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5 1 **Fe-Mg interdiffusion rates in clinopyroxene: experimental**  
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7 2 **data and implications for Fe-Mg exchange geothermometers**  
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43 26 *Keywords:* clinopyroxene, diffusion, thin film, geothermometry, geospeedometry, RBS, PLD  
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6 3 **Abstract**  
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9 4 Chemical interdiffusion of Fe-Mg along the c-axis [001] in natural diopside crystals ( $X_{Di}$   
10 = 0.93) was experimentally studied at ambient pressure, at temperatures ranging from 800 - 1200  
11 °C and oxygen fugacities of  $10^{-11}$  to  $10^{-17}$  bar. Diffusion couples were prepared by ablating an  
12 olivine ( $X_{Fo}=0.3$ ) target to deposit a thin film (20 – 100 nm) onto a polished surface of a natural,  
13 oriented diopside crystal using the pulsed laser deposition (PLD) technique. After diffusion  
14 anneals, compositional depth profiles at the near surface region (~ 400 nm) were measured using  
15 Rutherford Backscattering Spectroscopy (RBS). In the experimental temperature and  
16 compositional range, no strong dependence of  $D^{Fe-Mg}$  on composition of clinopyroxene (Fe/Mg  
17 ratio between  $Di_{93}$  –  $Di_{65}$ ) or oxygen fugacity could be detected within the resolution of the  
18 study. The lack of  $fO_2$ -dependence may be related to the relatively high Al content of the crystals  
19 used in this study. Diffusion coefficients,  $D^{Fe-Mg}$ , can be described by a single Arrhenius relation  
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$$D^{Fe-Mg} = 2.77 \pm 4.27 \times 10^{-7} \exp(-320.7 \pm 16.0 \text{ kJ mol}^{-1} / RT) \text{ m}^2/\text{s}.$$

45 19  $D^{Fe-Mg}$  in clinopyroxene appears to be faster than diffusion involving Ca-species (e.g.  $D^{Ca-Mg}$ )  
46 while it is slower than  $D^{Fe-Mg}$  in other common mafic minerals (spinel, olivine, garnet,  
47 orthopyroxene). As a consequence, diffusion in clinopyroxene may be the rate limiting process  
48 for the freezing of many geothermometers and compositional zoning in clinopyroxene may  
49 preserve records of a higher (compared to that preserved in other coexisting mafic minerals)  
50 temperature segment of the thermal history of a rock. In the absence of pervasive  
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1 recrystallization, clinopyroxene grains will retain compositions from peak temperatures at their  
2 cores in most geological and planetary settings where peak temperatures did not exceed ~ 1100  
3 °C (e.g. resetting may be expected in slowly cooled mantle rocks, many plutonic mafic rocks, or  
4 ultra-high temperature metamorphic rocks).

6 **Introduction**

7 Clinopyroxene is a common constituent of many igneous, metamorphic and mantle  
8 derived rocks and it is frequently found in extra-terrestrial samples (e.g. silicate meteorites from  
9 asteroids, the moon and Mars). Chemical compositions of clinopyroxenes are important  
10 indicators of magmatic and metamorphic evolution. Partitioning of Fe and Mg between  
11 clinopyroxene and many coexisting phases (e.g. orthopyroxene, garnet, olivine, spinel, or melt)  
12 is temperature dependent and can be used as geothermometers (e.g., Wood and Banno 1973;  
13 Råheim and Green 1974; Wells 1977; Ganguly 1979; Pattison and Newton 1989; Green and  
14 Adam 1991; Perkins and Vielzeuf 1992; Loucks 1996; Zack, et al. 1997; Ravna 2002; Putirka, et  
15 al. 2003). The fact that clinopyroxenes are frequently chemically zoned additionally opens up the  
16 prospect of using these for tracking the thermal evolution in diverse settings. However, their  
17 utility in this regard is compromised by the fact that interdiffusion rates of Fe-Mg in  
18 clinopyroxenes have not yet been experimentally measured. We have undertaken an  
19 experimental study making use of silicate thin films that are tens of nanometers thick, and  
20 analytical techniques that can resolve compositional profiles on this scale. In this paper we report  
21 diffusion data in the geologically relevant temperature range of 800 – 1200 °C from experiments  
22 carried out at atmospheric pressure under controlled oxygen fugacity conditions. We use our  
23 diffusion data to evaluate the conditions at which Fe-Mg exchange geothermometers involving

1 clinopyroxene may be expected to preserve temperatures without resetting; and in cases where  
2 resetting does occur, we consider the cooling rate information that might be extracted from the  
3 frozen zoning profiles.

## 4 **Experimental and analytical methods**

### 5 *Experimental setup*

6 Natural crystals of gem quality clinopyroxene (cpx 2, purchased from Excalibur Minerals  
7 and reported to be from Rajasthan, India) were used for the diffusion experiments.  
8 Representative compositions of the clinopyroxene crystals determined with the electron  
9 microprobe at the Ruhr-Universität Bochum are shown in Table 1. The average composition  
10 yields  $Ca_{0.98}Na_{0.02}Mg_{0.88}Fe_{0.02}^{2+}Fe_{0.04}^{3+}Al_{0.04}^{VI}Si_{1.93}Al_{0.07}^{IV}O_6$ . Although the analyses exhibit some  
11 heterogeneity in the Al-content, the Fe-Mg ratio seems to be constant and reveals a near end-  
12 member Fe-rich diopside composition of  $Di_{93}$ . Slices of about 2 mm thickness, approximately  
13 perpendicular to the c-axis, were cut out of the original cpx crystals (~ 1cm in diameter). The  
14 slices were polished progressively down to finer grit sizes using diamond compounds, followed  
15 by a final chemical-mechanical polishing step using colloidal silica. Finally, the polished slices  
16 were cut into squares of about 2 mm<sup>2</sup> (surface area of polished side) using a high precision  
17 diamond wire saw.

18 Finding a suitable source material for the diffusion experiments turned out to be  
19 problematic. Thin films deposited by pulsed laser deposition are originally amorphous and  
20 recrystallize in the early stages of the diffusion anneal, resulting in different microstructures  
21 depending on the composition, film thickness and temperature (e.g., Dohmen, et al. 2007;  
22 Watson and Dohmen 2010). In our case, thin films of a clinopyroxene composition have poor  
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1 wetting properties and on annealing they produce isolated, nanoscale, islands of clinopyroxene  
2 (of a different composition) on the surface of the crystal in a “bed of thorns” structure (see  
3 Watson and Dohmen 2010; figure 6). Therefore, we chose to use source materials of an olivine  
4 composition (Fo<sub>30</sub>). In our earlier studies (Dohmen, et al. 2007; Dohmen 2008) we have found  
5 that olivine thin films produce dense, continuous coverage on a variety of mineral substrates.  
6 This was found to be the case for clinopyroxene as well. A dense, polycrystalline (with grain size  
7 of about a micrometer) film of Fe-rich olivine therefore acted as the diffusive exchange partner  
8 for clinopyroxene (Fig. 1). It is important to note, however, that Dohmen et al. (2007) thoroughly  
9 investigated the geometry and chemistry of deposited olivine thin films and found a slight excess  
10 in SiO<sub>2</sub>, i.e. a systematic deviation in stoichiometry from an ideal olivine. Thus, it is likely that  
11 initial recrystallization of the thin film produced some orthopyroxene by the reaction of olivine  
12 and excess SiO<sub>2</sub> as observed by Dohmen et al. (2007). There are additional complexities that  
13 needed to be addressed in the design of these diffusion experiments. The film thickness had to be  
14 optimized such that there was enough material in the films to produce well resolved diffusion  
15 profiles, but that the film thickness or profile lengths of Fe were not long enough to be affected  
16 by overlap with Ca peaks in a RBS spectrum (see below and fig. 2). After several trials and error,  
17 it was found that film thicknesses between 20 and 100 nm fulfill these conditions. Olivine thin  
18 films (Fo<sub>30</sub>) of such thickness were produced by pulsed laser deposition (PLD) in our laboratory  
19 following procedures that have been described in detail in Dohmen et al. (2002) and Dohmen et  
20 al. (2007). Each deposition run was used to coat 2-6 samples. At least one crystal from each set  
21 was used as a reference sample to check the thickness and composition of the deposited layer.  
22 Measured thicknesses of thin films of reference samples ranged between 20-60 nm. In an earlier  
23 study, Dohmen et al. (2002) demonstrated that there is no detectable variation in composition

1 and less than 10 % variations in the thickness of the deposited layer within 5 mm<sup>2</sup> for samples  
2 placed in different positions in the central part within the vacuum chamber. Prior to the  
3 deposition the clinopyroxene crystals were heated up to approximately 600°C in vacuum for 10-  
4 15 minutes to degas any volatile adsorbents on the sample surfaces. Deposition times varied  
5 typically between 8 and 15 minutes depending on the actual measured intensity of the laser  
6 during the coating using a pulsed (10Hz, 20KV) UV laser with a wavelength of 193nm.

### 7 8 *Diffusion anneals*

9         Samples were annealed for 10–400 hours at 800–1200°C in gas mixing furnaces at one  
10 atmosphere total pressure in a continuous flow of a CO-CO<sub>2</sub> gas mixture under controlled  
11 oxygen fugacity. Temperatures were monitored continuously using a type B thermocouple and  
12 uncertainties arising from both, accuracy of the thermocouple as well as temperature variations  
13 during an experimental run, fall within ±2°C. Counting the diffusion anneal time was started  
14 when the run temperature of an experiment was reached. This was typically achieved within less  
15 than 10 minutes of insertion of the sample in the furnace. The time to attain anneal temperatures  
16 is assumed to be negligibly small compared to the overall run durations and no corrections are  
17 made for this. The oxygen fugacity was measured with a *f*O<sub>2</sub>-sensor made of yttria stabilized  
18 zirconia and is accurate within ±0.1 log units. Experiments were carried out at different partial  
19 pressures of oxygen between 1x10<sup>-11</sup> to 1x10<sup>-17</sup> bar over a range of temperatures. A summary of  
20 the experiments and details of the run conditions are provided in table 2. In order to test the  
21 reproducibility of our results, we performed a time series of experiments at 1000°C (6 – 40  
22 hours; fig. 3). A “zero-time” experiment (heating up to 1000 °C and removing the crystal  
23 instantaneously from the furnace) was carried out to test if any modifications of the film

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1 occurred during heating and cooling. After the diffusion anneals, samples were quenched by  
2 removing them from the furnace and cooling in air. The crystals were washed in an ultrasonic  
3 bath with distilled water, acetone and ethanol to clean the surface and run products were  
4 eventually inspected optically before measuring concentration profiles using RBS.

6 *Rutherford Backscattering Spectroscopy (RBS)*

7 In order to measure the nanoscale diffusion profiles that were induced in our experiments  
8 we used the non-destructive method of Rutherford Backscattering Spectroscopy (RBS) that  
9 allows both, the composition profile as well as the thickness of the film to be determined (see  
10 Feldmann 1986 for a review of the method). RBS analyses for this study were performed at the  
11 Dynamitron Tandem Accelerator facility of RUBION at the Ruhr-Universität Bochum. We used  
12 a 2 MeV beam of  $\alpha$ -particles that was focused onto the sample surface using a final aperture of  
13 0.5 mm in diameter. This setup allows measuring profiles from a surface area as small as 1 mm<sup>2</sup>  
14 on the polished sample. Acquisition conditions were chosen as follows: The beam current was in  
15 a range between 20 and 50 nA. The back-scattered particles were detected at an angle of 160° at  
16 an energy resolution of 16 – 20 keV. The sample was tilted slightly relative to the beam (~5°) for  
17 the acquisition to avoid channeling along a crystallographic axis. Concentration-depth profiles of  
18 Fe and Ca were extracted using the program RBX (Kótai 1994). Representative spectra and  
19 concentration-depth profiles (up to 400 nm) for Fe extracted from them are shown in Fig. 2&4  
20 for a sample before and after the diffusion anneal. A detailed description of the procedure  
21 followed for processing of RBS data in our laboratory is available in Dohmen et al. (2002; 2007).

23 *Determining diffusion coefficients*

1 The diffusion profiles in our experiments develop due to diffusion from a finite source of  
2 known concentration and thickness into an infinite medium with known initial concentration.  
3 There are possibilities that (a) diffusion rates in the film and the medium ( $C_{px}$ ) are different, (b)  
4 there is a compositional jump due to element partitioning at the film / crystal interface, and (c)  
5 diffusion rates are dependent on the concentration of the diffusing species i.e. Fe and Mg in this  
6 case. Additionally, if there is a compositional jump due to element partitioning at the film /  
7 crystal interface, the possible role of convolution in smearing out this discontinuity (Ganguly, et  
8 al. 1988) needs to be accounted for. Lovering (1936) developed an analytical solution for the  
9 simplified case of no compositional dependence of diffusivity and no partitioning between the  
10 film and substrate ( $K_D=1$ ) (see also Watson and Dohmen 2010 (eqns. 5-7) for details):

$$\frac{C_f(x,t) - C_s^0}{C_f^0 - C_s^0} = -\frac{1+p}{2} * \operatorname{erf}\left(\frac{x}{2\sqrt{D_f t}}\right) + \left(\frac{1+p}{2}\right) * \sum_{n=1}^{\infty} (-p)^{n-1} \left[ \operatorname{erf}\left(\frac{dn+x}{2\sqrt{D_f t}}\right) - p * \operatorname{erf}\left(\frac{dn-x}{2\sqrt{D_f t}}\right) \right]$$

and the equivalent expression for the concentration in the substrate (s):

$$\frac{C_s(x,t) - C_s^0}{C_f^0 - C_s^0} = -\frac{1+p}{2} * \operatorname{erf}\left(\frac{x}{2\sqrt{D_s t}}\right) + \left(\frac{1+p^2}{2}\right) * \sum_{n=1}^{\infty} (-p)^{n-1} \operatorname{erf}\left(\frac{d\sqrt{D_s/D_f}n+x}{2\sqrt{D_s t}}\right)$$

$$\text{With: } p := \frac{\sqrt{D_f D_s} - \sqrt{D_s D_f}}{\sqrt{D_f D_s} + \sqrt{D_s D_f}}$$

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1 These equations can be used to calculate concentration profiles in the film (*f*) and substrate (*s*)  
2 for the known initial concentrations at time = 0 ( $C_f^0$  and  $C_s^0$ ) and run durations (*t*), with diffusion  
3 coefficients ( $D_f$  and  $D_s$ ) as the only variable(s) (using  $d = 2 * \text{film thickness.}$ ). The calculated  
4 profiles may then be compared with the measured profiles and the diffusion coefficients varied  
5 until the best possible description of the measured profile shape is obtained. Alternately,  
6 numerical finite difference schemes may be used to calculate simulated profiles accounting for  
7 features such as partitioning at the film / crystal interface, convolution, and different diffusion  
8 rates in the film and the crystal. We have used both approaches to study the implications for  
9 retrieved diffusion coefficients (Fig. 4a).

10  
11 On the one hand, it is shown that the entire profile, i.e. the segment within the substrate as well  
12 as that within the thin film can be nicely described by the analytical solution given above and the  
13 diffusion coefficient in the clinopyroxene can be determined. Such a solution is shown in figure  
14 4a for sample 07-CPX-05. On the other hand, the measured Ca and Fe concentrations within the  
15 thin film permit the possibility that there is a compositional jump at the interface, and mixed  
16 analyses (i.e. convolved profiles) are extracted from the RBS spectra in the area around the  
17 interface. Plotting the data on a ternary diagram to visualize the exchange vectors (Fig. 4b)  
18 underscores this possibility. Hence, the extracted profile might also be the result of convolution  
19 of a profile showing a compositional jump due to element partitioning at the interface. Given that  
20 the thin film is a mixture of olivine + orthopyroxene, it is difficult to calculate an exact partition  
21 coefficient. However, the extracted profile gives the concentration in atomic percent iron in the  
22 thin film or the substrate respectively. Hence, the apparent partition coefficient between bulk thin  
23 film and substrate can be defined as

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$$K_P^{Fe} = \frac{at.\%Fe^{film}}{at.\%Fe^{substrate}}$$

For a given stoichiometry, as in the case of clinopyroxene substrate, this can be translated into atoms per formula unit as shown in figure 4b. The thin film, in contrast, consists of a mixture of olivine and orthopyroxene and thus the relative proportions of ol and opx as well as the different atomic ratios based on mineral formula needs to be taken into account. Therefore, we have explored the effects of somewhat extreme values of the effective partition coefficient ranging between 2 and 4 within the temperature range of the experiments. A hypothetical profile calculated using a finite difference scheme with the same, known initial concentrations, fast diffusion in the thin film, and a partition coefficient of 2 at the interface is shown in figure 4a. The profile is convolved for an effective spatial resolution of 20 nm ( $= 1\sigma$ ), and compared to the measured data as well as the analytical solution for the simplified case in figure 4a. It is found that while the overall profile shapes differ in detail, most of the difference lies in how compositions within the thin film are described. In particular, the diffusion coefficient in clinopyroxene is constrained primarily by the length of the profile within the clinopyroxene, and the values retrieved using the two approaches are indistinguishable from one another. This insensitivity to the choice of boundary conditions arises in this case because the film is thin, and the difference between profiles calculated using the two sets of boundary conditions are not pronounced (Fig. 4a). Therefore, we have used the analytical solution to determine diffusion coefficients from all our experimental runs and the results are reported in Table 2.

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4 1 We have analyzed some of the samples before and after the diffusion anneals in order to  
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6 2 determine the exact thickness of the source layer for each sample, and in order to document its  
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8 3 compositional evolution more accurately. This approach served one very critical purpose. Mass  
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10 4 balance could be verified for the experimental runs, i.e. the amount of Fe lost from the films was  
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12 5 matched by the amount of Fe that was found to have entered the clinopyroxene crystals by  
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14 6 diffusion. This is an added, quantitative check (in addition to optical observations and  
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16 7 observations of selected samples in SEM) that there are no unaccounted sources / sinks of Fe, i.e.  
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18 8 no process other than diffusion (e.g. chemical reaction, precipitate formation) affected our  
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20 9 samples. This is important for diffusion studies in clinopyroxene where phenomena such as early  
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22 10 partial melting (EPM) and formation of precipitates (Jaoul and Raterron 1994) are known to  
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24 11 occur.  
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### 33 **Results**

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36 14 Fits to the RBS spectra allowed us to extract compositional profiles of Fe and Ca;  
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38 15 compositional profiles of Mg were inferred from stoichiometry. It is found that in almost all  
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40 16 experiments, the process we observed was a pure Fe-Mg exchange and therefore, the diffusion  
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42 17 coefficient that is determined in these experiments is  $D^{\text{Fe-Mg}}$ , the chemical diffusion coefficient  
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44 18 for Fe-Mg exchange (Fig. 4b). In six experiments out of 23, slight concentration gradients of Ca  
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46 19 developed as well, indicating a ternary multicomponent exchange process. However, results from  
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48 20 these experiments lie on the same trend as data from all other runs and therefore these are not  
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50 21 treated differently in this study. Strictly speaking, an effective binary Fe-Mg diffusion coefficient  
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52 22 is obtained from these runs. The ability to describe the observed profile shapes using a constant  
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54 23 diffusion coefficient (in the analytical or the numerical solution) for clinopyroxene indicates that  
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1 the compositional dependence of diffusivity is limited (not resolvable in the form of asymmetry  
2 of profile shapes within the resolution of our measurement) over the range of compositions  
3 spanned by the concentration profiles. The compositional range of clinopyroxene for which  
4 diffusion coefficients are determined may be obtained by two methods: (a) Using the known film  
5 thickness to determine which part of the profile lies within the clinopyroxene and (b) using  
6 compositional vectors and assumed partition coefficients, such as those illustrated in Fig. 4b.  
7 Using either approach, we estimate the compositional range to be between  $Di_{93}$  and  $Di_{65}$ . Fe-Mg  
8 diffusion coefficient in clinopyroxene appears to be insensitive to composition over this range.

9 The time series of experiments carried out at 1000 °C (Fig. 3 and Table 2) indicate that  
10 reproducibility of diffusion coefficients is within 0.4 log units for our experiments. This is taken  
11 to be the uncertainty on the determination of diffusion coefficients in this study. The uncertainty  
12 could be a little higher even for runs at lower temperatures with substantially shorter profile  
13 lengths or where there is considerably overlap of Fe and Ca signals (e.g. run 07-CPX-06).

14 All data are plotted on an Arrhenius diagram in figure 5. We find that for experiments  
15 carried out at any given oxygen fugacity, diffusion rates decrease systematically with  
16 temperature. It is not possible to carry out experiments over the entire temperature range of this  
17 study using the same oxygen fugacity because neither the stability of clinopyroxene (as a  
18 function of  $fO_2$ ) nor the range of  $fO_2$  accessible by mixing CO and CO<sub>2</sub> (experimental constraints  
19 of our system) permit that. Within the uncertainties quoted above, diffusion coefficients  
20 determined at different  $fO_2$  at a single temperature (950, 1000, 1100 °C) are similar to each other  
21 (Table 2, Fig. 6), Therefore, we consider  $\log D^{Fe-Mg}$  to be insensitive to  $fO_2$  between  $fO_2 = 1 \times 10^{-11}$   
22 and  $1 \times 10^{-17}$  bar within the resolution of this study. Diffusion coefficients from experiments at  
23 all oxygen fugacities were considered together to obtain the temperature dependence of diffusion

1 coefficients. All data obtained between 800 – 1200 °C could be fitted to a single Arrhenius  
2 expression [ $D = D_0 \exp (-Q/RT)$ , where  $D_0$  is a pre-exponential factor and  $Q$  is an activation  
3 energy,  $R$  is the universal gas constant and  $T$  is the absolute temperature] to yield  $D_0 = 2.77$   
4  $(\pm 4.27) \times 10^{-8}$  m<sup>2</sup>/sec and  $Q = 320.7 (\pm 16.0)$  kJ/mol. The fit, with an estimated uncertainty  
5 envelope, is shown in figure 5b. Within the temperature range of the experiments, the Arrhenius  
6 expression reproduces the measured diffusion coefficients within 1 log unit. These parameters  
7 are valid for Fe-Mg diffusion along the c-axis of a clinopyroxene crystal. Previous studies have  
8 found some anisotropy for Mg and Ca tracer diffusion (Zhang, et al. 2010), but diffusion along c-  
9 axis is always fastest. Possible effects of diffusion anisotropy have not been explored in this  
10 study.

## 11 12 **Comparison with previous studies**

13 In spite of the wide interest in the diffusion rates of Fe-Mg in clinopyroxenes (e.g., Frost  
14 and Chacko 1989; Pattison, et al. 2003; Krogh Ravn and Terry 2004), no direct experimental  
15 determination of this rate is available for comparison. Comparison of profile lengths in  
16 clinopyroxene crystals coexisting with crystals of garnet, olivine or orthopyroxene (Smith and  
17 Wilson 1985) or inferences from the width of exsolution lamellae in natural pyroxenes from the  
18 Bushveld complex (Rietmeijer and Champness 1982; Rietmeijer 1983) indicate that diffusion in  
19 clinopyroxene is expected to be slow compared to other ferromagnesian minerals. Rietmeijer  
20 (1983) estimates the value of  $D^{\text{Ca-(Fe-Mg)}}$  to lie between  $6 \times 10^{-24}$  and  $2 \times 10^{-21}$  m<sup>2</sup>/s at 900 °C,  
21 which is consistent with the results of this study (Fig. 5, Table 2). A compilation and discussion  
22 of all diffusion data in clinopyroxene is available in Cherniak and Dimanov (2010).  
23 Experimental studies of chemical diffusion of major divalent elements in clinopyroxene that

1 could be compared to the results of the present study include Ca-(Mg+Fe) (1100 - 1250 °C;  
2 Brady and McCallister 1983), (Fe+Mn)-Mg (900 - 1240 °C; Dimanov and Sautter 2000; 1000 -  
3 1200 °C; Dimanov and Wiedenbeck 2006) and Ca-Mg (950 - 1150 °C; Zhang, et al. 2010). In  
4 addition, there is one study published in abstract form, which gives a single value of Ca-(Mg+Fe)  
5 interdiffusion at 1100 °C (Fujino, et al. 1990). All of these data are compared in figure 7.

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7 Our results are practically identical to the data of Dimanov and Wiedenbeck (2006) ((Fe+Mn)-  
8 Mg) diffusion) within the experimental range, although the activation energy obtained by them  
9 from experiments carried out over a smaller temperature range is slightly lower (297 kJ/mol vs.  
10 320 kJ/mol in this study). However, these authors observed a dependence of the interdiffusion  
11 coefficient on  $fO_2$  (Fig. 6), which is in contrast to our results. Dimanov and Wiedenbeck (2006)  
12 found the (Fe,Mn)-Mg interdiffusion coefficients to be independent of  $fO_2$  only at partial oxygen  
13 pressures above  $1 \times 10^{-7}$  or below  $1 \times 10^{-15}$  bar. In the range in between, their experimental  
14 results indicate a decrease of the diffusion coefficients by about two log units with decreasing  
15  $fO_2$ . We plotted their data points for (Fe,Mn)-Mg interdiffusion at 1100 °C in figure 6 for  
16 comparison with our data. Inspection of figure 6 reveals that extracted diffusion coefficients  
17 from our experiments (Fe-Mg interdiffusion at 1100 °C with  $\log D^{Fe-Mg} \approx -18.7$  at  $fO_2 = 1 \times 10^{-11}$   
18 bar) are practically indistinguishable from their value ( $\log D^{(Fe,Mn)-Mg} = -18.65$ ) at  $fO_2 = 1 \times 10^{-9}$   
19 bar. Furthermore, the derived diffusion coefficients are in agreement with their data even for  
20 oxygen fugacities  $\geq 1 \times 10^{-11}$  bar if the analytical uncertainties are taken into account. They  
21 explained the observed dependence of diffusivity on  $fO_2$  using a point defect model in which,  
22 simply speaking,  $Fe^{2+}$  oxidizes with increasing  $fO_2$  to form  $Fe^{3+}$  and a vacant metal site to  
23 maintain charge balance. Consequently, diffusion rates increase with  $fO_2$ , and the  $fO_2$ -

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4 1 dependence is a function of the iron-content of clinopyroxene. We note that the Fe-content of the  
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6 2 clinopyroxenes used as starting materials in our study and those of Dimanov and Wiedenbeck  
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8 3 (2006) are very similar. On the other hand, there is a marked difference in the Al content of the  
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10 4 pyroxenes used in the two studies. Incorporation of tetrahedrally coordinated Al in the  
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12 5 clinopyroxene structure needs to be charge balanced, for example, by the presence of Fe<sup>3+</sup> on  
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14 6 the octahedrally coordinated metal sites. In the event that high Al-concentrations are dominantly  
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16 7 charge balanced by Fe<sup>3+</sup> in the initial clinopyroxene structure, variation of  $fO_2$  and the resulting  
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18 8 change in concentration of Fe<sup>3+</sup> does not have any significant influence on vacancy  
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20 9 concentrations and hence, on diffusion rates. Our clinopyroxene contains ~0.1 atoms of Al per  
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22 10 formula unit, whereas the starting material used by Dimanov and Wiedenbeck (2006) is almost  
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24 11 Al-free. It is therefore likely, that the difference in  $fO_2$  dependence of diffusion rates observed in  
25  
26 12 the two studies may be attributed to the different Al-contents of the pyroxene crystals used in the  
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28 13 two studies. The higher Al content of the pyroxenes used by us would have produced charge  
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30 14 compensating Fe<sup>3+</sup> that overwhelmed the concentration of vacancies generated by oxidation of  
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32 15 Fe<sup>2+</sup>. If this explanation is correct, then in the terminology of Dohmen and Chakraborty (2007),  
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34 16 diffusion in the study of Dimanov and Wiedenbeck (2006) was in the transition metal extrinsic  
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36 17 (TaMED) regime whereas diffusion in our study was by a pure extrinsic diffusion mechanism  
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38 18 (PED). An experimental study with pyroxene crystals containing a range of Al-contents for the  
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40 19 same (or similar) Fe-contents would help to clarify and quantify this aspect.

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42 20 Ca-(Mg+Fe) or Ca-Mg exchange in clinopyroxene (Brady and McCallister 1983; Zhang,  
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44 21 et al. 2010) appear to be consistently slower than Fe-Mg exchange rates within the temperature  
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46 22 ranges of measurement. Arrhenius fits to data from these studies over smaller temperature ranges  
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48 23 (1100 – 1250 °C for Brady and McCallister, 1983 and 950 – 1150 °C for Zhang et al., 2010)

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4 1 yield somewhat different activation energies. As a result, the data of Zhang et al. (2010) would  
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6 2 imply that Ca-Mg and Fe-Mg diffusion rates might be similar at temperatures of 900 – 700 °C,  
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8 3 which are relevant for metamorphic petrology. At lower temperatures, Ca-Mg diffusion would  
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10 4 even be faster than Fe-Mg diffusion according to these results. However, low temperature  
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12 5 determinations of Ca-Mg diffusion rates and additional constraints on the activation energy are  
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14 6 required for establishing such trends.

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19 7 It is noteworthy that the data from this study could be described by a single set of  
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21 8 Arrhenius parameters over the entire temperature range (800 – 1200 °C) of this study and this  
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23 9 range includes the point (1100 – 1150 °C) where breaks in slopes were observed for Ca tracer  
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25 10 diffusion in diopside (e.g., Dimanov, et al. 1996). The significance of this break in slope (change  
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27 11 in mechanism? Early partial melting?) remains a topic of discussion (e.g. see Cherniak and  
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29 12 Dimanov 2010). However, this aspect as well as the comparison with Ca-Mg(+Fe) diffusion  
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31 13 rates discussed above indicate that the diffusion behavior of Fe-Mg exchange is distinct from  
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33 14 cases where Ca, the larger M2 cation in the pyroxene structure, plays a prominent role. This may  
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35 15 bear important implications for the closure of different geothermometers involving cpx,  
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37 16 depending on whether Fe-Mg or exchange of a Ca-bearing component is involved.

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43 17 Fe-Mg diffusion rates in clinopyroxene may be compared with experimentally  
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45 18 determined Fe-Mg diffusion rates in related mafic minerals. We compare Fe-Mg diffusion rates  
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47 19 in spinel (Liermann and Ganguly 2002), olivine (Dohmen, et al. 2007), garnet (Borinski, et al.  
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49 20 2012) and orthopyroxene (Dohmen et al., *in prep.*) in figure 8. The data are illustrated for typical  
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51 21  $X_{\text{Fe}}$ -contents of coexisting mafic minerals and a  $fO_2$  of  $1 \times 10^{-12}$  bar where a  $fO_2$ -dependence is  
52  
53 22 relevant. It is found that  $D^{\text{Fe-Mg}}$  decreases in the order spinel > olivine > garnet ~ orthopyroxene  
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55 23 > clinopyroxene. Diffusion in clinopyroxene is therefore rate limiting and may be responsible for  
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1 the freezing of many geothermometers (e.g. in eclogites). Similarly, of all the common  
2 ferromagnesian minerals, clinopyroxene is expected to preserve the highest temperature record in  
3 any given situation.

4  
5 **Implications for geothermometry, geospeedometry and timescales of geological and**  
6 **planetary processes**

7 Compositions of clinopyroxenes are widely used in geothermometers because the  
8 partitioning of Fe and Mg between clinopyroxene and common rock forming mafic minerals  
9 (e.g. garnet, olivine, spinel, orthopyroxene) and melts often depends strongly on temperature. So  
10 it is necessary to identify sets of conditions (peak temperatures, cooling rates, grain size) for  
11 which information from the peak of a thermal history would be retained in crystals of  
12 clinopyroxene. If the compositions are reset, it is necessary to evaluate by how much. As  
13 discussed above, the diffusion rates of Fe-Mg in the exchange partners of cpx may be only  
14 slightly (e.g. in orthopyroxene, garnet) or considerably (e.g. olivine, spinel, melt) faster than in  
15 cpx. Consequently, a formulation such as Dodson (1973) or its modifications (e.g., Dodson 1986;  
16 Ganguly and Tirone 1999) that assumes exchange with an effectively infinite reservoir cannot be  
17 used to evaluate the compositional resetting of clinopyroxene. Evaluation of recorded  
18 temperatures by element exchange is further complicated by the different grain sizes, modal  
19 abundances and transport properties along grain boundaries in natural rocks (e.g., Eiler, et al.  
20 1994). Ganguly et al. (2013) stated in a different context that there is no analytical solution to  
21 cover all possibilities that may arise in such a two phase, non-isothermal exchange problem and  
22 that it is necessary to use numerical tools. We consider some illustrative examples here using a  
23 numerical method to provide some sense of where resetting may be expected. We model

1 diffusive exchange between two adjacent phases i.e. we assume that there is no / negligible  
 2 interface resistance. However, Dohmen and Chakraborty (2003) and Müller et al., (2010) have  
 3 shown that even when the phases exchanging Fe-Mg are not in mutual contact, the development  
 4 of compositional zoning in a phase such as clinopyroxene will often be determined by the  
 5 diffusion rates in the phase with the slowest diffusion coefficient i.e. clinopyroxene, for  
 6 comparable grain sizes and modal abundances of exchanging mineral phases (most common  
 7 mineralogical situations). Therefore, our results will also be applicable to many situations where  
 8 diffusive exchange occurs between phases that are not immediately adjacent to each other as in  
 9 the model calculations.

10 We solve the diffusion equation

$$\left( \frac{\partial C_{Fe/Mg}}{\partial t} \right)_{\alpha} = \frac{\partial}{\partial X} \left( D_{Fe-Mg}^{cpx} \left( \frac{\partial C_{Fe/Mg}}{\partial X} \right)_{\alpha} \right)$$

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 13 in two adjacent phases (where each phase is denoted by  $\alpha$ ) using a finite difference scheme. The  
 14 concentration distribution is taken to be initially homogeneous in both phases. Concentrations at  
 15 the interface between the two phases are set by partitioning using

$$K_D^{grt-cpx} = \frac{\left( Fe/Mg \right)_{grt}}{\left( Fe/Mg \right)_{cpx}} = f(T),$$

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 17  
 18 where  $K_D$  is the equilibrium partition coefficient. For the purpose of this study, we use the  
 19 temperature and pressure dependent expression for  $K_D$  between garnet and clinopyroxene  
 20 derived by Ganguly et al. (1996). As will be seen below, the choice of garnet as an illustrative

1 exchange partner allows us to infer the behavior of several other phases. Mass balance is  
2 maintained at the interface using

$$D_{Fe-Mg}^{grt} \left( \frac{\partial C_{Fe/Mg}}{\partial X} \right)_{grt} = D_{Fe-Mg}^{cpx} \left( \frac{\partial C_{Fe/Mg}}{\partial X} \right)_{cpx}$$

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6 The temperature and compositionally dependent interdiffusion coefficients for Fe-Mg in garnet  
7 have been calculated using the data of Borinski et al. (2012). The Fe-Mg interdiffusion data for  
8 cpx are from this study. Concentration profiles are calculated iteratively, where the partition- and  
9 diffusion- coefficients are updated at each time step to correspond to the temperature attained at  
10 that time according to the prescribed cooling rate. The results are presented as final, frozen  
11 concentration profiles (Fig. 9) as well as in the form of temperatures that would be calculated  
12 (Fig. 10) using the geothermometer by pairing either the compositions at the core of each crystal  
13 (under the assumption that they have not been reset, referred to as *core-core* temperatures  
14 henceforth), or the compositions at the rims of the two crystals (*rim-rim* thermometry). See  
15 Onorato et al. (1981) for more details on the evolution of calculated temperatures at different  
16 points of the crystal in such a cooling system.

17 We consider two examples for peak temperatures corresponding to cases that may arise  
18 in mantle (1300 °C) and crustal metamorphic (900 °C) samples, respectively. For our illustrative  
19 examples we consider grains that are 0.2, 1, and 4 mm in diameter. Larger grains will retain peak  
20 concentrations at the core for longer times whereas smaller grains would be reset sooner. We  
21 illustrate the evolution of compositional profiles for cooling rates between 10 °C/my and 1000  
22 °C/my. In our model garnet crystals have an initial  $X_{Fe} = 0.3$  and  $X_{Mg} = 1 - X_{Fe}$ . Clinopyroxene  
23 compositions are chosen to be in equilibrium at the initial temperature of a model calculation.

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1 The boundary conditions in our numerical code imply equilibrium conditions at the interface (i.e.  
2 the boundary node) at every time. Therefore, rim compositions for calculating rim-rim  
3 temperatures are taken from the first interior node, i.e. about 2-3  $\mu\text{m}$  away from the interface,  
4 which is also a reasonable proxy for typical electron microprobe analyses.

5         Considering the “mantle samples” first, we find that on cooling from 1300  $^{\circ}\text{C}$  the initial,  
6 peak compositions are not retained in both garnet and clinopyroxene for even the very fastest  
7 cooling rates on the order of 1000  $^{\circ}\text{C}/\text{my}$ . For slower cooling rates, garnet homogenizes  
8 completely and adjusts compositions to lower temperatures during cooling. As a result, core  
9 temperatures of only 1100  $^{\circ}\text{C}$  (for 100  $^{\circ}\text{C}/\text{my}$  cooling rate) or lower can be retained; the rim  
10 compositions freeze at an even later stage of cooling and indicate temperatures on the order of  
11 900  $^{\circ}\text{C}$  for the cooling rates considered in this study. In contrast, the “crustal samples”,  
12 commencing cooling from a lower temperature, are able to retain compositions from the peak  
13 temperature at the core. For only very slow cooling rates (or for smaller grains, on the order of  
14 200  $\mu\text{m}$ ) are the core compositions reset. Rim compositions are reset here as well, and indicate  
15 temperatures of 550 – 600  $^{\circ}\text{C}$  for the cooling rates used in our simulations.

16         We can now use our knowledge of Fe-Mg diffusion rates in other phases (Fig. 8 and  
17 discussion above) to evaluate how geothermometers involving those phases may behave. As core  
18 compositions in garnets tend to get reset for all but the slowest cooling rates and the lower peak  
19 temperature, the core compositions of all phases (e.g. olivine, spinel, melt – all of which have  
20 much faster diffusivity) other than orthopyroxene will be reset in most situations (excepting  
21 extremely rapid cooling, as in volcanic systems, or where unusually large grain sizes are  
22 involved). Opx-Cpx pairs are the most refractory and may preserve compositions from the peak  
23 conditions in many cases where the peak temperatures did not exceed 1100  $^{\circ}\text{C}$ .

1 Summarizing, we can conclude that in the absence of pervasive recrystallization,  
2 geothermometers involving clinopyroxene hold the potential to record the peak temperature  
3 conditions from most settings, with the exception of a few extremes such as slowly cooled  
4 mantle or ultra-high temperature metamorphic samples. Compositional zoning would develop at  
5 the rims of clinopyroxenes in these cases, and these offer a window of opportunity for  
6 determining the timescale of such high temperature cooling processes. For all but the most rapid  
7 cooling rates (e.g. volcanic systems), clinopyroxene rims will show zoning (particularly when  
8 modern advances in spatially resolved chemical analysis are considered) and these may be used  
9 to infer timescales (e.g. cooling rates) of a variety of processes.

## 12 Acknowledgements

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14 Bochum to S. Chakraborty that funded the positions of TM, RD and JTH as well as the running  
15 of the experimental petrology and the thin film deposition labs. We gratefully acknowledge the  
16 constructive comments of Daniele Cherniak, an anonymous reviewer, and the handling editor  
17 Jon Blundy.

## 19 Figure and Table captions

20 Table 1: Representative electron microprobe analyses of natural clinopyroxene crystals used for  
21 diffusion experiments. Mineral formulae are calculated based on four cations and six  
22 oxygens.  $Fe^{3+}$  is calculated as  $12 - \sum$  of all positive charges normalized to four cations.  
23 Distribution of cations to structural positions assume tetrahedral site to be occupied by Si  
24 and Al, M2 site by Ca, Na, and M1 site by  $Fe^{2+/3+} + Mg + Al^{VI} + Mn$ . ( $Al^{IV} = 2 - Si$ ). Diopside  
25 component is computed as  $X_{Di} = (Mg / Mg + Fe + Mn)$ .

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4 1 Table 2: Summary of experimental run conditions and determined diffusion coefficients. Source  
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6 2 material for the thin film deposition was a synthesized fayalite-rich pellet of olivine  
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8 3 stoichiometry ( $\text{Fo}_{30}$ ). See text for more details.  
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10 4  
11 5 Figure 1: Experimental setup for the Fe-(Ca+Mg) interdiffusion couple. Thin films of olivine  
12 6 ( $\text{Fo}_{30}$ ) were deposited using the pulsed laser deposition technique (PLD) onto a polished  
13 7 surface, perpendicular to the c-axis, of a natural diopside crystal (2x2 mm). Typical  
14 8 thickness of thin films ranged between 20 and 100 nm.  
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16 10 Figure 2: Typical measured RBS spectrum of reference sample (gray) and samples after  
17 11 diffusion anneal (black) of sample 07-CPX-5. Steps correspond to  $\alpha$ -particles  
18 12 backscattered by the major species of the sample. The originally high Fe content limited  
19 13 to the depth of the thin film in the reference sample decreases and broadens during the  
20 14 diffusion anneal, indicating a depth penetration by Fe diffusing into the crystal.  
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22 16 Figure 3: Time series of Fe-(Ca+Mg) interdiffusion experiments for diffusion parallel to the c-  
23 17 axis of natural diopside crystals ( $\text{Di}_{93}$ ) performed at 1000 °C and an oxygen fugacity of  
24 18  $1 \times 10^{-16}$  bar. Diffusivities are consistent within 0.4 log units over the investigated time  
25 19 range indicating the absence of other processes such as surface reaction or dissolution-  
26 20 reprecipitation during the experiment. The error of a single analysis is smaller than the  
27 21 symbol size.  
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29 23 Figure 4: A) Extracted profiles for Fe of diffusion experiment 07-CPX-5 for Fe-Mg diffusion in  
30 24 clinoproxene 1000 °C and  $f\text{O}_2 = 1 \times 10^{-12}$  bar (filled circles). Extracted depth profiles  
31 25 have been fitted with 1) an analytical solution with no partitioning, but different  
32 26 diffusivities in the film and substrate (Lovering 1936) and 2) numerical solution with Fe-  
33 27 Mg partitioning using a  $K_p^{\text{Fe}}$  = 2, fast diffusion in the thin film and convolution due to  
34 28 limited spatial resolution ( $1\sigma = 20$  nm). Both approaches yield the same extracted  
35 29 interdiffusion coefficient. B) Ca-profiles extracted from diffusion experiments 07-CPX-5  
36 30 before and after the experiment. C) Ternary diagram showing the chemical composition  
37 31 from the interface towards the center of diopside crystal. Initial compositions of the Ca-

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4 1 free thin film and the natural cpx crystal are marked with stars. Note the increase in Ca in  
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6 2 the region around the interface suggesting the presence of mixed analyses or little  
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8 3 diffusion of Ca into the thin film. Clinopyroxene compositions have been normalized to  
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10 4 one M-cation, i.e. MeSiO<sub>3</sub>.  
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13 6 Figure 5: Arrhenius plot summarizing experimental results for Fe-Mg cation diffusion in  
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15 7 clinopyroxene. A) Extracted diffusion coefficients as a function of the partial oxygen  
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17 8 pressure. Note, that no systematic trend of changes in the diffusivity can be observed  
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19 9 within the experimental range of  $10^{-17} < fO_2 < 10^{-11}$  bar. B) All data obtained between 800  
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21 10 – 1200 °C can be fitted to a single Arrhenius expression shown with an envelope for the  
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23 11 estimated uncertainty. The error of an individual data point is covered by the symbol size.  
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26 13 Figure 6: Plot of extracted Fe-Mg interdiffusion coefficients as a function of the partial oxygen  
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28 14 pressures for experiments at 950, 1000, and 1100 °C. Diffusion coefficients are constant  
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30 15 within the analytical limits for each temperature and thus, no  $fO_2$ -dependence can be  
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32 16 observed. This is in contrast to the data of Dimanov and Wiedenbeck (2006) for  
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34 17 experiments at 1100 °C, see text for details.  
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39 20 Figure 7: Comparison of interdiffusion data in clinopyroxene. Ca-Mg data from Brady and  
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41 21 McAllister are corrected for the pressure effect to 1 atm. Results from Dimanov and  
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43 22 Wiedenbeck for (Fe,Mn)-Mg are plotted for an oxygen fugacity of  $1 \times 10^{-12}$  bar and are  
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45 23 indistinguishable from our result at temperatures above 1000 °C and high oxygen  
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47 24 fugacities (fig. 6). Ca tracer diffusion data from Dimanov et al. (1994) and Zhang et al.  
48  
49 25 (2010) show systematically slower diffusivities.  
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52 27 Figure 8: Arrhenius relations for Fe-Mg interdiffusion data in ferromagnesian minerals.  
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54 28 Diffusion coefficients decrease in the following order: spinel > olivine > orthopyroxene ~  
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56 29 garnet.  
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4 1 Figure 9: Modeling results showing the development of Fe-zonation during Fe-Mg exchange  
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6 2 between garnet and clinopyroxene along a linear cooling path (cooling from two different  
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8 3 peak T: 1300 °C and 900 °C to mimic mantle and granulite facies conditions). The  
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10 4 numerical model assumes equilibrium at the interface and diffusive fluxes across the  
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12 5 interface are constrained by mass balance (see text for details).  
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15 7 Figure 10: Modeling results showing the recorded temperatures for core-core (dashed lines) and  
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17 8 rim-rim (solid lines) thermometry using the Fe-Mg exchange between garnet and  
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19 9 clinopyroxene with different grain sizes (0.2, 1, and 4 mm) and for a linear cooling path.  
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21 10 Note that only very high cooling rates in combination with low peak temperatures (900  
22  
23 11 °C) will preserve the peak compositions at the core of clinopyroxene crystal.  
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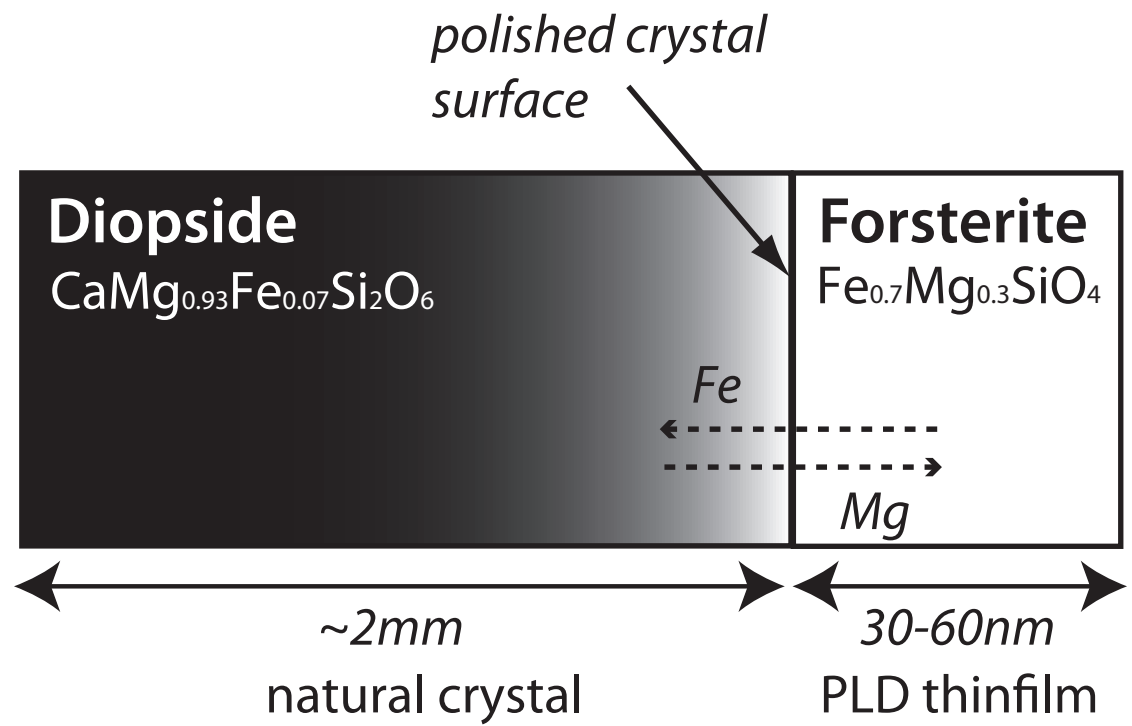


Figure 1  
Müller et al. - Fe-Mg diffusion in cpx

Figure 2

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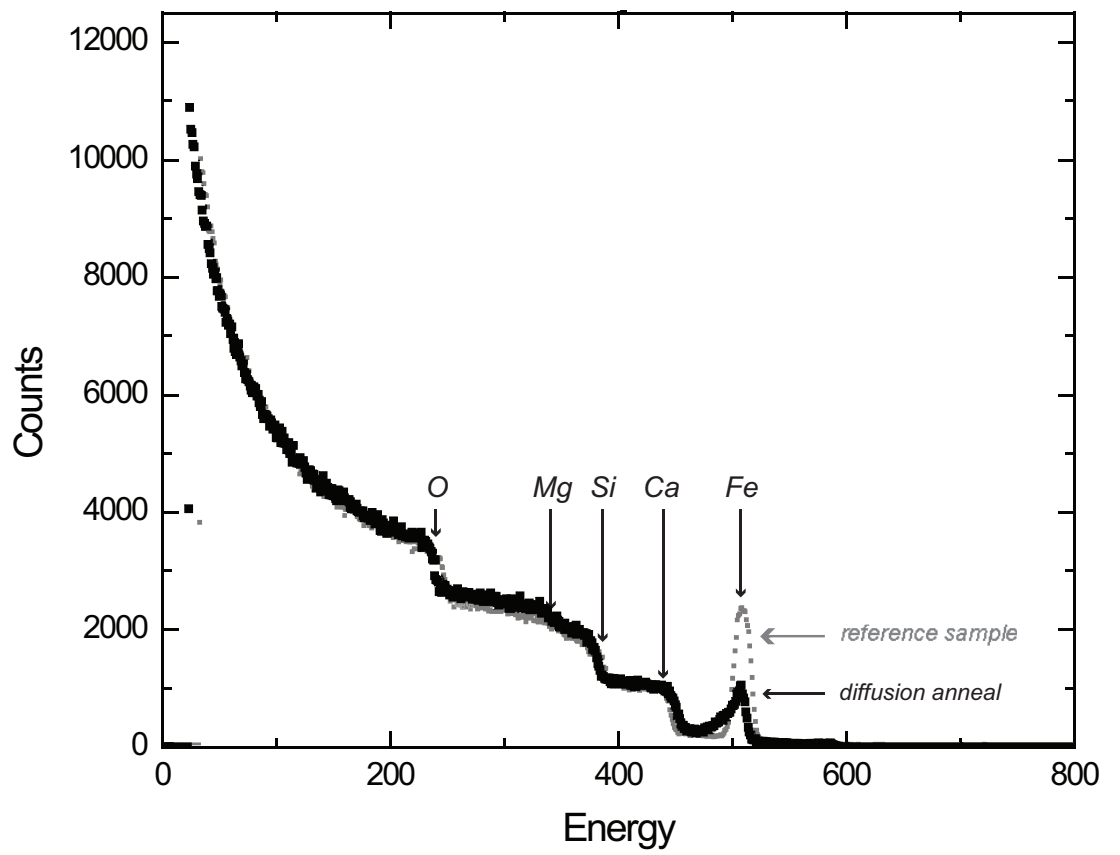


Figure 2

Müller et al. -Fe-Mg diffusion in cpx

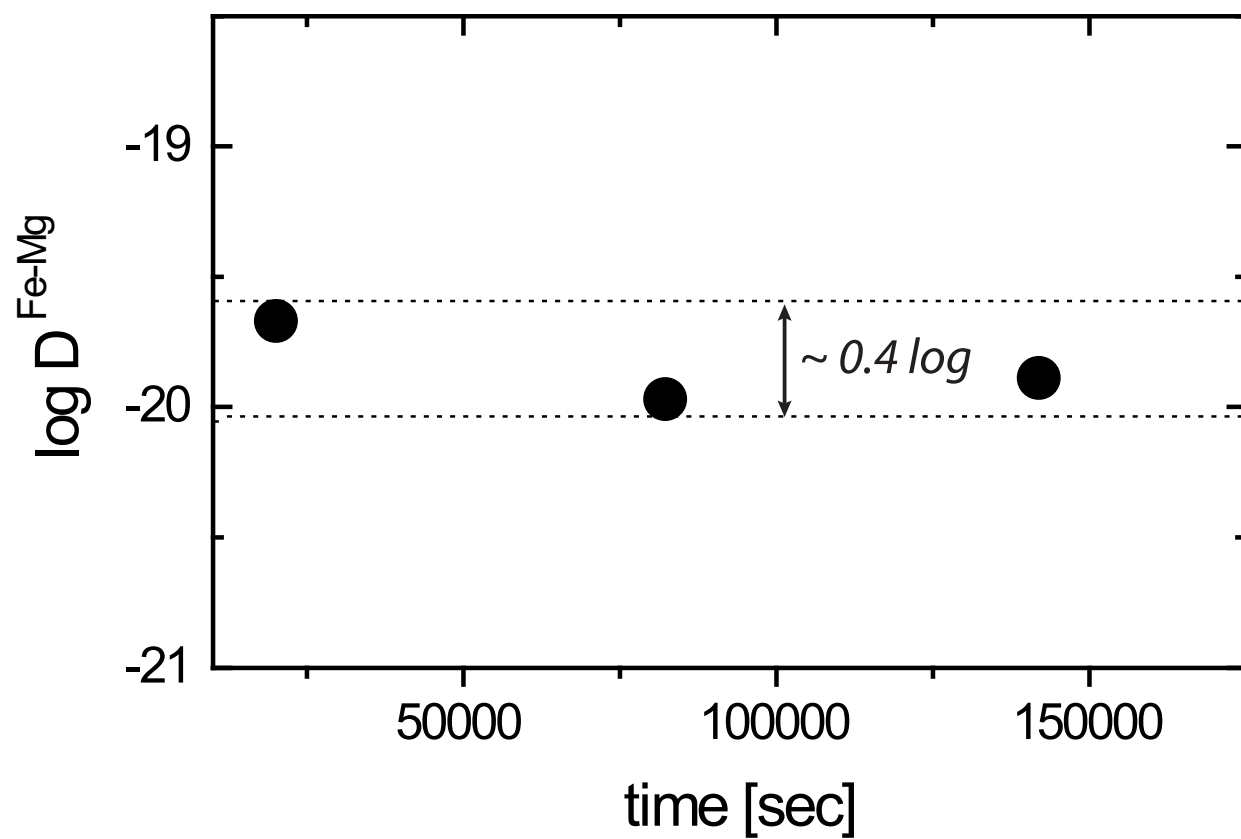


Figure 3

Müller et al. -Fe-Mg diffusion in cpx

Figure 4

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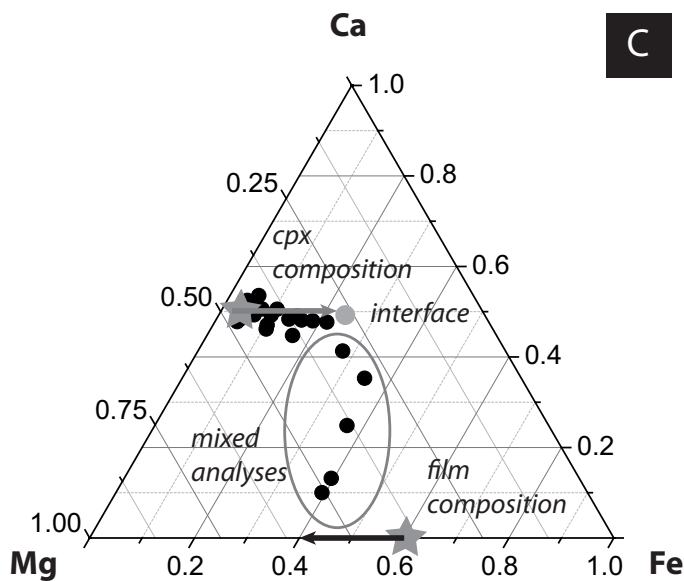
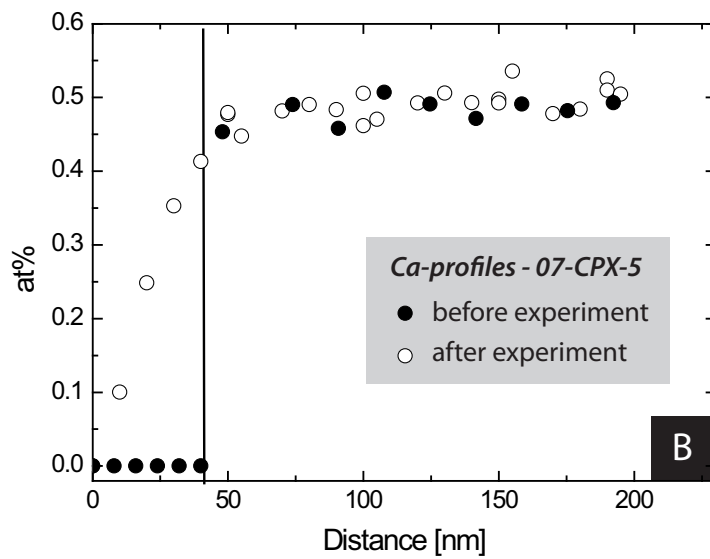
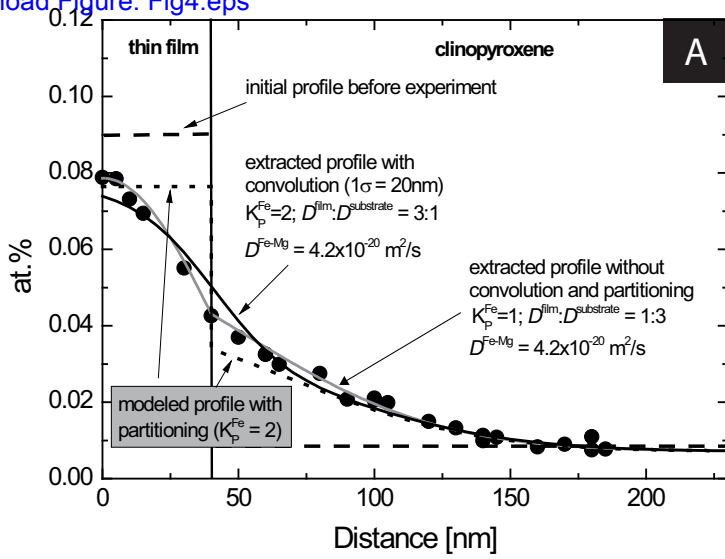


Figure 4

Müller et al. -Fe-Mg diffusion in cpx

Figure 5

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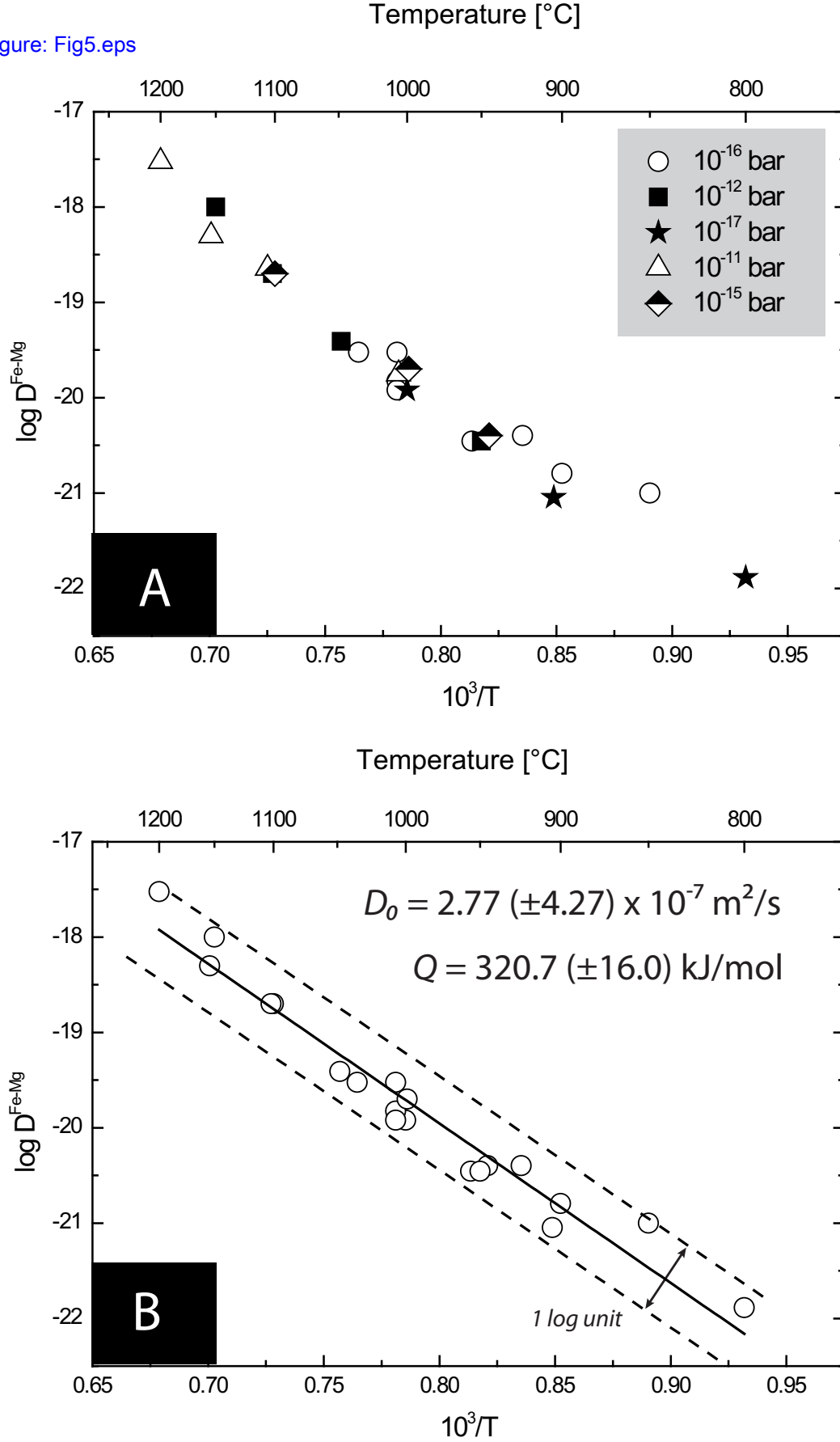


Fig. 5

Mueller et al. - Fe-Mg diffusion in cpx

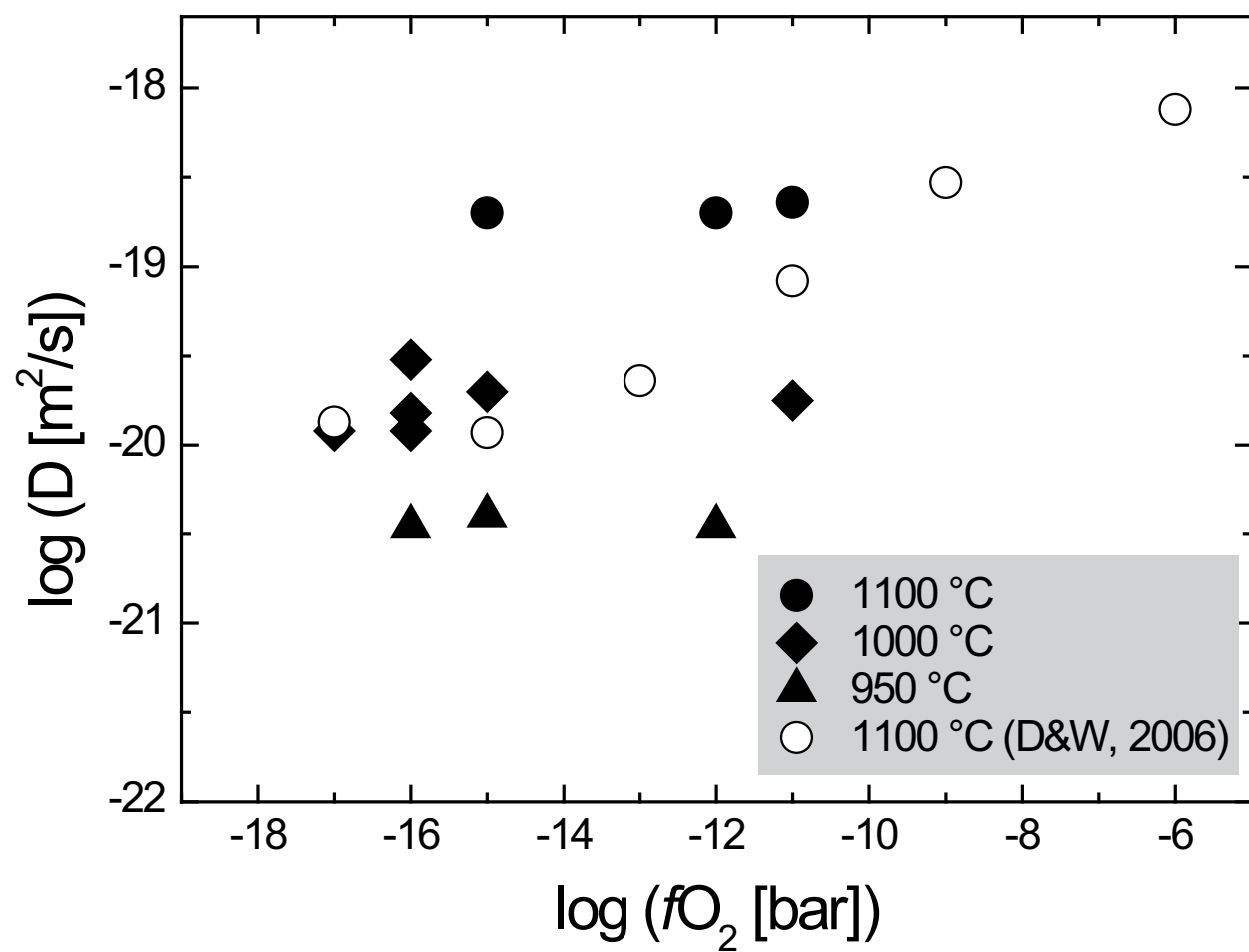


Fig. 6

Mueller et al. - Fe-Mg diffusion in cpx

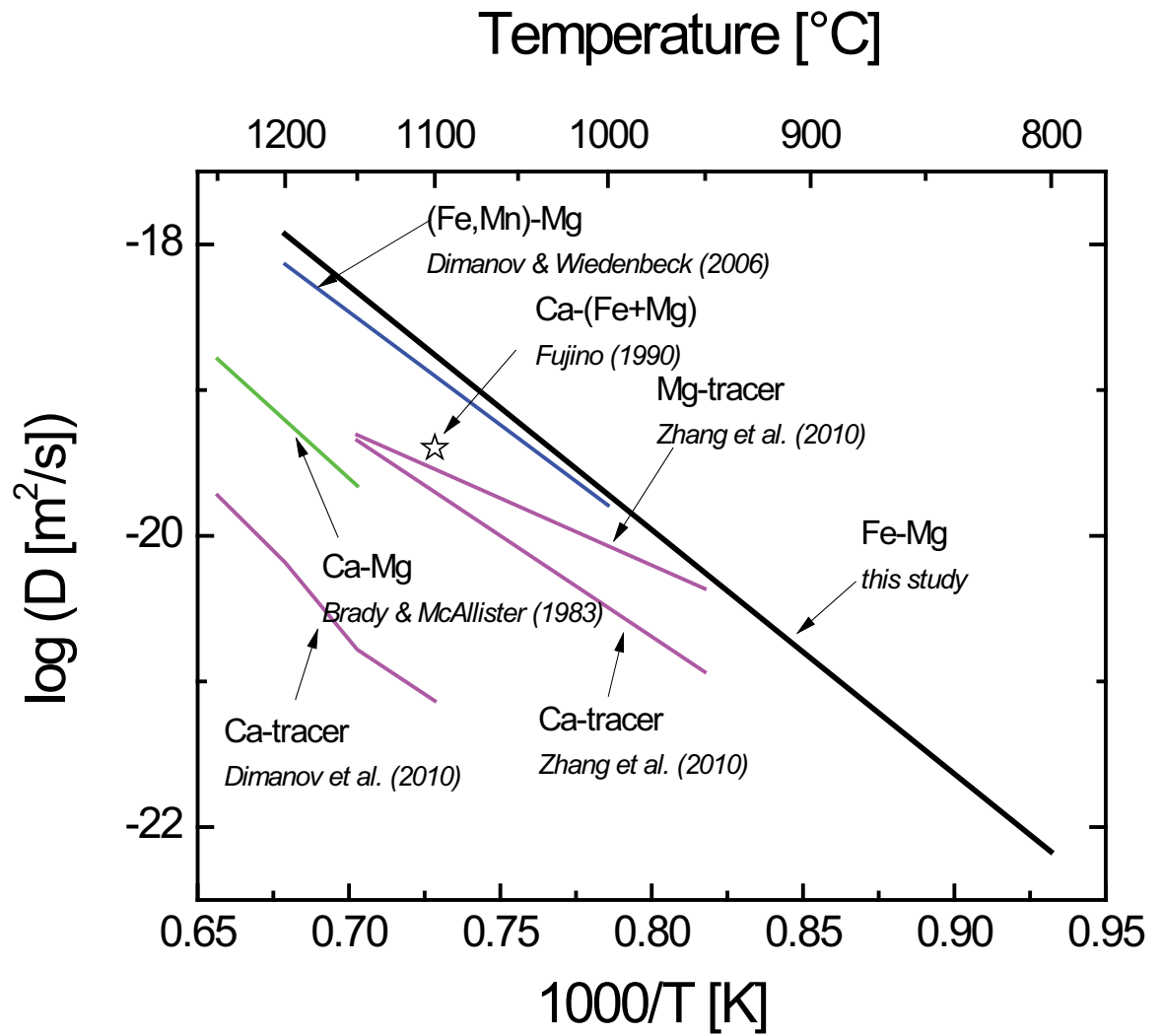


Fig. 7  
Mueller et al. - Fe-Mg diffusion in cpx

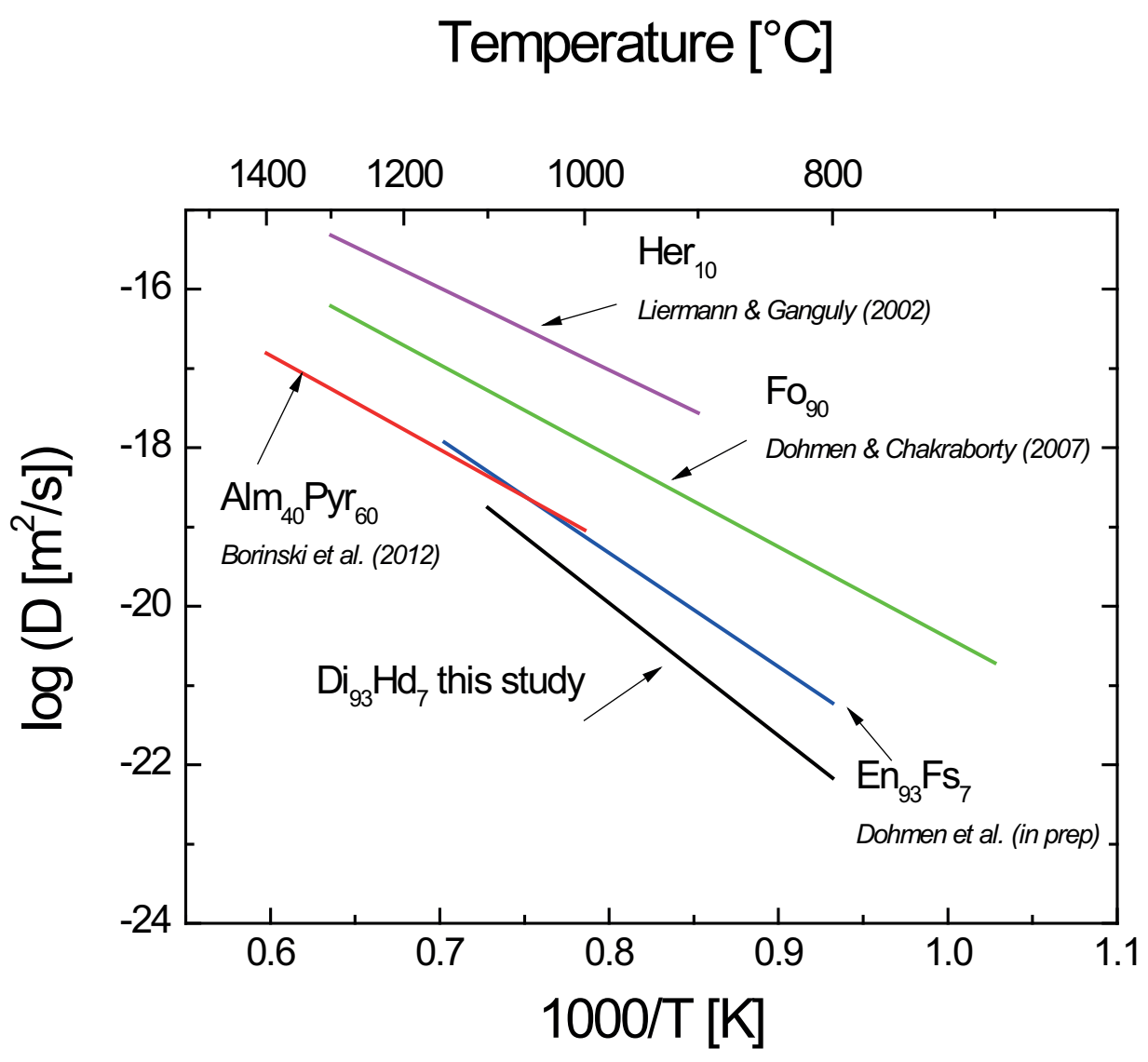


Fig. 8  
Mueller et al. - Fe-Mg diffusion in cpx

Figure 9

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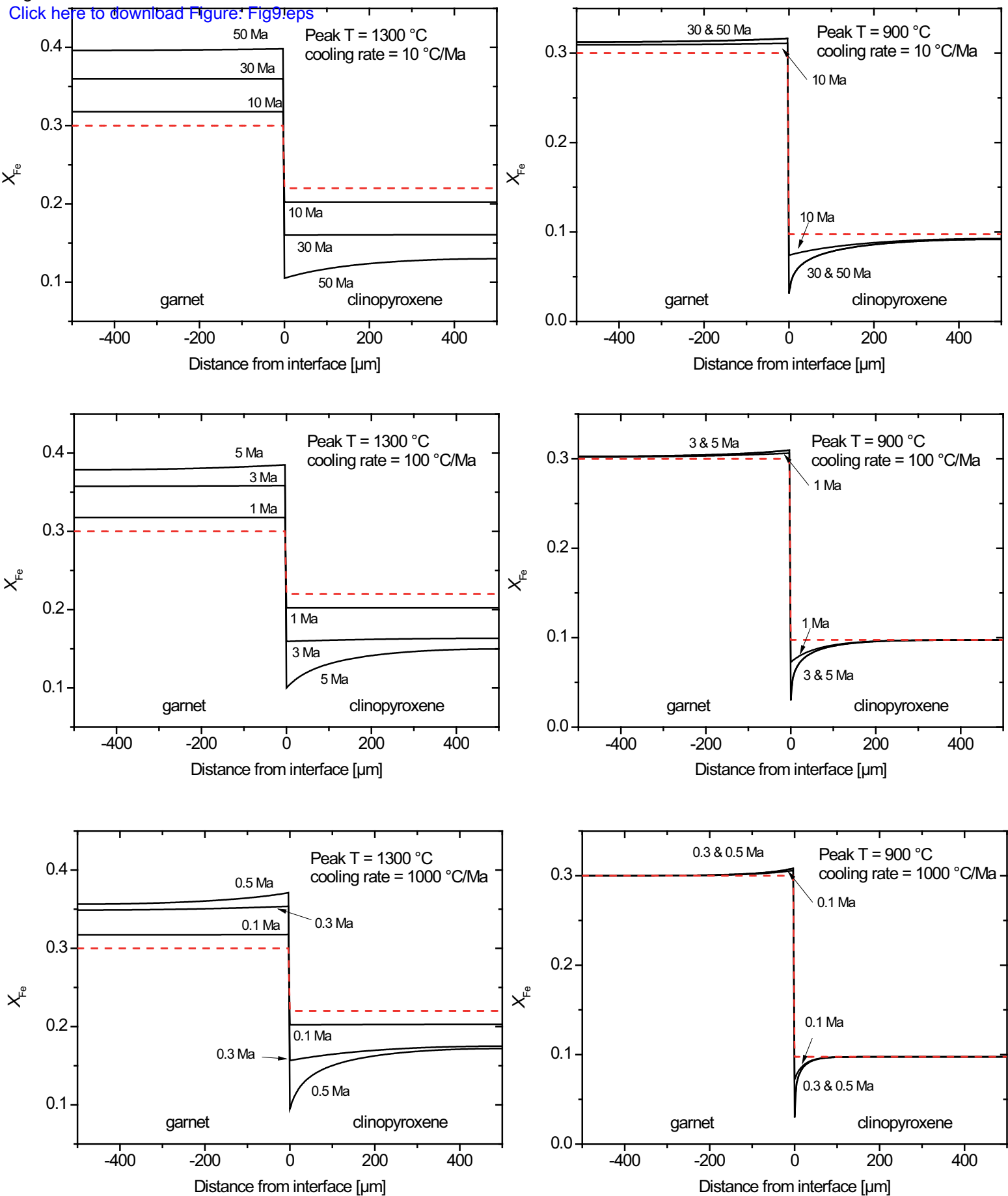


Figure 9

Müller et al. - Fe-Mg diffusion in cpx

Figure 10  
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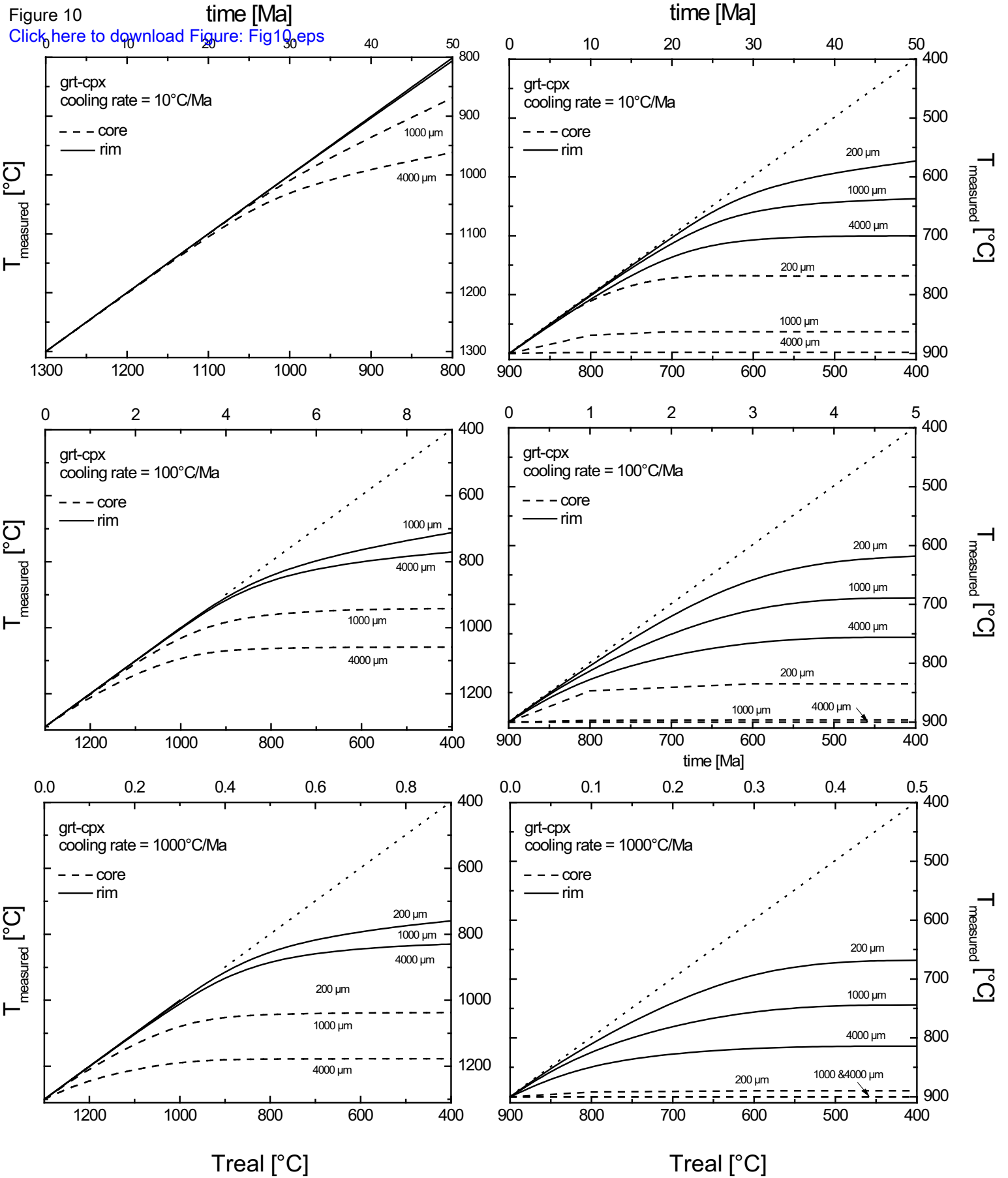


Figure 10  
 Müller et al. - Fe-Mg diffusion in cpx

<b><i>measured wt% Oxide</i></b>			
SiO <sub>2</sub>	52.9	52.84	52.65
Al <sub>2</sub> O <sub>3</sub>	2.72	2.6	2.65
TiO <sub>2</sub>	0.11	0.11	0.11
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.04	0.03
MgO	15.95	15.99	16.07
FeO	2.21	2.23	2.08
MnO	0.08	0.06	0.08
CaO	25.2	25.08	25.24
Na <sub>2</sub> O	0.24	0.26	0.2
<b>Total</b>	<b>99.42</b>	<b>99.21</b>	<b>99.11</b>
<b><i>structural position normalized to 4 cations and 6 oxygens</i></b>			
Si (T)	1.94	1.93	1.93
Al <sup>IV</sup> (T)	0.06	0.07	0.07
Al <sup>VI</sup> (M1)	0.05	0.04	0.04
Ti (M1)	0.00	0.00	0.00
Fe <sup>3+</sup> (M1)	0.02	0.05	0.06
Mg (M1)	0.87	0.87	0.88
Fe <sup>2+</sup> (M1)	0.04	0.02	0.00
Mn (M2)	0.00	0.00	0.00
Ca (M2)	0.99	0.98	0.99
Na (M2)	0.02	0.02	0.01
<b>X(Di)</b>	<b>0.93</b>	<b>0.93</b>	<b>0.93</b>
<b>X(Hd)</b>	<b>0.07</b>	<b>0.07</b>	<b>0.07</b>

table 2

[Click here to download table: Table 2 word97.xls](#)

Experiment	T [°C]	1000/T [K]	t [sec]	log fO <sub>2</sub> [bar]	D [m <sup>2</sup> /s]	log D [m <sup>2</sup> /s] <sup>*</sup>
07-CPX-01	850	0.890	492000	-16.0	1.0x10 <sup>-21</sup>	-21.00
07-CPX-02	900	0.852	264000	-16.0	1.6x10 <sup>-21</sup>	-20.80
07-CPX-04	950	0.818	240060	-12.0	3.5x10 <sup>-21</sup>	-20.46
07-CPX-06	1150	0.703	4320	-12.0	1.0x10 <sup>-18</sup>	-18.00
08-CPX-07	800	0.932	1355820	-17.0	1.3x10 <sup>-22</sup>	-21.89
08-CPX-11	905	0.849	423720	-17.0	9.0x10 <sup>-22</sup>	-21.05
08-CPX-15	1106	0.725	7200	-11.0	2.3x10 <sup>-19</sup>	-18.64
08-CPX-16	1006	0.782	57600	-11.0	1.8x10 <sup>-20</sup>	-19.75
08-CPX-17	1154	0.701	3600	-11.0	5.0x10 <sup>-19</sup>	-18.30
08-CPX-18	1200	0.679	1800	-11.0	3.0x10 <sup>-18</sup>	-17.52
09-CPX-02	1035	0.764	44400	-16.0	3.0x10 <sup>-20</sup>	-19.52
09-CPX-03	924	0.835	78600	-16.0	4.0x10 <sup>-21</sup>	-20.40
09-CPX-06	1000	0.785	360	-16.0	1.0x10 <sup>-18</sup>	NA
09-CPX-09	956	0.814	249360	-16.0	3.5x10 <sup>-21</sup>	-20.46
09-CPX-11	1048	0.757	31080	-12.0	3.9x10 <sup>-20</sup>	-19.41
09-CPX-12	1102	0.727	7440	-12.0	2.0x10 <sup>-19</sup>	-18.70
09-CPX-13	945	0.821	225000	-15.0	4.0x10 <sup>-21</sup>	-20.40
09-CPX-14	999	0.786	54600	-15.0	2.0x10 <sup>-20</sup>	-19.70
09-CPX-15	1100	0.728	9360	-15.0	2.0x10 <sup>-19</sup>	-18.70
09-CPX-16	1000	0.785	45240	-17.0	1.2x10 <sup>-20</sup>	-19.92
09-CPX-17	1007	0.781	20100	-16.0	3.0x10 <sup>-20</sup>	-19.52
09-CPX-18	1007	0.781	82260	-16.0	1.5x10 <sup>-20</sup>	-19.82
09-CPX-19	1007	0.781	141600	-16.0	1.2x10 <sup>-20</sup>	-19.92

\*Uncertainties on logD are ±0.2. See figure 3 and text for details.