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Kinetics of Anorthite Dissolution in Basaltic Melt

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6 Abstract

7 We report convection-free anorthite dissolution experiments in a basaltic melt at 1280-
8 1500 °C and 0.5 GPa on two different crystallographic surfaces, $(12\bar{1})$ and $(\bar{3}02)$ to investigate
9 dissolution kinetics. The anisotropy of the anorthite dissolution rate along these two surfaces is
10 negligible. Time series experiments at ~ 1280 °C show that anorthite dissolution is mainly
11 controlled by diffusion in the melt within experimental uncertainty. Analytical solutions were
12 used to model the dissolution and diffusion processes, and to obtain the diffusivities and the
13 saturation concentrations of the equilibrium-determining component (Al_2O_3) for anorthite
14 dissolution into the basaltic melt. For the first time, we are able to show the physical and
15 chemical characteristics of quench growth effect on the near-interface melt using high spatial
16 resolution (0.3 μm) EDS analyses. For anorthite ($\text{An}\# \geq 90$) saturation in a melt with 39-53 wt%
17 SiO_2 and ≤ 0.4 wt% H_2O , the concentration of Al_2O_3 in wt% depends on temperature as follows:

$$18 \quad \ln(\text{Al}_2\text{O}_3) = 8.032(\pm 0.192) - \frac{7884(\pm 287)}{T},$$

19 where T is temperature in K, and errors are given at 1σ level. Al_2O_3 diffusivity in basaltic melt
20 during plagioclase dissolution can be expressed as:

$$21 \quad \ln D_{\text{Al}_2\text{O}_3}^{\text{EBD,plag diss}} = -13.69(\pm 1.57) - \frac{19313 \pm 2485}{T},$$

22 where D is in m^2/s , and the activation energy is 161 ± 21 kJ/mol. These results are applied to
23 model the convective dissolution of anorthite in basaltic melts. The model indicates that though
24 anorthite crystals can survive for a longer time compared to olivine crystals of the same size in
25 the same melt, the former would rise for a much smaller distance compared to the olivine sinking
26 distance, due to the smaller density contrast between anorthite and melt.

Keywords: Crystal dissolution kinetics, diffusion, interface reaction, quench overgrowth

1. INTRODUCTION

Mineral dissolution and crystallization are basic processes for understanding more complicated geological processes such as magma crystallization and assimilation, xenolith digestion and many other processes. Information such as diffusivity, interface melt composition, and mineral dissolution rate obtained from mineral dissolution/growth studies can be used to quantify processes such as crystal growth rate, and magma ocean evolution and differentiation.

Many authors have studied the mechanisms and rates of dissolution/growth of various minerals in a variety of silicate melts (e.g., Harrison and Watson, 1983; Donaldson, 1985; Zhang et al., 1989; Liang, 1999, 2000, 2003; Shaw, 2000, 2004, 2006, 2012; Acosta-Vigil et al., 2002, 2006; Morgan et al., 2006; Chen and Zhang, 2008, 2009). In general, convection-free mineral dissolution may be controlled either by interface reaction, by diffusion, or by both (e.g., Zhang, 2008, p. 50-54). If interface reaction plays a role, the interface melt composition would gradually evolve with time from the initial to the final “steady-state” composition. If interface reaction is rapid, the interface melt composition would quickly reach the “steady-state” composition and be constant within error, and the dissolution would be controlled by diffusion. Such experiments can be used to extract diffusivity in the melt and the saturation melt composition. Convection can also influence the mineral dissolution rate. Zhang et al. (1989) investigated diffusive mineral dissolution in an andesitic melt and pointed out that some earlier experiments in the literature did not differentiate convective dissolution from diffusive dissolution, rendering the extracted

diffusion data unreliable. Kerr (1995) quantified the convective dissolution of minerals in silicate melts for Reynolds Number (Re) less than 1. Zhang and Xu (2003) expanded the application of the convective dissolution model to regimes with Re up to 10^5 . Within the framework of their approach, melt viscosity, and the diffusivity and interface melt concentration of the equilibrium-determining component are the three critical parameters needed to quantify convective dissolution (Levich, 1962; Clift et al., 1978; Kerr, 1995; Zhang and Xu, 2003; Chen and Zhang, 2008). Among these three parameters, saturation concentration and diffusivity can be obtained from diffusive mineral dissolution experiments. Therefore, recent studies on mineral dissolution have experimentally investigated diffusive dissolution and applied the results to quantify convective dissolution or growth in nature (Chen and Zhang, 2008, 2009; Zhang, 2013).

In this work, we investigate the kinetics of convection-free dissolution of Ca-rich plagioclase (An₉₄). One goal is to examine the role of interface reaction and diffusion (Donaldson, 1985; Zhang et al., 1989; Liang, 1999; Acosta-Vigil et al., 2002, 2006; Baker et al., 2002; Shaw 2004, 2006, 2012; Morgan et al., 2006; Chen and Zhang, 2008, 2009) for anorthite dissolution. Another goal is to check for possible anisotropy of anorthite dissolution rate. The third goal is to extract the relevant diffusivities and saturation conditions for anorthite. The results will be applied to model the kinetics of anorthite dissolution in basaltic melts.

With these issues in mind, time-series experiments on convection-free anorthite dissolution in a basaltic melt are conducted at different temperatures to examine the role of interface reaction in controlling mineral dissolution. Important parameters, including the effective binary diffusivity of Al₂O₃ and the interface Al₂O₃ concentration, are obtained. To evaluate the possible anisotropy of anorthite dissolution rate, experiments along two different

crystallographic directions of anorthite are conducted. Finally, modeling of anorthite dissolution in basaltic melt is discussed.

2. EXPERIMENTAL AND ANALYTICAL METHODS

We followed the experimental procedure of Chen and Zhang (2008, 2009) to investigate anorthite dissolution in basaltic melt. Almost gem-quality anorthite crystals with molar compositions of $\text{Ca}/(\text{Ca}+\text{Na}+\text{K})=0.94$ and $\text{Na}/(\text{Ca}+\text{Na}+\text{K})=0.06$ (Waythomas et al., 2010), and a piece of MORB glass from Juan de Fuca Ridge (Dixon et al., 1986, 1988) were used to conduct anorthite dissolution experiments in a ½ -inch piston-cylinder apparatus. The compositions of the anorthite and tholeiitic basaltic glass are listed in Table 1. We chose a plagioclase with high An# so that the solidus of the plagioclase is much higher than the liquidus of the basaltic melt for our dissolution experiments. Otherwise either the temperature interval is too small to constrain the Arrhenius relation, or there would be partial melting of the plagioclase crystal or partial crystallization of the basaltic melt, complicating the experiments. The basaltic glass (containing 0.25 to 0.40 wt% H₂O) used in this study is the same as that used by Chen and Zhang (2008, 2009); therefore, cross comparisons can be made with their olivine and clinopyroxene dissolution results.

Two large anorthite crystals were cut and ground into round cylinders of 2.4-2.6 mm in diameter. The Miller indices of the base of one cylinder were (12 $\bar{1}$), and the other ($\bar{3}$ 02), as determined using single crystal X-Ray Diffraction (XRD). The angle between the normal directions of these two plane systems was calculated to be 50.5°. The cylinders were cut into wafers of ~0.5 mm in thickness. The MORB glass was prepared into discs in a similar way, with dimensions of ~2.0 mm in thickness and 1.80 mm in diameter. As shown in Fig. 1, the diameter

of the glass was intentionally made smaller than that of the anorthite crystal so that the dissolution distance can be measured directly from the quenched experimental sample (Morgan et al., 2006; Chen and Zhang, 2008, 2009). For each experiment, one anorthite disc and one basaltic glass disc were packed into a cylind graphite capsule. The contact surfaces of the anorthite disc and the glass disc were polished to ensure the best surface contact. The experimental design (Fig. 1) followed that of Chen and Zhang (2008), except that the crystal disc was on top of the basaltic glass to ensure gravitational stability.

Time-series experiments were conducted for dissolution on $(12\bar{1})$ surfaces (orientation 1) to examine the evolution of the interface melt composition with experimental duration at 0.5 GPa and three temperatures (1280°C, 1330°C, and 1400°C). For comparison, dissolution experiments (orientation 2) on another crystallographic surface, $(\bar{3}02)$, were also conducted at 1280 °C and 0.5 GPa to study possible anisotropy of the anorthite-melt interface reaction. A third set of time-series experiments (orientation 3, not determined) was carried out with extra care to examine whether the correlation between the interface melt composition and the experimental duration was reproducible. The experimental temperatures (T_1 in Table 2) were chosen to be above the liquidus of basalt and below the solidus of anorthite. The feasible temperature range is between ~1243°C (the liquidus of this basalt at 0.5 GPa based on the MELTS program; Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998; Ghiorso et al., 2002) and ~1527 °C (the solidus of plagioclase An₉₄ at 0.5 GPa, interpolated from the phase diagram of plagioclase; Morse, 1980). Allowing uncertainties in the calculated and experimental temperatures, experiments were conducted at nominal temperatures of 1280, 1330, 1400 and 1500°C.

During an experiment, the sample assembly is first brought to the desired pressure and then heated to the planned temperature. The reported experimental temperature (T_2 in Table 2)

is the temperature at the plagioclase-melt interface using the calibration of Hui et al. (2008). The pressure was manually maintained during the whole experimental duration to within about 4 MPa. In total, 25 successful experiments were conducted (Table 2), although three experiments (214, 223, and 229) had other problems (discussed later).

After quench, the sample assembly was taken out, mounted in epoxy, and then ground and polished to expose the anorthite and basaltic glass parallel to the center axis of the graphite capsule until the exposed area of the sample reached or was near the maximum. Epoxy was applied as needed during grinding/polishing to seal cracks in the sample. Well-polished samples were cleaned using ultrasonic cleaner and dried in a vacuum oven, and then prepared for measurement of composition profiles using a Cameca SX100 electron microprobe at the University of Michigan. The electron microprobe analysis conditions are: 15 kV and 10 nA focused beam (defocused beam was used for experiment 230 to obtain melt composition from glass containing quenched crystals), counting time of 30 s for Si, Mg, K, 40 s for Al, Fe, Ca, and Na; 20 s for Ti; and 10 s for Mn. Na was analyzed as one of the first elements on a spectrometer by counting for five 8-seconds periods, and the Na_2O concentration was calculated by extrapolating to zero time.

Two to three traverses (Fig. 2a) in the basaltic melt were analyzed for each experimental sample. When there were cracks, we used multiple traverses to estimate the actual gap across cracks as explained in Zhang et al. (1989) and Chen and Zhang (2008, 2009). A typical concentration profile is shown in Fig. 2b. The electron microprobe data of all samples is available in the Supplementary Materials.

Selected samples were also examined using the new JEOL JSM 7800FLV SEM at the University of Michigan for high-spatial-resolution and semi-quantitative Energy-Dispersive

Spectroscopy (EDS) analyses (Salge, 2012) using an acceleration voltage of 7 kV, line scan spacing of 0.3 μm , and counting time of 30 s. An initial test run at 7 kV with a step size of 0.2 μm across a quartz-rhyolite interface showed that the spatial resolution of the EDS analyses is about 0.3 μm .

3. RESULTS

3.1. General

A list of run conditions of all successful anorthite dissolution experiments is shown in Table 2. PDisBa-201 to PDisBa-209, PDisBa-221 to PDisBa-227, and AnDisBa-301 to AnDisBa-304 are three sets of time-series experiments at 1280°C and 0.5 GPa. PDisBa-210 to PDisBa-216 are time-series experiments at 1330°C. Figure 2a shows a Back Scatter Electron (BSE) image of an experimental sample. Locations of the measured traverses were marked on it, and Figure 2b displays the three measured Al_2O_3 profiles of the sample. The horizontal offset is slightly exaggerated to better show the analysis procedure.

Complications in some experiments are discussed below:

1. In experiments at and above 1400°C, the melt layer within 10-50 μm distance of the interface typically contains numerous oriented and needle-like crystals (Figs. 3c and 3d), extending off the anorthite-melt interface. The thickness of the layer increases with the experimental temperature. Experiments at lower temperatures typically show crystal-free interface regions, except for experiments PDisBa-214 and PDisBa-223 (discussed below). All the observed crystal needles are long (5~20 μm) but thin ($\sim < 1$ μm). The electron microprobe cannot directly determine their composition. SEM-EDS analyses indicate that they have plagioclase compositions. These crystals are attributed to plagioclase growth during quench due

to high degrees of plagioclase super-saturation when the temperature cooled from the experimental temperature. At 1280 and 1330°C, there is smooth cryptic overgrowth that can generate local artificial concentration profiles, which are not caused by the dissolution and diffusion at the experimental temperature. More details of the latter type of quench overgrowth can be found in section 3.2.

2. For PDisBa-214 (nominal temperature of 1330°C) and PDisBa-223 (1280°C), a 10-20 μm thick layer of well-oriented needle-like crystals near the interface were observed. These are typical features of experiments conducted at higher temperatures. These two experiments also show other characteristics (higher output power during experiments, much higher interface concentration and effective binary diffusivity of Al_2O_3 compared to other experiments at the same temperature) that suggest that the temperatures during these two experiments were significantly higher than the planned temperatures of 1330°C and 1280°C, respectively. The likely cause of the unexpectedly high experimental temperatures is the off-center placement of the crystal-melt interface when the capsules were prepared. The two experiments will not be used in the quantitative treatments below.

3. For PDisBa-229 (1404°C), the anorthite-melt interface has been preserved, but a major part of the concentration profile was lost due to heavy cracking. Diffusivities cannot be reliably obtained, though the interface melt composition can be roughly estimated by averaging the points near the interface.

Concentration profiles of a selected experiment are shown in Fig. 4, and important features are discussed below. The concentration profiles at the far field are generally flat, except for some cases where CaO concentrations of the far-field melt were altered due to the rapid

diffusion of CaO. The altered far-field concentration of CaO violated the semi-infinite condition. In such cases, the effective binary diffusivity for CaO was not extracted.

Three methods are used to evaluate whether there was convection in the experiments. One is by comparing three concentration traverses in a single sample (Fig. 2 and all other samples). The three traverses are typically in excellent agreement (Figs. 2 and 4), consistent with no convection. The second is to make elemental maps of some sections (Fig. 5) that would reveal “fingers” or convection cell patterns if there were convection (Morgan et al., 2006). Such features are absent in all the mapped sections. Thirdly, time series experiments have been conducted with experiment duration varying by a factor of 20 (PiDisBa-201 to PiDisBa-209, 200 to 6000 s), and the extracted Al_2O_3 diffusion coefficients from these experiments agree within a factor of 2.5. These lines of evidence together demonstrate that the experiments were not affected by convection.

3.2. Crystal overgrowth at the interface during quench

Zhang et al. (1989) observed that even though the general trend of MgO concentration profile in the melt during olivine dissolution is to increase towards the olivine-melt interface, very near the interface (within about 10 μm), the trend reverses and MgO concentration decreases toward the interface (Fig. 6 in Zhang et al., 1989). This was explained to be a consequence of cryptic overgrowth of olivine as the interface melt becomes supersaturated with olivine during quench. Other authors have also observed the same phenomenon (Chen and Zhang, 2008, 2009), and we also observed this phenomenon for the Al_2O_3 concentration profile during anorthite dissolution. However, the quench overgrowth layer of the crystal is thin (1 μm or less), and the spatial resolution of the electron microprobe analysis at 15 kV is about 2 μm .

Hence, the quench overgrowth layer has never been resolved before. We analyzed the quench overgrowth layer using an SEM (JEOL 7800 FLV) equipped with a silicon drift detector (SDD) that is able to perform high-spatial-resolution semi-quantitative EDS analyses at low voltages (Salge, 2012). EDS traverses with 0.3 μm step sizes were made across the anorthite-basalt interface. Figure 6 shows a BSE image across the interface between the anorthite crystal and the basaltic glass, with an EDS traverse (the yellow horizontal line) marked. EDS data are calibrated using electron microprobe analyses in spots near the EDS traverse, and the resulting concentration profiles are shown in Fig. 6 below the BSE image. The compositional data clearly reveal the layer of overgrown plagioclase with high SiO_2 , high Na_2O , and nearly zero MgO , roughly matching a plagioclase formula of An_{67-74} . The newly grown plagioclase has lower Ca and higher Na concentrations compared to the original anorthite. In the BSE image, this newly grown plagioclase can be seen as the dark grey band between the original anorthite (less dark) and the basaltic glass (light grey). The quench overgrowth produced a narrow (1 μm thick) bright band next to the dark band, and caused SiO_2 and Al_2O_3 depletion in a melt layer of about 3 μm , and Na_2O depletion and MgO enrichment in a melt layer of about 5 μm in this example. The composition of this melt layer near the interface is hence not part of the normal concentration profile for crystal dissolution. The width of the layer increases as the experimental temperature increases. The bent concentration trend near the interface (known as the quench effect) is excluded from profile fitting (Zhang et al., 1989; Chen and Zhang, 2008, 2009).

3.3. Interface Al_2O_3 concentration

The interface Al_2O_3 concentration in each experiment (Table 4) is obtained by extrapolating the non-quench-affected Al_2O_3 profile to the interface ($x = 0$). Some authors have

argued that convection-free plagioclase dissolution may be partially controlled by interface reaction (Acosta-Vigil, 2002, 2006; Shaw, 2004, 2006, 2012), which would manifest itself as gradual evolution of the interface Al_2O_3 from the initial concentration in the melt to the saturation concentration for the case of anorthite dissolution. To test this, we determined the interface Al_2O_3 concentrations in experiments of different durations. Initial data appeared to indicate a trend of systematic variation of interface Al_2O_3 concentration with the experimental duration, especially at 1280°C, but data scatter made it difficult to determine whether the trend is real. A third set of experiments was therefore carried out at 1280°C (exp. 301, 302, and 304 in Tables 2-4; “1280°C, v3” in Fig. 7) and showed that there is no systematic trend (Fig. 7); e.g., the Al_2O_3 interface concentration of the shortest duration (2 min.) experiment is almost the same as that for the 60-minute experiment (19.1 vs. 19.7 wt%). That is, we are not confident that our experiments can resolve the possible evolution of the interface melt composition with time and we will treat the interface melt composition at a given temperature to be constant within error. In addition, anorthite growth rates in its own melt are high according to Kirkpatrick et al. (1976), about 100 $\mu\text{m/s}$ at $\sim 1350^\circ\text{C}$, indicating rapid interface reaction rate and therefore diffusion control of non-convective dissolution. Hence, below we assume that the interface reaction is rapid and plagioclase dissolution is controlled by diffusion.

3.4. Concentration profiles and fits

Figure 4 displays concentration profiles of major components in the basaltic glass in selected experiments. Concentrations of SiO_2 , TiO_2 , MgO and FeO in the melt decrease toward the anorthite-melt interface, whereas Al_2O_3 and CaO concentrations increase toward the interface. These are expected because the dissolving anorthite crystal contains lower SiO_2 , TiO_2 ,

MgO, and FeO concentrations, and higher Al₂O₃ and CaO concentrations than the basaltic melt. SiO₂ shows weak uphill diffusion with a small maximum. Despite the relatively large data scatter, Na₂O shows obvious uphill diffusion with a minimum in the middle of the profile (e.g., Fig. 4), and sometimes even both a minimum and a maximum, demonstrating complicated multicomponent diffusion effects. MnO and K₂O concentration profiles are scattered due to their low concentration. Compositional profiles and digital data of all the experiments are provided in Supplementary Materials.

Monotonic concentration profiles C vs. x are fitted by the following equation (Zhang et al., 1989):

$$C = C_{\infty} + (C_0 - C_{\infty}) \frac{\operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}} - \alpha\right)}{\operatorname{erfc}(-\alpha)}, \quad (1)$$

where x is the distance in the melt from the crystal-melt interface, t is the experimental duration, C , C_{∞} , and C_0 are the concentrations of the oxide at x , in the initial (far-field) melt ($x = \infty$), and the interface melt ($x = 0$), α is related to the melt growth distance L ($L = 2\alpha\sqrt{Dt}$), and C_0 and α satisfy:

$$\exp(\alpha^2) \operatorname{erfc}(-\alpha) \sqrt{\pi} \alpha = \frac{C_0 - C_{\infty}}{C_c - C_0}. \quad (2)$$

All the fit D values are listed in Table 3, and the fits are shown in Fig. 4 and in the Supplementary Materials.

3.5. Dissolution distance

The dissolution distances of anorthite for each sample are determined by two methods. One is based on the direct measurement of how much the melt moved into the anorthite wafer

using BSE images (L1 in Table 2). However, L1 is not always measurable. Sometimes, the experimental charge is too cracked and L1 cannot be estimated reliably. In other samples, melt encroachment into the anorthite crystal can only be seen from one side, with anorthite on the other side either missing or cracked. In these cases, L1 estimation is not reliable and not reported. In the second method, dissolution distance is calculated from the measured Al_2O_3 concentration profiles based on mass balance using eq. 16 in Zhang et al. (1989) assuming constant density in the glass and $\rho_{\text{anorthite}}/\rho_{\text{glass}} = 1$ (L2 in Table 2). The dissolution distance given by these two methods are generally consistent with each other. The directly measured dissolution distance L1 is a good independent (though redundant) determination of the dissolution distance. The independent verification by the two methods strengthens our data and discussion. Both L1 (when available) and L2 were used in figures.

The dissolution distance is plotted against the square root of the experimental duration in Fig. 8. The dissolution distance at each temperature is roughly proportional to $t^{1/2}$ considering data scatter, consistent with the diffusion controlled dissolution. At $\sim 1400^\circ\text{C}$, the fit equation is $L = (3.43 \pm 0.11)t^{1/2}$ (blue short-dashed line) with t in s, L in μm and errors at 1σ level hereafter. At $\sim 1330^\circ\text{C}$, $L = (1.79 \pm 0.06)t^{1/2}$ (red solid line). At $\sim 1280^\circ\text{C}$, $L = (0.99 \pm 0.05)t^{1/2}$ (black long-dashed line).

4. DISCUSSION AND APPLICATIONS

4.1. Al_2O_3 concentration at anorthite saturation

Concentrations of oxides in the interface melt can be estimated from the concentration profiles by extrapolation. When the MELTS program (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998) is used to calculate the liquidus temperature and phase using the interface melt

composition, the calculated liquidus phase is plagioclase (the calculated composition of the liquidus plagioclase is An₇₄₋₈₃ at 1280 °C, ~An₈₂₋₈₇ at 1330 °C, ~An₉₀ at 1400 °C, and ~An₉₅ at 1500 °C) and the calculated liquidus temperatures are within 33°C of our experimental temperature at 1280-1330°C (excluding the two outliers described above), but are lower by 51°C to 93°C at 1400°C to 1500°C. When the thermobarometers of Putirka (2005) are used to estimate the temperature or pressure, the calculated temperatures are higher than the experimental temperature by 15°C to 58°C, and the calculated pressures are off by 5 kb to 28 kb. When the model of Namur et al. (2012) is applied to estimate the temperature at which the interface melt is in equilibrium with plagioclase An₉₄, the calculated equilibrium temperatures are 1267-1317°C for experiments at 1280°C, and 1190-1197°C for experiments at 1400°C. At experimental temperatures of 1400°C and 1500°C, the large differences between the calculated and experimental temperatures by the different models are likely due to the paucity of experimental data at such high temperatures when these models were calibrated.

Plagioclase-melt equilibrium is controlled by multiple components (Al₂O₃, CaO, SiO₂, and Na₂O in the melt; e.g., Drake, 1976; Panjasawatwong et al., 1995; Putirka, 2005; Namur et al., 2012) whose activities depend on factors such as H₂O concentration (Lange et al., 2009). The anorthite-melt equilibrium can be expressed as:

The equilibrium constant can be written as:

$$K = \frac{a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{plag}}}{a_{\text{CaO}} a_{\text{AlO}_{1.5}}^2 a_{\text{SiO}_2}^2}, \quad (4)$$

where a is the chemical activity in the plagioclase (indicated by superscript “plag”) and the melt (not indicated). However, models based on eqs. 3 and 4 cannot be applied easily to model crystal

growth and dissolution unless the multicomponent activity model and diffusivity matrix are available (e.g., Liang, 1999; Alexander, 2011). Therefore, there is a need to develop simpler models for Ca-rich plagioclase saturation.

To simplify the problem, we will consider only “dry” systems (with less than 0.4 wt% H₂O in the melt) and for plagioclase with $X_{An} > 0.90$, which would be applicable to the formation of anorthosite crust on Moon. During plagioclase dissolution, the Al₂O₃ concentration gradient (or the difference between Al₂O₃ concentration in the interface melt and that in the far-field melt) clearly is the largest compared to the gradients of other components. For example, in experiment P1DisBa-228 (1408 °C, 142.7 s), the CaO concentration varies from 10.9 wt% in the far field to 13.0 wt% at the interface (a relative variation of about 19%), and the SiO₂ concentration varies from 51.2 wt% to 45.7 wt% (about –11% relative variation), whereas the Al₂O₃ concentration varies from 13.6 wt% to 26.9 wt% (a relative variation of about 97%). In addition, the CaO concentration in the melt increases toward the interface and the SiO₂ concentration decreases toward the interface, leading to only small variations of $C_{CaO}C_{SiO_2}^2$ (where C is concentration) across the whole diffusion profile. The calculated activity product of $a_{CaO}a_{SiO_2}^2$ using MELTS (Ghiorso and Stack, 1995) also does not vary much across the whole diffusion profile either. That is, the Al₂O₃ concentration largely controls the saturation of anorthite in our experiments. In Figs. 9a-9c, we plot all available literature plagioclase-melt equilibrium data in “dry” melts (including terrestrial basalts and komatiite, lunar basalts, a chondritic melt, and eucrites) with $X_{An} > 0.90$ and compare the dependence of $-\ln K$ (either activity- or concentration-based) and $\ln(Al_2O_3)$ on $1000/T$, where the activities of SiO₂, Al₂O₃ and CaO are calculated using MELTS (Ghiorso and Stack, 1995), and $-\ln K$ (rather than $\ln K$) is used so as to enable a more straightforward comparison. Figure 9 shows that:

(1) The equilibrium melt compositions from phase equilibrium experiments and interface melt saturation compositions from anorthite dissolution experiments are similar. For example, at 0.5 GPa, our anorthite dissolution data are consistent with the equilibrium data of Panjasawatwong et al. (1995). That is, there is no need to distinguish between phase equilibrium data and anorthite dissolution data.

(2) Experimental data on lunar basalts (Grove and Raudsepp, 1978; Grove and Beaty, 1980; Finnilla et al., 1994) are broadly consistent with data on terrestrial basalts. Hence, it is not necessary to develop special models for lunar basalts with low SiO₂ and alkali contents, high FeO contents, and highly variable TiO₂ contents.

(3) The available experimental data do not show systematic variations of either $\ln K$ or $\ln(\text{Al}_2\text{O}_3)$ with pressure. For example, the 10⁻⁴ GPa data (black symbols) and the 0.5 GPa data (red symbols) fall on the same trend within error, the 0.6 GPa data (purple symbols) are above the trend, the 0.8 GPa point (green symbols) is below the trend, and the 1 GPa point (blue symbols) is on the trend. Lange et al. (2009) showed that the fusion volume of anorthite is small (the corresponding contribution to ΔG is at most 0.7 kJ/mol; while that for albite is larger, 3 to 4 kJ/mol at 0.5 GPa) and varies weakly with pressure, with a contribution to $\ln K$ of no more than 0.09 when pressure is less than 1 GPa. Therefore, it is difficult to accurately obtain the pressure dependence using the above dataset due to the experimental uncertainties within and between studies.

(4) The data scatter in $\ln K$ vs. $1/T$ is not noticeably smaller than in $\ln(\text{Al}_2\text{O}_3)$ vs. $1/T$ (in fact, the r^2 value for the $\ln(\text{Al}_2\text{O}_3)$ vs. $1/T$ fit is slightly better than that for the $\ln K$ vs. $1/T$ fit). That is, using K to characterize the anorthite saturation condition is not noticeably more accurate.

(5) The data of Morgan et al. (2006) are slightly off the trend in the three plots.

In conclusion, the multicomponent treatment using K as shown in Figs. 9a-b does not have much advantage over simply using Al_2O_3 concentration at least for the subset of data we are considering. We also tried to relate $\ln(\text{Al}_2\text{O}_3/X_{\text{An}})$ vs. $1/T$ to characterize anorthite saturation. It turns out that the simple approach of $\ln(\text{Al}_2\text{O}_3)$ vs. $1/T$ (Fig. 9c) provides a more consistent linear correlation, and hence it is adopted. We realize that our approach to use Al_2O_3 rather than K to characterize the saturation is an approximation. Nevertheless, the simple saturation model for anorthite is useful in modeling anorthite growth and dissolution kinetics, similar to the use of MgO to model olivine saturation (e.g., Niu et al., 2002; Chen and Zhang, 2008).

From Fig. 9c, excluding the data of Morgan et al. (2006), the Al_2O_3 concentration data in the melt at plagioclase-melt equilibrium can be fitted as a function of temperature by the following equation:

$$\ln C_{\text{s},\text{Al}_2\text{O}_3} = 8.032(\pm 0.192) - \frac{7882(\pm 287)}{T}, \quad (5)$$

where the errors provided in the parentheses are at 1σ level, and $r^2 = 0.948$. The above equation can reproduce the experimental $\ln C_{\text{s},\text{Al}_2\text{O}_3}$ to within 0.16 $\ln C$ units with 1σ prediction error of 0.07 $\ln C$ units, and the experimental temperatures to within 44°C with 1σ prediction error of 20°C , except for the data of Morgan et al. (2006), for which the errors are 0.18-0.26 in $\ln C$, and 65 - 99°C in temperature. That is, for plagioclase saturation in “anhydrous” melts when $X_{\text{An}} \geq 0.90$ and when SiO_2 in the silicate melt is between 39 wt% to 53 wt%, the simple equation above (eq. 5) is about as good as the more sophisticated models of MELTS (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998) and Putirka (2005).

4.2. Effective binary diffusivity of Al_2O_3

The effective binary diffusivity (EBD) of Al_2O_3 is another essential parameter in modeling anorthite dissolution and growth rates and is also of general interest, and it is well constrained from our experiments, by fitting the concentration profiles with the analytical solution (eq. 1). The fits are shown in Fig. 4 and Supplementary Materials. The fitting results are listed in Table 3 and Supplementary Materials. The Al_2O_3 diffusion data in our study can be fitted by the following Arrhenius relation (Fig. 10a):

$$\ln D_{\text{Al}_2\text{O}_3}^{\text{EBD, plag diss}} = -13.69(\pm 1.57) - \frac{19313(\pm 2485)}{T}, \quad r^2 = 0.75 \quad (6)$$

where T is in K and uncertainties are given at 1σ level. The above equation can reproduce experimental $\ln D$ values to within 0.49 $\ln D$ units, with 1σ uncertainty of 0.24 $\ln D$ units. Note that the above equation can only be applied to the case of anorthite dissolution in a basaltic melt due to limitations of EBDs.

Al_2O_3 diffusivity in lunar basalts (Finnila et al., 1994; Morgan et al., 2006) and terrestrial basalts during anorthite dissolution experiments (this study) are compared in Fig. 10a. Note that the Al_2O_3 diffusivities determined by Finnila et al. (1994) are only order-of-magnitude estimates according to the authors. The data in Fig. 10a show that limited Al_2O_3 diffusion data in lunar melts are scattered, though the calculated viscosity (calculated at 1300 °C) of the basaltic melt (~ 1.0 Pa·s) used by Finnila et al. (1994) is similar to those of the very low Ti and low Ti basaltic melts (~ 1.2 Pa·s and ~ 1.3 Pa·s) used by Morgan et al. (2006). The scatter is likely due to the fact that the diffusivities reported by Finnila et al. (1994) are only order-of-magnitude estimates.

To better understand the factors controlling the EBDs of Al_2O_3 , diffusion data during dissolution experiments of various minerals (olivine, diopside, quartz, anorthite, and spinel) and diffusion couple experiments in natural melts (lunar basalt, terrestrial basalt, and andesite) are compared in Fig. 10b. The mineral dissolution data include those for corundum dissolution into

413 CaSiO₃-Al₂O₃ melt (Cooper and Kingery, 1964) at 0.0001 GPa, dissolution of olivine, diopside,
414 spinel, and quartz into an andesitic melt at 0.5-2 GPa (Zhang et al., 1989), anorthite dissolution
415 into a lunar basalt at 0.0001 GPa (Finnila et al., 1994) and 0.6 GPa (Morgan et al., 2006), olivine
416 and diopside dissolution into a basaltic melt (Chen and Zhang, 2008, 2009), and this study. The
417 diffusion couple data include those in the diopside-anorthite system (Kubicki et al., 1990), the
418 dacite-rhyolite system (Baker et al., 1988), and the tholeiite-basanite system (Lunstrom, 2003).
419 The data are displayed in Fig. 10b and show that:

420 (1) Experimental pressure does not significantly affect the EBDs of Al₂O₃, at least within the
421 0.5 to 2.0 GPa pressure range, consistent with the conclusion of weak pressure dependence by
422 Chen and Zhang (2008, 2009).

423 (2) EBDs of Al₂O₃ during diffusive mineral dissolution experiments depend on the initial (far-
424 field) melt composition or viscosity. For example, Fig. 10b shows that the Al₂O₃ diffusivities
425 during mineral dissolution in andesitic melt obtained by Zhang et al. (1989) are less than those in
426 basaltic melt (Chen and Zhang, 2008, 2009; this study), as expected. When the diffusivity model
427 of Mungall (2002) is applied to calculate EBDs of Al₂O₃ (Mungall's model for Al diffusivity is
428 largely related to melt viscosity) from mineral dissolution experiments (Fig. 11a), it works well
429 for the data in this study and in Chen and Zhang (2008, 2009), but not so well for the data in
430 Zhang et al. (1989) and Morgan et al. (2006).

431 (3) EBDs of Al₂O₃ during mineral dissolution experiments also vary with the interface melt
432 composition. For instance, Al₂O₃ diffusivities in basaltic melts during olivine dissolution and
433 during diopside dissolution are similar (Chen and Zhang, 2008, 2009), but they are different
434 from those during plagioclase dissolution (Fig. 10b). In particular, the activation energy for
435 Al₂O₃ diffusion during plagioclase dissolution is lower than that during olivine and diopside

dissolution. Another example is quartz dissolution in andesitic melt (Zhang et al., 1989) in which the Al_2O_3 diffusivity is much smaller (Fig. 10b, labeled as “Qz, 234”) due to the very silicic composition of the interface melt. Preliminary modeling using a few simple compositional parameters cannot reconcile this datum with other data, but more complicated relations are not well constrained by the data.

After some trials, we approximate the compositional effect of $D_{\text{Al}_2\text{O}_3}$ in mineral dissolution experiments using a linear relation between $\ln D$ and $X_{\text{Si+Al}}$ of the far-field (initial) melt as well as that of the mineral. Because our goal is to understand the variation of $D_{\text{Al}_2\text{O}_3}$ in the melt during mineral dissolution experiments, and because the diffusion couple data cannot be treated the same way due to the presence of two far-field compositions, the diffusion couple data are not included in the treatment. For olivine, diopside and anorthite dissolution in basaltic melt JDF, we obtain

$$\ln D_{\text{Al}_2\text{O}_3}^{\text{EBD in basalt}} = -15.630(\pm 1.451)X_{\text{Si+Al}}^{\text{mineral}} - \frac{39863(\pm 158) - 23366(\pm 2255)X_{\text{Si+Al}}^{\text{mineral}}}{T} \quad (7)$$

where $X_{\text{Si+Al}}^{\text{mineral}}$ is cation mole fraction of Si+Al in the mineral, errors are given at 1σ level, and $r^2 = 0.938$. The above equation can reproduce the data in Chen and Zhang (2008, 2009) and this study within 0.50 $\ln D$ units with 1σ reproducibility of 0.23 $\ln D$ units.

For the more extensive data on mineral dissolution in andesitic to basaltic melts (including lunar melts), excluding one quartz dissolution data point from Zhang et al. (1989) and the order-of-magnitude data from Finnila et al. (1994), the Al_2O_3 diffusivity data of Zhang et al. (1989), Morgan et al. (2006), Chen and Zhang (2008, 2009) and this study can be fitted as a function of experimental temperature, $X_{\text{Si+Al}}$ in the far-field melts and in the minerals as follows:

$$\ln D_{\text{Al}_2\text{O}_3}^{\text{EBD}} = -15.332(\pm 1.537)X_{\text{Si+Al}}^{\text{mineral}} - \frac{31983(\pm 898) + 12991(\pm 1303)X_{\text{Si+Al}}^{\text{melt},\infty} - 23157(\pm 2414)X_{\text{Si+Al}}^{\text{mineral}}}{T}, \quad (8)$$

where $X_{\text{Si+Al}}^{\text{melt},\infty}$ is the cation mole fraction of Si+Al in the far-field melt (H is included in the calculation), and $r^2 = 0.928$. The above equation can reproduce the data to within $0.72 \ln D_{\text{Al}_2\text{O}_3}$ units with a 1σ uncertainty of 0.264 $\ln D$ units. The fit quality of this equation is shown in Fig. 11b. Cross-validation analyses (2-folds and 10-folds) of this model (eq. 8) and other models with fewer parameters were carried out, and the results show that eq. (8) gives the smallest mean square error (MSE) and hence does not over-fit the data. The effect of very high SiO_2 concentration in the melt on diffusivity (such as that during quartz dissolution) is not resolved in this study.

Comparing the fit of $D_{\text{Al}_2\text{O}_3}$ using eq. (8) as shown in Fig. 11b and the prediction using the model of Mungall (2002) as shown in Fig. 11a, it can be seen that our specific model predicts $D_{\text{Al}_2\text{O}_3}$ significantly better than the general model of Mungall (2002). Note that the model of Mungall (2002) is for tracer diffusivity and not for effective binary diffusivity. In addition, Mungall (2002) modeled the diffusivity of Al_2O_3 , SiO_2 and other high field strength elements to be the same and controlled primarily by viscosity. Hence, in a way, eq. (8) is modeling $D_{\text{Al}_2\text{O}_3}$ in a similar fashion to the model of Mungall (2002) in that $X_{\text{Si+Al}}$ in the melt is a main control of melt viscosity. On the other hand, melt viscosity cannot be the single control for the effective binary diffusivity of Al_2O_3 , SiO_2 and other high field strength elements, because effective binary diffusivity of Al_2O_3 is about 50% larger than that of SiO_2 (e.g., Zhang et al., 1989), contrary to the assumption of identical diffusivities by Mungall (2002).

4.3. Effective binary diffusivities of TiO_2 , FeO , MgO , and CaO

The EBDs of TiO_2 , FeO_t , and MgO are also obtained using the analytical solution (listed in Table 3); while fitting for CaO is only carried out when the semi-infinite boundary condition holds (Table 3). The EBDs of SiO_2 are not fitted, due to weak uphill diffusion of this component, a manifestation of multicomponent diffusion.

The diffusivity of TiO_2 is about 16% smaller than that of Al_2O_3 in the same anorthite dissolution experiment. The EBDs of FeO_t and MgO are similar and about 2.5 times that of Al_2O_3 . Compared with the EBD data from olivine and clinopyroxene dissolution experiments (Chen and Zhang, 2008, 2009), the EBDs of TiO_2 , FeO_t and MgO from this study are significantly smaller and give much smaller activation energies for diffusivity, indicating compositional as well as compositional-gradient dependences for EBDs of TiO_2 , FeO_t and MgO . TiO_2 and FeO_t often show uphill diffusion in various dissolution situations (Zhang et al., 1989; Chen and Zhang, 2008, 2009), indicating multicomponent effects.

Though we have attempted to fit the EBDs of CaO using eqs. 1-2, there is sometimes systematic misfit (Fig. 4). CaO often displays multicomponent diffusion effects, manifested by the uphill diffusion in the CaO concentration profiles of in previous dissolution studies on olivine, forsterite, spinel, and rutile (Zhang et al., 1989; Chen and Zhang, 2008). Although no uphill diffusion pattern is apparent in our CaO concentration profiles, the multicomponent diffusion effect may still result in complicated diffusion behavior of CaO . In other words, the cross-component terms of the diffusivity matrix are as significant as the diagonal term for CaO , resulting in the complicated diffusion feature in CaO concentration profiles. It is likely that using multicomponent approach can solve the issue. However, the set of experiments in this study cannot constrain the diffusivity matrix in an 8-component basaltic system (Trial and Spera, 1994).

4.4. Convective dissolution of anorthite in basaltic melt

The theory of convective crystal dissolution has been developed by Kerr (1995) and Zhang and Xu (2003), further verified by Zhang (2005) and Zhang and Xu (2008), and reviewed in Zhang (2008, 2013) and Liang (2010). To model convective dissolution or growth of anorthite in a basaltic melt requires knowledge of the densities of the melt and anorthite, the solubility and diffusivity of Al_2O_3 in the melt, the viscosity of the melt, the initial crystal size, the temperature and the pressure. The procedure for this modeling has been explained in Chen and Zhang (2008, 2009) in detail. The following calculation uses the basalt composition in Table 1 with 0.3 wt% H_2O (Chen and Zhang, 2008). We have verified that ≤ 0.3 wt% H_2O does not affect significantly the anorthite-melt equilibrium temperature and viscosity at $\geq 1280^\circ\text{C}$, using the MELTS program and the viscosity model of Shaw (1972).

We calculated the melt density based on the model of Lange and Carmichael (1987) and Ochs and Lange (1999), the anorthite density ($\text{An}\# > 90$) based on the equation of state model of Angel (2004), and the melt viscosity based on the model of Hui and Zhang (2007). The dependence of anorthite density on temperature was obtained using the thermal expansion coefficient data from Tribaudino et al. (2010). The upper limit of pressure for applying the anorthite density model is 3 GPa. No viscosity model is available for basaltic melt at 1 GPa, but pressure does not significantly affect viscosity in this pressure range (e.g., Hui et al., 2009). Hence, the viscosity model at 1 bar pressure conditions is used for pressures of ≤ 1 GPa pressure range. Based on the above models, anorthite dissolution in basaltic melt was modeled over a temperature range from 1100°C to 1500°C , a pressure range of 10^{-4} GPa to 1 GPa, and an anorthite composition range from An_{90} to An_{100} .

The modeling results show that the Reynolds number (Re) ranges from 4×10^{-11} to ~ 1 for anorthite crystals of 1-8 mm effective radius. The steady-state falling/rising velocity of anorthite crystals in the melt is determined using Stokes' law, because Re is smaller than 1. The steady-state falling/rising velocity of anorthite is $\leq 2 \times 10^{-4}$ m/s for a 1-mm-radius single crystal, and ≤ 0.01 m/s for a 8-mm-radius crystal. Compared to the olivine dissolution estimates of Chen and Zhang (2008), the largest steady-state rising velocity in our anorthite convective dissolution model is about 1 order of magnitude smaller than the corresponding values of olivine, due to the smaller density difference between anorthite and the basaltic melt than that between olivine and the basaltic melt. Figure 12 shows the difference in density between anorthite (An#94) and MORB under different temperature and pressure conditions. In MORB, the typical density difference is less than 0.05 g/cc for anorthite, while that for olivine is about 0.5 g/cc. According to the Stokes' Law or eq. 7a-c in Chen and Zhang (2008), the steady rising/sinking velocity of a crystal is proportional to the crystal-melt density difference, while the boundary layer thickness increases as the crystal-melt density difference decreases. A thicker boundary layer slows the convective dissolution rate (Eq. 20 of Zhang et al, 1989). According to our modeling results, anorthite crystals of the same size can survive about 1 order of magnitude longer than olivine at the same temperature and pressure, while the maximum rising distance is about an order of magnitude smaller than olivine's sinking distance (Fig. 13). When the temperature rises, the dissolution rate increases, and both the survival time and distance of the same-size anorthite crystal shorten. Unlike for olivine dissolution, the density difference between anorthite and basalt (with 0.3 wt% H_2O) becomes zero when temperature reaches $\sim 1220^\circ C$ at 0.2 GPa (but the density crossover depends on the H_2O content; e.g., a completely dry basaltic melt would have a density crossover at $\sim 1455^\circ C$ at 0.2 GPa). At zero density difference, the

dissolution would be controlled by pure diffusion. When temperature further increases to above ~1220°C, the density of MORB drops below that of anorthite, resulting in anorthite sinking in the basaltic melt.

We hoped to model convective growth and flotation of anorthite crystals in the late stages of lunar magma ocean, which presumably led to the formation of the anorthosite crust of the moon. However, because the pressure effect of anorthite-melt equilibrium is not resolved and is necessary in such modeling, this application must wait for future progress in understanding plagioclase-melt equilibrium in more detail. On the other hand, the weak pressure dependence is an advantage in predicting anorthite equilibrium temperature, and in predicting convective plagioclase crystallization/dissolution rate and rising/falling velocity in a magma chamber (Fig. 13) where the pressure variation is small. Moreover, the small pressure effect suggests that a small degree of undercooling would lead to plagioclase oversaturation in a large range of depths, resulting in the formation, growth and flotation of plagioclase, and possibly rapid formation of anorthosite crust.

5. CONCLUSIONS

1. Our time-series experiments (covering 1280~1400 °C, at 0.5 GPa) on olivine dissolution in a basaltic melt were unable to confidently resolve the variation of the interface Al_2O_3 concentration. Experiments for dissolution from two different crystallographic surfaces ($12\bar{1}$) and $(\bar{3}02)$ of anorthite do not show anisotropic dissolution.

2. The overgrowth of the dissolution crystal during quench has been resolved well by high-spatial resolution EDS analyses.

3. The effective binary diffusivity of Al_2O_3 , FeO , MgO and TiO_2 , and the interface concentration of Al_2O_3 were obtained from experiments. The effective binary diffusivity of Al_2O_3 depends on the melt composition, which is approximately characterized by the cation mole fraction of (Si+Al) in the melt. The effective binary diffusivity of TiO_2 is just slightly smaller than that of Al_2O_3 , whereas those of FeO and MgO are about 2.5 times Al_2O_3 diffusivity.

4. The interface melt Al_2O_3 concentration data at anorthite near-saturation obtained in this work are consistent with literature data on anorthite-melt equilibrium. The pressure effect on anorthite-melt equilibrium temperature cannot be resolved from available data.

5. Our new data coupled with literature data allow quantitative modeling of the dissolution rate of a rising or sinking plagioclase in magma. Compared to the convective dissolution of olivine at a similar degree of undersaturation, plagioclase can survive for a longer time but would rise/sink for a shorter distance in a magma.

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APPENDIX

Supplementary file and data associated with this article include: (1) a pdf file for oxide concentration profiles in all experiments, (2) an excel file for electron microprobe data of the concentration profiles, and (3) an excel file for all Al₂O₃ diffusion data (including literature and our own data) we used in obtaining eq. (8). These can be found in the online version, at [xxxxxxxxxx](#).

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Figure Captions

Fig. 1. Sketch of the experimental capsule design. A is the graphite cap, B is the graphite capsule, C is the anorthite wafer, D is the basalt glass wafer, and E is the graphite ring that surrounds the basalt.

Fig. 2. (a) Back-scattered electron image of the experiment sample PDisBa-210. The dissolution distance was obtained by directly measuring the distance between the anorthite-melt interface and the edge of the anorthite; (b) Al_2O_3 concentration profiles for the same sample. Three traverses were measured across the sample section (their locations are indicated in Fig. 2a). The fit by Eq. (1) is also plotted (solid purple curve).

Fig. 3. Types of anorthite-melt interface features at (A) 1280°C, (B) 1330°C, (C) 1400°C, and (D) 1500°C. At 1280 °C and 1330 °C, the interface is straight and sharp without visible quench crystals. At 1400 °C and 1500 °C, the interface region has numerous oriented dendritic plagioclase crystals.

Fig. 4. Concentration profiles of major oxide components in PDisBa-228 (1408 °C, 143 s) with fits of monotonic profiles using Eq. (1).

Fig. 5. Elemental mapping of sample PDisBa-202. Al, Mg, Fe, and Ca are mapped using wavelength-dispersive spectroscopy. (a) Back-scattered electron image of the whole sample; (b) a blow-up of the boxed region in (a), for which elemental mapping was carried out. (c), (d), (e) and (f) are elemental maps of Al, Fe, Mg, and Ca.

Fig. 6. BSE image and high-spatial-resolution EDS analysis across the plagioclase-melt interface. EDS analysis is calibrated using the electron microprobe analysis on the same sample. From the anorthite into the basaltic melt (from left to right), four units can be recognized: the original anorthite (gray), the overgrown plagioclase An₆₇₋₇₄ (narrow darker region), the plagioclase-constituent-depleted melt due to quench growth (narrow bright region), and basaltic melt with the normal diffusion profile.

Fig. 7. Al_2O_3 concentrations in interface melts versus the experimental duration. Orientation 1 (v1) represents crystallographic surface ($\bar{3}02$); orientation 2 (v2) represents ($12\bar{1}$); orientation 3 (v3) is not determined. Experiments 223 and 214 are considered as outliers, and not included in the quantitative results.

Fig. 8. Variation of anorthite dissolution distance with time. L1 represents the directly measured dissolution distance under BSE image, 1σ error of L1 (solid symbols) is also drawn on the plot, and error is not shown when it is smaller than the symbol size; L2 is the calculated dissolution distance based on mass conservation using Al_2O_3 concentration profiles. v1 represents the crystallographic direction $[\bar{3}02]$; while v2 represents the direction $[12\bar{1}]$. v3 is not determined. The straight-line (linear proportionality) fits assume pure-diffusion control.

Fig. 9. Experimental plagioclase saturation data from phase equilibrium and plagioclase dissolution experiments in “dry” melts for $X_{\text{An}} \geq 0.90$. (a) $-\ln K$ vs. $1000/T$, where K is defined by

eq. (4) with calculated activities using MELTS. (b) $-\ln K_{\text{oxides}}$ vs. $1000/T$, where K_{oxides} is calculated based on the concentrations of SiO_2 , Al_2O_3 and CaO . (c) $\ln(\text{Al}_2\text{O}_3)$ vs. $1000/T$, where Al_2O_3 is saturation concentration in wt%. The line is a fit to all data except for Morgan et al. (2006). The data appear to indicate weak nonlinearity in $\ln K$ vs. $1000/T$, which is ignored. Different pressures are indicated using different colors: black for 1 bar data, red for 5 kb (0.5 GPa), purple for 6 kb (0.6 GPa), green for 8 kb (0.8 GPa), and blue for 10 kb (1 GPa). References: S2001 = Sugawara (2001) phase equilibrium experiments on basalt to dacite; J1993 = Jurewicz et al. (1993) on chondritic high-FeO basalts; Grove = Grove and Raudsepp (1978) on Apollo 15 basalts, Grove and Beaty (1980) on Apollo 11 basalts; F1994 = Finnila et al. (1994) on plagioclase dissolution in lunar basalt; others = two points from Kinzler and Grove (1985) on komatiite, one point from Yang et al. (1996) on MORB, one point from Stolper (1977) on eucrite and one point from Longhi and Pan (1988); P1995 = Panjasawatwong et al. (1995) on basalts; M2006 = 0.6-GPa data of Morgan et al. (2006) on plagioclase dissolution in lunar basalts; G1992 = 0.8-GPa point from Grove et al. (1992) on MORB; J1986 = 1-GPa point from Johnston (1986) on island arc basalts.

Fig. 10. (a) A comparison of effective binary diffusivity (EBD) of Al_2O_3 from anorthite dissolution experiments. (b) EBD of Al_2O_3 from dissolution experiments of various minerals. References: Zhang89 = Zhang et al. (1989) various minerals dissolution into andesite melt at 0.5 to 2 GPa Finnila94 = Finnila et al. (1994), anorthite dissolution in lunar basalt at 10^{-4} GPa; Morgan06 = Morgan et al. (2006), anorthite dissolution in lunar basalt at 0.6 GPa; Chen08 and Chen 09 = Chen and Zhang (2008, 2009), olivine and diopside dissolution in terrestrial basalt at from 0.5 to 2 GPa; Baker88 = Baker and Watson (1988), Cl- and F-bearing silicate melt diffusion couples; Kubicki90 = Kubicki et al, 1990, diffusion couples of diopside to $\text{Di}_{40}\text{An}_{60}$ composition; Lundstrom03 = Lundstrom, 2003.

Fig. 11. (a) Comparison of the calculated Al_2O_3 diffusivity using Mungall's model (2002) and the fitted EBD of Al_2O_3 of literature data. The solid line is the 1:1 line. The dashed lines are 0.5 $\log_{10} D$ units off the 1:1 line. (b) Comparison of the calculated EBD of Al_2O_3 using Eq. (8) and the fitted EBD of Al_2O_3 of literature data. The solid line is the 1:1 line.

Fig. 12. Density difference between anorthite (An#94) and MORB at 1100 – 1500°C and 10^{-4} – 1 GPa.

Fig. 13. Falling/rising distance and survival time of a convectively dissolving anorthite crystal as a function of temperature and initial radius of the anorthite crystal (An#94) in MORB at 0.2 GPa.

TABLES

827 Table 1. Composition of anorthite crystal and basalt glass in experiments.

Oxides	Anorthite		Basalt (JDF)	
	Composition (wt%)	StdDev (wt%)	Composition (wt%)	StdDev (wt%)
SiO ₂	44.77	0.15	51.49	0.48
TiO ₂	bdl	-	1.85	0.16
Al ₂ O ₃	35.07	0.24	13.40	0.22
FeO _t	0.50	0.03	12.23	0.23
MnO	nd	-	0.21	0.09
MgO	0.06	0.02	6.74	0.13
CaO	18.96	0.16	11.00	0.14
Na ₂ O	0.66	0.02	2.73	0.11
K ₂ O	0.01	0.01	0.18	0.03
H ₂ O			0.32	0.07
Total	100.03	-	99.84	

828
829 bdl means below detect limit, nd means not determined.
830 StdDev means one standard deviation.
831

832 Table 2. Summary of experimental conditions

Exp No.	Crystallographic surface (<i>hkl</i>)	T1 (°C)	T2 (°C)	Duration (s)	L1 (μm)	L2 (μm)
201	(302)	1280	1293	1826	--	37.6
202			1284	6010	--	87.6
203			1280	338	--	11.9
205			1286	201	--	5.2
207			1278	1223	22±4	18.9
208			1278	6015	102±1	98.2
209			1280	3615	--	43.9
221	(121̄)		1284	1827	42±1	40.9
222			1279	329	--	8.6
223			1280	6005	--	141.8
227			1283	6009	66±4	71.1
301	-		1284	319	--	8.9
302			1284	3615	--	52.9
304			1281	149	--	9.4
210	(121̄)	1330	1333	1819	78±1	79.3
211			1333	919	47±1	40.2
212			1334	443	47±12	32.8
213			1328	3615	103±4	104.5
214			1327	2538	152±5	151.7
215			1327	143	--	14.6
216			1326	2540	103±1	95.7
228		1400	1408	143	--	37.1
229			1404	621	--	-
233			1405	620	--	87.4
230		1500	1506	134	123±16	132.1

833 T1 is the planned experimental temperature, and T2 is the corrected experimental temperature (Hui et al., 2008). All
834 the experiments were done at 0.5 GPa.

835 L1 is the directly measured dissolution distance using the electron microscope. Sometimes L1 cannot be determined
836 reliably because the plagioclase edge is missing from one side of the polished glass section, or because of many
837 cracks. L2 is the dissolution distance calculated from Al₂O₃ concentration profiles using mass balance.

838 The crystallographic directions for experiments 301, 302 and 304 were not determined.

844 Table 3. Fitted effective binary diffusivities (EBD) of Al₂O₃, TiO₂, FeO_t, MgO and CaO

Exp No.	Diffusivity (10 ⁻¹² m ² /s)				
	Al ₂ O ₃	TiO ₂	FeO _t	MgO	CaO
201	4.7(1)	4.0(6)	8.3(5)	8.2(6)	-
202	6.5(2)	6.0(6)	12.7(4)	15.8(3)	-
203	4.5(1)	3.7(5)	11.1(6)	9.8(4)	44.2(4.5)
205	3.0(1)	2.7(6)	6.6(6)	5.3(6)	-
207	3.6(1)	3.5(4)	5.9(2)	6.4(4)	-
208	7.2(1)	6.6(4)	15.8(1)	15.6(4)	-
209	5.1(1)	4.3(4)	10.5(4)	10.8(5)	-
221	4.1(1)	3.8(4)	8.3(4)	9.6(5)	-
222	4.0(1)	3.2(7)	7.5(6)	7.4(6)	-
301	2.9(1)	2.2(4)	5.9(4)	5.6(5)	-
302	5.5(2)	3.8(6)	9.8(7)	11.0(8)	-
304	5.1(2)	5.6(1.4)	9.8(8)	7.4(7)	-
227	5.5(1)	5.2(5)	11.7(4)	11.4(4)	-
210	6.8(1)	6.5(4)	16.6(3)	17.3(4)	-
211	5.0(1)	4.1(3)	10.5(3)	10.6(3)	29.2(2.1)
212	6.4(1)	4.9(4)	15.7(4)	15.4(5)	40.6(2.5)
213	7.5(1)	6.7(4)	19.3(5)	18.4(5)	-
215	6.5(1)	5.8(7)	16.6(7)	15.0(7)	27.1(22.8)
216	8.0(1)	7.4(3)	20.7(4)	20.2(5)	-
228	10.1(1)	8.5(4)	27.5(6)	25.6(5)	56.4(3.1)
233	13.3(1)	11.6(4)	36.6(6)	35.0(8)	83.9(5.9)
230	22.3(3)	17.6(4)	57.9(1.5)	56.1(1.3)	100.1(4.2)

845
846 The value in parentheses indicates 1σ error on the last digit of the diffusivity. EBDs of CaO are not provided when
847 the semi-infinite boundary condition is not satisfied.
848

856 Table 4. Interface melt composition of all the experiments

Sample#	SiO ₂ ^a	TiO ₂	Al ₂ O ₃	FeO	MnO ^a	MgO	CaO ^a	Na ₂ O ^a	K ₂ O ^a
201	47.5	1.17(2)	20.14(5)	9.51(3)	0.18	5.18(3)	11.9	2.7	0.17
202	47.3	1.16(1)	20.61(2)	9.52(1)	0.20	5.07(1)	12.0	2.7	0.16
203	48.7	1.36(2)	18.59(3)	10.17(3)	0.20	5.56(1)	11.6	2.8	0.16
205	49.2	1.46(2)	17.12(4)	10.44(3)	0.23	5.83(3)	11.3	2.9	0.17
207	48.8	1.36(2)	18.42(3)	10.14(2)	0.20	5.60(2)	11.6	2.8	0.17
208	47.2	1.11(1)	21.12(2)	9.19(1)	0.17	4.99(1)	12.2	2.7	0.16
209	47.8	1.31(1)	18.98(3)	10.01(2)	0.18	5.49(1)	11.6	2.8	0.17
221	48.2	1.10(2)	21.22(3)	9.44(3)	0.20	5.15(2)	12.0	2.8	0.17
222	48.9	1.44(3)	17.66(3)	10.43(3)	0.20	5.83(2)	11.4	2.8	0.17
227	48.1	1.24(1)	20.20(2)	9.80(2)	0.19	5.35(1)	11.7	2.8	0.16
301	47.8	1.36(2)	18.27(5)	10.88(3)	0.20	5.61(2)	11.3	2.9	0.18
302	47.0	1.21(2)	19.68(3)	9.83(4)	0.21	5.30(2)	11.6	2.9	0.17
304	49.0	1.29(2)	19.14(6)	9.78(5)	0.19	5.51(3)	11.3	2.9	0.18
210	45.8	0.84(1)	24.33(3)	8.37(2)	0.15	4.50(2)	12.5	2.6	0.14
211	46.7	0.98(2)	22.83(2)	8.92(2)	0.16	4.79(2)	12.1	2.8	0.16
212	46.7	0.92(2)	22.91(3)	8.52(2)	0.18	4.60(2)	12.3	2.7	0.14
213	47.4	0.90(1)	23.36(3)	8.49(2)	0.16	4.57(1)	12.3	2.5	0.15
215	48.5	1.09(3)	21.35(4)	8.91(3)	0.15	4.99(2)	12.0	2.8	0.16
216	46.8	0.89(1)	23.76(4)	8.39(2)	0.15	4.44(1)	12.6	2.6	0.13
228	45.7	0.62(2)	26.92(4)	7.39(3)	0.11	3.87(2)	13.0	2.6	0.12
229 ^b	45.2	0.6	26.8	6.5	0.1	3.4	13.5	2.7	0.12
233	45.9	0.61(1)	26.87(4)	7.27(3)	0.14	3.85(2)	13.1	2.6	0.12
230 ^c	44.5	0.02	34	2.66	0.05	1.26	16.6	2.0	0.04

857 Interface melt compositions are extrapolated by fitting the diffusion profiles using the analytical solution to the
858 diffusion equation (eqs. 2a-2b), 1 σ fitting errors are given in the parentheses, meaning the uncertainty on the last
859 digit.

861 a. SiO₂, Na₂O, K₂O and MnO do not have obvious “normal” diffusion profiles. Therefore, the interface
862 concentrations of these components are estimated by finding the mean of the points near the interface, and the error
863 is not provided for these three components.

864 b. Sample PIDisBa-229 is heavily cracked near the interface, losing a majority of the diffusion profile. Therefore
865 estimation of the interface composition is obtained by averaging the points near the interface.

866 c. Quench crystals near the interface of PIDisBa-230 disrupt the diffusion profiles near the interface. Therefore, the
867 interface composition is roughly obtained by averaging the near-interface data points.

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871 Fig. 1

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Fig. 3

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Fig. 6

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Fig. 10

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903 Fig. 13