D_{o} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( /a )</td>
<td>222.21 (20.51)</td>
<td>9.20 (16.74) ( 10^{-6} )</td>
</tr>
<tr>
<td>( /b )</td>
<td>262.09 (41.80)</td>
<td>1.91 (7.14) ( 10^{-7} )</td>
</tr>
<tr>
<td>( /c )</td>
<td>217.93 (21.23)</td>
<td>1.20 (2.23) ( 10^{-8} )</td>
</tr>
<tr>
<td>( /c ) (unw)</td>
<td>234.53</td>
<td>4.16 ( 10^{-8} )</td>
</tr>
</tbody>
</table>

Fig. 3. Arrhenius plot of Nd diffusion data parallel to the three crystallographic axes (also principal diffusion directions) of enstatite. The solid lines are weighted least squares fits whereas the dashed lines are unweighted fits to the data. The lower right panel shows a composite plot of all Arrhenius relations (weighted fits). Error bars: \( \pm 1\sigma \). The dotted lines represent the 1σ error envelopes of the log D values predicted from the Arrhenius relations and 1σ errors of the Arrhenius parameters. All diffusion profiles were determined by SIMS depth profiling, except for one experiment marked by a cross in the lower left panel for which the profile was measured by RBS.
Fig. 3(d) shows a comparison of Arrhenius relations determined by the weighted least squares fits to the diffusion data parallel to the a, b and c axial directions. The dotted lines in all panels represent 1σ error envelopes of the log $D$ values predicted from the above Arrhenius parameters, taking into account the covariance of the errors of $Q$ and log $D_n$ values, according to Tirone et al. (2005). The comparative relations suggest statistically significant anisotropy of diffusion parallel to the c and b axial directions, with $D(//c) > D(//a)$. The weighted least squares fits of the data suggest an intermediate behavior for $D(//a)$ (i.e. $D(//c) > D(//a) > D(///b)$), which is similar to the anisotropic Ca and Mg diffusion in diopside (Zhang et al., 2010). However, since the 1σ error envelopes of the least squares fit to the $D(//a)$ and $D(///b)$ data overlap (Fig. 3), it may be argued that our data do not reveal a statistically significant difference between the diffusivities parallel to the a and b axial directions.

To address the issue of diffusion anisotropy in a different way, we illustrate in Fig. 4 the concentration profiles and model fits to the SIMS depth profiling data for Nd-diffusion parallel to the three axial directions in oriented samples that were annealed simultaneously at 1 bar, 1025 °C and $f(O_2)$ corresponding to that of WM buffer, and analyzed in the same SIMS depth profiling session. Within 2σ error limits, the spatial positions of the data points, taking into account the errors in the crater depth measurements and crystal surface locations, have errors of ~20%, 10% and 6% for diffusion parallel to the a, b and c axial directions, respectively. These data clearly show that the diffusion parallel to the c axis is significantly faster than that parallel to the a and b axes. Also, in order to invoke that $D(//a)$ and $D(///b)$ are effectively the same, one would need to assume that the spatial positions of the two sets of SIMS data have errors in the opposite directions up to their respective 2σ limits. This is not impossible, but unlikely. Furthermore, the fit to the data parallel to the a and b axes with a single $D$ value would have a larger scatter than the separate fits shown in Fig. 4. The possible physical mechanism of Nd$^{3+}$ diffusion discussed below also suggest that diffusion parallel to the c-axis should be significantly greater than those in the other two orthogonal directions, and also $D(//a)$ is likely to be somewhat greater than $D(///b)$. We, thus, conclude that at $T < 1150$ °C, Nd$^{3+}$ diffusion in enstatite is anisotropic, with $D(//c) > D(//a) > D(///b)$, but the difference between the last two values may not be significant for the purpose of applications to natural problems.

Because of its orthorhombic symmetry, the directions of the principal diffusion axes of orthopyroxenes are parallel to those of the crystallographic axes. Thus, according to diffusion tensor theory (Carslaw and Jaeger, 1959; Nye, 1985), the diffusion coefficient along an arbitrary direction, $n$, that is normal to the concentration contours is given by:

$$D_n = D(//a)(\cos Q_a)^2 + D(///b)(\cos Q_b)^2 + D(//c) \times (\cos Q)^2$$

where $Q$ is the angle between the specified axial direction and $n$.

### 3.4. Effect of $f(O_2)$

The results for the study of $f(O_2)$ dependence of Nd diffusion in orthopyroxene are illustrated in Fig. 5. The diffusion direction was chosen to be parallel to the b-axis for the simple reason that it is easier to polish (0 1 0) surface than (0 0 1) and (1 0 0) surfaces. The experimental data show a weak positive dependence of $D$ on $f(O_2)$, but can also be interpreted in terms of $D(///b)$ being effectively independent of $f(O_2)$ within the investigated range of $f(O_2)$ conditions, which essentially covers the range of geological and planetary conditions of interest. In contrast, $D(Cr^{3+})$ in orthopyroxene has been found to have a negative dependence on $f(O_2)$ at 950–1050 °C, with the diffusion coefficient decreasing by a factor of 2–3 for an increase of log($O_2$) by 4 from that defined by the IW buffer (Ganguly et al., 2007). The weak dependence of $D(Nd^{3+})$ on $f(O_2)$ for diffusion parallel to the b-axis is discussed below on the basis of possible diffusion pathways of Nd$^{3+}$, as suggested by crystal structure/
chemical considerations and the effect of \( f(O_2) \) on the diffusion coefficient through its effect on the concentration of lattice vacancies.

3.5. Comparison with previous studies

Our data on the effect of \( f(O_2) \) on Nd diffusion in orthopyroxene (Fig. 5) are compatible with the conclusion of Cherniak and Liang (2007) (on the basis of their diffusion data in air and IW-buffer conditions) that \( D(Nd) \) in orthopyroxene is effectively independent of \( f(O_2) \). Our data (Figs. 3 and 4) clearly show that the diffusion of Nd in orthopyroxene is anisotropic. In contrast, Cherniak and Liang (2007) suggested, on the basis of diffusion data of Eu \(^{2+}\) in orthopyroxene normal to (2 1 0) and (0 0 1) planes at 1100–1250 °C, that the diffusion of rare earth ions (both Eu \(^{2+}\) and trivalent rare earths) in orthopyroxene is effectively isotropic.

As discussed above, Cherniak and Liang (2007) presented a single Arrhenius relation using the RBS data for the diffusion of all REE\(^{3+}\) ions normal to (2 1 0) within the experimental temperature range of 850–1200 °C. This relation is compared in Fig. 6 with the Arrhenius relation normal to (2 1 0) calculated from our anisotropic diffusion data and Eq. (4). The direction normal to (2 1 0) makes angles of 45.93°, 44.07° and 90° with the \( a \), \( b \) and \( c \) axial directions, respectively (note that, according to Eq. (4), \( D(\perp 2 1 0) \) is not affected by \( D(\// c) \)). For \( D(\perp 2 1 0) \), our calculated values are in good agreement with the Arrhenius relation for \( D(\text{REE}) \) by Cherniak and Liang (2007) at \( \sim 1200 \) °C, but diverge to progressively higher values at lower temperatures. These authors have, however, made two direct measurements of \( D(Nd) \) normal to (2 1 0) at 1200 and 1250 °C. These results are illustrated in Fig. 6 by open circles, which are in very good agreement with the Arrhenius relation for Nd diffusion normal to (2 1 0) calculated from our data.

Ganguly and Tirone (2001) made a single determination of the tracer diffusion coefficient of \(^{145}\text{Nd} \) parallel to the \( c \)-axis of a natural enstatite crystal of very similar composition as that used in the present study. The experiment was done at 1 bar, 827 °C and \( f(O_2) \) of IW buffer. Their result is illustrated by a filled triangle Fig. 6. It is greater by a factor of \( \sim 10 \) than the \( D(\// c) \) determined in this study. The reason for this discrepancy is not clear, but is likely to be due to diffusion through a fast-diffusing path in the crystal. At any rate, the Arrhenius relation for \( D(\// c) \) presented in this study should supersede the single determination of Ganguly and Tirone (2001) from the same laboratory.

3.6. Possible Nd diffusion pathways in orthopyroxene

In order to understand the observed diffusion anisotropy and lack of any significant effect of \( f(O_2) \) on Nd\(^{3+}\) diffusion parallel to the \( b \)-axis in enstatite, we examined the crystal structure of orthopyroxene in different orientations, using the American Mineralogist Crystal Structure (AMCS) database. The enstatite structure consists of alternating tetrahedral and octahedral layers. The configurations of these layers, as projected on the \( b \)-c and \( a \)-b planes, are illustrated in Fig. 7. The \( b \)-c projection shows the presence of an open channel along the \( c \)-axial direction between two octahedral groups, each of which consists of a pair of zigzag M1–M2 chains. These channels appear as large rhombohedra in the \( a \)-b projection.

According to Shanon (1970), the ionic radius of Nd\(^{3+}\) in the 6- and 8-coordinated sites is 0.983 and 1.109 Å, respectively, relative to a 4-coordinated \( O^{2-} \) radius of 1.40 Å. Thus, the \( \text{Nd}–O \) radius ratio in enstatite is 0.702, which is much larger than the ideal ratio of 0.414 for a regular six-coordinated polyhedron (Pauling 1960). Consequently, the host lattice site for Nd\(^{3+}\) in enstatite must be the larger of the two octahedral sites, namely M2, which has six nearest and two next-nearest neighbors. Even then, substitution of Nd\(^{3+}\) in enstatite would cause significant lattice strain, and consequently its diffusion pathway should involve, as much as possible, the open channels in the octahedral and tetrahedral layers. Thus, one would expect the diffusion parallel to the \( c \)-axial direction to proceed via M2 \( \rightarrow V_{\text{C(O)}} \rightarrow M2 \) jump sequence of Nd, where \( V_{\text{C(O)}} \) stands for an octahedral channel, or to involve two or more consecutive jumps in the open channel before hopping into an M2 site and jumping back into the open channel again (Fig. 7a, paths a and b, respectively). (The creation of an M2 vacancy to which a Nd atom could jump into, if the appropriate M2 site is not vacant, would involve additional atomic jumps, the details of which are not important for the present purpose of qualitative discussion of diffusion pathway). On the other hand, diffusion parallel to the \( b \)-axial direction should proceed via M1/(M2) \( \rightarrow M2/(M1) \rightarrow V_{\text{C(O)}} \rightarrow M1/(M2) \) (Fig. 7a), whereas that parallel to the \( a \)-axial direction should proceed via M2 \( \rightarrow V_{\text{C(O)}} \rightarrow M2 \)
where V(M) stands for a vacancy in an M-site. If the diffusion of Nd is controlled by octahedral site hopping, then it can be shown that $D(Nd^{3+}) \propto f(O_2)^{1/6}$ (e.g. Morioka and Nagasawa, 1991). On the other hand, the jump of Nd$^{3+}$ from an octahedral site to V$_{C(O)}$ involves an exchange reaction, which, following the treatment of Dieckmann and Schmalzreid (1975) for Fe$^{2+}$ diffusion in spinel, can be written as

$$Nd(M) + V_{C(O)} \leftrightarrow Nd_{C(O)} + V(M) \quad \text{(b)}$$

Now, according to the reaction (a), increasing $f(O_2)$ raises the activity of V(M). Consequently, increasing $f(O_2)$ tends to drive the reaction (b) to the left hand side and thus works against the transfer of Nd$^{3+}$ from an M-site to the adjacent open channel. Thus, increasing $f(O_2)$ has opposing effects on two successive jumps, involving M-site vacancy and octahedral channel, along the $b$-axial direction. This explains the insensitivity of the overall value of $D(Nd/b)$ on $f(O_2)$. (The sign and magnitude of the net effect of $f(O_2)$ depend on the diffusivities associated with the M1–M2 and M–V$_{C(O)}$ jumps of Nd$^{3+}$). With the same microscopic or structural picture, we should expect the diffusivities parallel to both $a$- and $c$-axial directions to be insensitive to $f(O_2)$ as well. For $D(a/b)$, two successive jumps ($M_2 \rightarrow V_{C(O) // a} \rightarrow M_2$) should be characterized by similar jump frequencies and activation energy barriers but be affected by $f(O_2)$ in exactly opposing ways (negative effect for the first jump and positive effect for the second jump). The same picture also holds for two successive jumps along path (a) in Fig. 7a, whereas $f(O_2)$ plays no role for diffusion along path (b).

### 4. APPLICATIONS TO GEOLOGICAL AND PLANETARY PROBLEMS

#### 4.1. Melting and subsolidus cooling of mantle rock

Cherniak and Liang (2007) calculated the equilibrium length scales of REE in ortho- and clinopyroxene during melt percolation in reactive porous flow using velocity of melt transport of 0.1 m/year and 1 m/year, 1 mm grain size, and the available data on mineral-melt partition coefficients. The diffusion coefficients of the trivalent REE were taken from Van Orman et al. (2001) for clinopyroxene and from their own data for diffusion normal to (2 1 0) for orthopyroxene that are illustrated in Fig. 6. Cherniak and Liang (2007) concluded that while kinetic signatures of disequilibrium melting within a melting column in the mantle would be difficult to detect in routine ion-probe or laser ablation ICP-MS analysis of the compositional zoning of clinopyroxene, the REE$^{3+}$ ions in Opx grains would develop more easily detectable compositional zoning that could be used to extract information about disequilibrium partial melting and melt-rock reaction in the mantle. Although our data for Nd diffusion in Opx differ from those of Cherniak and Liang (2007) at subsolidus conditions, the two data sets essentially converge at conditions of partial melting (1200–1300 °C) (Fig. 6). Thus, the conclusion of Cherniak and Liang (2007) about the possible preservation...
of kinetic signatures of disequilibrium partial melting in REE$^{3+}$ in Opx seems to hold.

On the basis of their diffusion data for REE$^{3+}$ in Opx, Cherniak and Liang (2007) have also shown that Opx grains would develop “mushroom shaped” compositional profile of trivalent REE, or in other words a flat compositional profile within the interior of a grain and decreasing concentrations toward the rims (akin to the familiar retrograde zoning profile of Mg in metamorphic garnets cooled from granulite facies conditions), during subsolidus cooling of peridotites from 1400 to 1000 °C at a rate of 20 °C/Myr, with the core compositions of 2 mm (or larger) grains remaining essentially unaffected. Thus, they suggested that core compositions of REE$^{3+}$ (and also Y$^{3+}$) of relatively large (>2 mm) Opx grains may be used to retrieve information of high temperature magmatic processes, while the core–rim compositional variation of these ions, which appears to be of measurable magnitude in their simulations, may be used to infer subsolidus cooling rates of the host rocks. While this seems to be a viable and potentially rewarding approach to pursue, especially with the advent of nanoSIMS, it is emphasized here that, depending on the temperature, a core–rim compositional profile of a REE$^{3+}$ ion could have significant dependence on the crystallographic orientation of the line traverse because of the diffusion anisotropy, as demonstrated in this study. Thus, the inference about cooling rate from compositional zoning measured along a traverse normal to an interface between an Opx grain and matrix phase would be more robust if one determines the crystallographic orientation of the traverse line by EBSD (electron back scattered diffraction) study, and use the diffusion coefficient calculated from Eq. (4). This approach was followed by Costa and Chakraborty (2004) and Hewins et al. (2009) to model diffusion induced compositional zoning in olivine to infer time scales of magmatic and planetary processes, respectively. 2D mapping of concentration profiles within a grain could reveal the effect of anisotropic diffusion (e.g. Costa et al., 2008, also Fig. 9b), and modeling of these profiles would provide tight constraints on the cooling history of the host rock.

The simulations of compositional zoning of REE$^{3+}$ in Opx presented by Cherniak and Liang (2007) would be valid for somewhat different cooling rate than that used by them (20 °C/Myr), if one uses the diffusion data from this study. The readjusted cooling rate may be calculated by noting that for the type of diffusion problem considered by Cherniak and Liang (2007) that does not involve growth/dissolution of the crystals, the information that a zoning profile carries is not the time but the value of $\int D(t) dt$ (henceforth represented as $\langle D(t) \rangle$) through the time period of cooling. From the treatment of this integral quantity by Ganguly et al. (1994) and Ganguly (2002), it can be easily shown that for a given value of $\langle D(t) \rangle$ corresponding to a zoning profile, the ratio of the cooling rates corresponding to two different diffusion data sets, I and II, is given by:

$$\frac{\langle D(T) \rangle_I}{\langle D(T) \rangle_{II}} \approx \frac{(D(T_o))_I}{(D(T_o))_I} \frac{(Q(T_o))_I}{(Q(T_o))_II}$$

where $D(T_o)$ stands for the diffusion coefficient at the initial temperature (since Ganguly et al., 1994, used a nonlinear cooling model whereas Cherniak and Liang (2007) used a linear model, the above relation is valid through a temperature domain over which the $T$–$t$ relation is nearly linear from the initial temperature). Using this relation, we find that the compositional profiles in orthopyroxene calculated by Cherniak and Liang (2007), on the basis of a cooling rate of 20 °C/Myr from 1400 to 1000 °C and their diffusion data normal to (2 1 0), would be effectively valid for cooling rate of ~10 °C/Myr if one uses the $D(b/a)$ from this study or $D(\perp 2 1 0)$, calculated according to the anisotropic diffusion data presented in this study (Figs. 3 and 6). On the other hand, if the diffusion is parallel to the c-axial direction and one uses $D(c/c)$ from our study, then the cooling rate corresponding to a simulated profile of Cherniak and Liang (2007), using $D(\perp 2 1 0)$, is approximately the same as in their input value (i.e. 20 °C/Myr).

### 4.2. Closure temperature and resetting of Sm–Nd mineral age

Planetary samples are sometimes dated on the basis of whole rock-mineral Sm–Nd isochrons involving the pyroxenes (e.g. Prinzhofer et al., 1992; Shih et al., 2009). Interpretation of these ages in the context of the thermal history of parent bodies requires an understanding of the closure temperature of the Sm–Nd decay system in ortho- and clino-pyroxenes. Here we do not deal with any specific planetary problem, but present the closure temperature of Nd diffusion in orthopyroxene as function of cooling rate for specific grain size, initial temperature and crystal geometry. By analogy with the Sm and Nd diffusion data in garnet (Ganguly et al., 1998; Tirone et al., 2005), we expect Sm and Nd to have very similar diffusivities in orthopyroxene.

![Fig. 8. Illustration of closure temperature ($T_c$) of Nd diffusion (or the Sm–Nd decay system) in orthopyroxene as a function of cooling rate, grain size (0.5 mm (solid lines) and 1 mm (dashed line) radii or half-lengths), initial temperature (900 °C and 800 °C) and diffusion direction. $T_c$ for an initial temperature of 900 °C has been calculated on the basis of diffusion coefficient parallel to the $a$-axial direction that represents intermediate values between the largest and smallest diffusion coefficients, which are parallel to the $c$- and $b$-axial directions, respectively (Figs. 3 and 4). The effects of crystal geometry and grain size are illustrated by $T_c$ vs. cooling rate relation for $T_o = 900$ °C whereas that of diffusion anisotropy is illustrated for $T_o = 800$ °C, using a cylindrical geometry.](image-url)
so that the diffusive closure temperature of Nd in orthopyroxene represents its closure temperature for the Sm–Nd decay system.

No analytical formulation has yet been derived for calculating closure temperature in a mineral exhibiting anisotropic diffusion properties. Thus, we use the analytical formulation of Ganguly and Tirone (1999), which is an extension of the classic Dodson formulation (1973) for closure temperature of isotropic diffusion in crystals of different geometries, and illustrate the limiting effects of anisotropy along with the effects of grain size, crystal geometry and initial temperature on the closure temperature of Nd diffusion in orthopyroxene. The results, which are presented in Figs. 8–10, would serve as a framework for interpretation of Sm–Nd mineral age of orthopyroxene, and perhaps for pyroxenes in general, in planetary samples.

For any specific case, the closure temperature in an isotropic system may be calculated from the following relation (Ganguly and Tirone, 1999, 2001).

\[ T_c = \frac{E}{R} \left( \frac{1}{\ln M + G + g} \right) \]  

where \( G \) is a geometric parameter (Dodson, 1973) and \( g \) is a function of a dimensionless parameter \( M \) that is defined as

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Fig. 9. Three (left panels) and two (right panels) dimensional views of the simulation of the development of concentration profiles of Nd in the \( a\)-\( c \) plane at 900 °C after (a and b) 1.3 Myr and (c and d) 6.7 Myr in a \( 10 \times 10 \times 10 \) mm\(^3\) orthopyroxene crystal with initial homogeneous (unit) and fixed boundary (zero) concentration.

Fig. 10. Approximate lengths parallel to the \( c \)- and \( b \)-axial directions of orthopyroxenes (l//c and l//b, respectively) of plane sheet geometry (inset) vs. initial cooling rate such that there is no significant diffusive flux along these directions. The curves for \( T_o = 900 \) °C (l//c) and \( T_o = 800 \) °C (l//b) are essentially coincident.
\[ M = -\frac{RD(T_o)T^2}{Qa^2(DT/\partial t)_{ax}} \]  
(7)

Here \( a \) is a characteristic grain dimension (radius for sphere and cylinder, and half-length for a plane sheet). The analytical expression for \( g \) is given by Ganguly and Tirone (1999) and values of \( g \) for different values of \( M \) are tabulated by Ganguly and Tirone (2001) for three different grain geometries (sphere, infinite cylinder and infinite plane sheet). Eq. (6) was derived by assuming a nonlinear (asymptotic) \( T - t \) relation of the form:

\[ \frac{1}{T} = \frac{1}{T_o} + t \]
(8)

where \( \eta \) is a time constant with the dimension of \( K^{-1}t^{-1} \). In Eq. (7), \( dT/dt \) is a cooling rate at a specified temperature that appears in the numerator on the right hand side. The results for closure temperature calculations as function of \( T_o \), initial cooling rate, grain size, grain geometry and diffusion direction are illustrated in Fig. 8. It is clear that grain geometry has larger effect on \( T_o \) than the diffusion direction, and the latter effect is not significant at cooling rate above 20 °C/Myr. Since, according to the above cooling model, the cooling rate is proportional to \( T^2 \), the cooling rate at any temperature, \( T \), can be calculated by multiplying the cooling rate at \( T_o \) (shown as \( x \)-axis values in Fig. 8) by \((T/T_o)\eta\), with the temperatures in Kelvin.

We have calculated the evolution of compositional profile of Nd in an orthopyroxene crystal of \( 10 \times 10 \times 10 \) mm\(^3\) geometry at 1 bar, 900 °C, using the \( D(Nd) \) value calculated from the Arrhenius relations presented above. For simplicity, the initial concentration is set to unity and the boundary concentration to zero. In this case, the concentration profiles in two (or three) dimension may be expressed as the product of solutions of the one dimensional problems (Carslaw and Jaeger, 1959). The concentration profiles in the \( a - c \) plane at 1.3 and 6.7 Myr are illustrated in Fig. 9. It is clear that the simple infinite plane-sheet model is inadequate for the treatment of the overall diffusive flux out of the crystal in this simple case if the time scale exceeds a few Myr. Thus, the simulations serve to illustrate the point that \( T_o \) values for the Sm–Nd decay system in orthopyroxene calculated on the basis of infinite plane sheet model may not be applicable to natural crystals unless the horizontal and vertical lengths parallel to the planes have certain minimum values such that the fluxes along those directions are negligible compared to the flux normal to the planes.

Let us now consider an orthopyroxene crystal, as shown in the inset of Fig. 10, for which we want to evaluate the applicability of the infinite plane sheet model for the calculation of \( T_o \) using Nd diffusion data parallel to the \( a \)-axial direction, which is illustrated in Fig. 8. In order to roughly evaluate the length of the \( c \)-axial direction such that there is no significant Nd-flux along that direction, we consider a plane sheet in which, effectively, the diffusion is parallel only to the \( c \)-axis. In other words, we consider an effectively infinite plane sheet with the \( c \)-axial direction being normal to the planes. For an infinite plane sheet with homogeneous initial concentration and fixed boundary concentration, there is no significant diffusive flux normal to the planes when \( Dl^2 \leq 0.005 \), where \( l \) is the half-thickness of the plane sheet (Crank, 1975, Fig. 4.1) and \( D \) is the diffusion coefficient normal the planes. For a system subjected to cooling according to an asymptotic \( T - t \) relation (Eq. 8), \( Dl^2 \) equals \( M \) (Eq. 7) (Ganguly et al., 1994). Thus, there is no significant flux into/out of an infinite plane sheet if the thickness of the plane sheet is given by the following relation:

\[ l \geq \left( \frac{R(D(T_o))(T_o)^2}{0.005Q(DT/\partial t)_{ax}} \right)^{1/2} \]
(9)

Although we have considered above an orthopyroxene plane sheet of specific crystallographic orientation, it should be evident that Eq. (9) is a general equation that may be used to calculate the approximate minimum horizontal and vertical lengths of a plane satisfying the no-flux restriction. Thus, using the above relation and diffusion data parallel to the \( c \) and \( b \) axial directions, we have calculated the approximate minimum lengths parallel to these directions as function of \( T_o \) and initial cooling rate such that an infinite plane sheet model is satisfied for Nd closure temperature in orthopyroxene with the plate-normal direction being parallel to the \( a \)-axis. The results are illustrated in Fig. 10. If the plate-normal direction is given by the \( b \) or \( c \) axial directions, then the minimum lengths of the plate-parallel directions can be easily calculated using Eq. (9) and diffusivities along those directions.

4.3. Discrepancy between Sm–Nd mineral age and Pb-Pb age of mesosiderite

The mesosiderites are stony-iron meteorites with nearly equal amounts of metals and silicates. Bogard et al. (1990) and Mittlefehldt et al. (1998) presented critical reviews of the various hypotheses about the origin and evolution of mesosiderites. Ganguly et al. (1994) presented a two-step cooling history model of these planetary materials and discussed its implications for the size of the parent body and impact and burial history (see also Ruzicka et al. 1994). Prinzhofer et al. (1992) determined a Sm–Nd mineral age of 4470 ± 20 Ma for Morristown mesosiderites on the basis of an internal isochron defined by plagioclase, phosphate and orthopyroxene. They noted that this age is ~90 Ma younger than the U–Pb age (4560 ± 31 Ma) for the Estherville mesosiderite, determined by Brouxel and Tatsumoto (1991). The latter workers determined a Sm–Nd whole rock-mineral age for Estherville as 4533 ± 94 Ma, which is similar to the U–Pb age, but also agrees, within the limits of statistical uncertainties, with the younger Sm–Nd mineral age for the Morristown mesosiderites.

In order to explain the younger Sm–Nd mineral age of the Morristown mesosiderite relative to the U–Pb age of Estherville, Prinzhofer et al. (1992) proposed an “impulsive disturbance” model that could result from a short-lived metamorphic episode. It was proposed that the Sm–Nd isotopic compositions of plagioclase, which had the lowest \(^{143}\text{Sm}/^{144}\text{Nd} \) ratio, was disturbed after a period of closed-system growth of the \(^{143}\text{Nd}/^{144}\text{Nd} \) ratio (due to the β-decay
of $^{147}\text{Sm}$ to $^{143}\text{Nd}$ such that it achieved equilibrium (or nearly so) with phosphates that had higher $^{147}\text{Sm}/^{144}\text{Nd}$ ratio. On the other hand, the Nd isotopic ratio of orthopyroxene, which had the highest $^{147}\text{Sm}/^{144}\text{Nd}$ ratio, remained unaffected due to its relatively much slower diffusivity of Sm and Nd, as one would infer by analogy with the Sm diffusion data in clinopyroxene determined by Sneeringer et al. (1984). This effect of “impulsive disturbance”, if correct, should cause a clockwise rotation of the mineral isochron, thereby leading to an apparent younger Sm–Nd age. Ganguly and Tirone (2001) have, on the other hand, suggested that the younger Sm–Nd age of the Morristown mesosiderite could be a consequence of the difference between U–Pb and Sm–Nd closure temperatures during slow cooling of the mesosiderites. Here we revisit the problem of younger Sm–Nd age on the basis of the diffusion data of Nd in orthopyroxene and plagioclase.

Cherniak (2003) determined the Nd diffusion kinetics of plagioclase normal to (0 1 0) as function of temperature and composition at 1 bar pressure. In mesosiderites, the anorthite content of plagioclase is between 91 and 93 mol% (Mittlefehldt et al., 1998). The Nd diffusion coefficient of Plag(An93), as determined by Cherniak (2003), is compared with that in enstatite in Fig. 6. The Nd diffusion in plagioclase is expected to be anisotropic, but nonetheless, from the data summarized in Fig. 6 it seems highly unlikely that Sm–Nd isotopic ratios in plagioclase could be sufficiently disturbed without disturbing those in enstatite.

For the model of resetting of Sm–Nd mineral age by an “impulsive disturbance” at a certain time, say $t$, to work, the process must lead to the same or sufficiently similar bulk $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the different minerals such that the subsequent growth of $^{147}\text{Sm}/^{144}\text{Nd}$ ratio up to the present time defines a linear array of the data, within the resolution of mass spectrometric measurements, in a Sm–Nd isochron plot. For the ideal case of attainment of uniformity of the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio between and within the minerals at $t$, the Nd isotopic ratio needs to be completely reset or homogenized by the thermal effect of the impulsive disturbance.

The solution to the problem of progressive homogenization of a phase with isotopic diffusion property and fixed boundary concentration is given in Crank (1973) and Caruslaw and Jaeger (1959) for spherical, cylindrical and plane sheet geometries as function of a dimensionless variable $Di/a^2$, where $a$ is a characteristic length of the grain (radius for sphere and infinite cylinder and half-thickness for infinite plane sheet). For effectively complete equilibration with the matrix, $Di/a^2$ is $-0.4, 0.8$ and $1.5$ for spherical, infinite cylindrical and infinite plane sheet geometries, respectively. Using the diffusion coefficient parallel to the $a$-axis, which has an intermediate value between $Di/(jb)$ and $Di/(bc)$ (Fig. 3), we have calculated the required time scale of the supposed “impulsive disturbance” to completely reset the Sm–Nd decay system in orthopyroxene of spherical and infinite plane sheet geometries that represent the limiting cases of diffusive flux. The results are illustrated in Fig. 11. It shows that even for a short-lived metamorphic episode with a peak thermal duration of 5 Myr, the rock needs to be heated above 750°C in order to completely reset the Nd isotopic ratio. It is possible that effective uniformity of the bulk Nd isotopic ratio of the minerals could be achieved without requiring it to be uniform within individual grains. In that case, the required time scale for resetting would be somewhat shorter than that inferred from Fig. 11. However, it is still likely to be of the order of million years. It is not clear if such $T–t$ relation could be satisfied by a reasonable scenario of planetary metamorphism or thermal pulse. We, thus, explore below an alternative scenario for resetting of the Sm–Nd age during cooling that was suggested earlier by Ganguly and Tirone (2001).

The two-stage cooling model for mesosiderites of Ganguly et al. (1994) envisions a transition from very rapid cooling at an average rate of $\sim 4^\circ$C/10$^3$ year at high temperature to very slow non-linear cooling, according to the asymptotic form of the Eq. (8), at low temperature with a transition temperature ($T_{tr}$) between 500 and 850°C. They arbitrarily assumed a temperature of 1000 K (727°C) for the onset of slow cooling and suggested a cooling time constant, $\eta$, of $\sim 1.8(10^{-12})$ K$^{-1}$year$^{-1}$ that leads to a $T–t$ path satisfying a number of constraints on the cooling rates at different temperatures below 727°C.

Ganguly and Tirone (1999, 2001) developed the formulation for calculating the bulk resetting time scale of mineral age as a function of cooling rate, grain size and geometry, and initial (peak) temperature ($T_{st}$), which is as follows:

$$\Delta t = \frac{R}{Q} \left( \ln M + G + g \right)$$  (10)

Using this formulation, the $\eta$ value inferred by Ganguly et al. (1994) and Nd diffusion data parallel to $a$-axis in orthopyroxene and cylindrical grain geometry (infinite cylinder), which leads to an intermediate diffusive flux (Fig. 8) and may, thus, be viewed roughly as an average scenario, we find that resetting of Sm–Nd age of orthopyroxene by $\sim 90$ Ma could be achieved if we set the $T_{st}$ at 770°C, which falls within the $T_{tr}$-range suggested by Ganguly et al. (1994). Following the procedure of Ganguly et al. (1994), the calculated $T–t$ curve yields 138 K as the present temperature of mesosiderite. This estimate is $\sim 30$ K lower than the mean black body temperature of an object in the asteroidal belt (Wood 1964). However, it is clear that the desired
resetting of Sm–Nd age could be achieved by imposing the cooling model proposed by Ganguly et al. (1994), and without any need for “impulsive disturbance”. The values of \( \eta \) and \( T_i \) that lead to a \( T–t \) path best satisfying the mean black body temperature, resetting of the Sm–Nd age, and the constraints on cooling rate used by Ganguly et al. (1994) adhering to the diffusion data parallel to the \( a \)-axis and effectively infinite cylindrical geometry, is \( 1.65 \times 10^{-12} \) K \(^{-1}\) year\(^{-1}\) and 750 °C, respectively. This \( \eta \) value is slightly smaller (by a factor of \( \sim 0.9 \)) than that suggested by Ganguly et al. (1994). It yields a present day temperature of \( \sim 150 \) K, as compared to the mean black body temperature of 170 K and resetting of the Sm–Nd age of enstatite by \( \sim 90 \) Ma. The cooling rate corresponding to the new value of \( \eta \) (given by \( dT/dt = -\eta T^2 \)) is \( \sim 0.5 \) °C/Ma at 250 °C and \( \sim 1 \) °C/Ma at 500 °C, the latter value being compatible with the cooling rates constrained by metallocraphic data and the Fe–Mg intra-crystalline ordering data of orthopyroxenes in mesosiderites, as summarized by Ganguly et al. (1994).

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