Noble Gas Partition between Basaltic Melt and Olivine Crystals at High Pressures

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Abstract. Noble gas solubilities for basaltic melt and olivine crystals were determined for temperatures of 1250°C, 1300°C, and 1600°C and pressures of 0.5 Kbars, 1 Kbar, and 2 Kbars.

Solubilities in basaltic melt increased with temperature, but were almost independent of pressure. The solubilities in olivine increased with temperature, and were smaller at higher pressures. Olivine-basalt distribution coefficients (\(D_l\)) of noble gases were as follows; 0.02 < \(D_{\text{He}}\) < 0.7, 0.03 < \(D_{\text{Ne}}\) < 0.6, 0.087 < \(D_{\text{Ar}}\) < 2.0, 0.1 < \(D_{\text{Kr}}\) < 3.0.

Surface tensions for basaltic melt calculated from the noble gas solubility data were almost independent of temperature and pressure up to 2 Kbars with value of 130 ± 10 dyne/cm.

1. Introduction

Noble gases are inert and rare in the Earth, so that they serve as an excellent tracer in resolving the Earth evolution processes such as magma generation and its transportation, mantle degassing, atmospheric evolution, and so on. The fundamental physical process controlling the noble gas behavior in the above processes is described by noble gas distribution between melt and crystal. So far, few attempts have been made to estimate distribution coefficients of noble gases between silicate melt and crystal in spite of their great importance. This may be due to a common feeling that noble gases are extremely incompatible elements and cannot be accommodated in any significant amount in a crystal structure. A preliminary attempt to estimate distribution coefficients of noble gases was made by Batiza et al. (1979). They compared the noble gas content of volcanic rock matrix and its constituting minerals, and estimated distribution coefficients. They obtained values of about 0.1 for Ne. However, values for heavy noble gases ranged from 2 to 8. Since the results were unexpected, Batiza et al. concluded that noble gases had been lost from the samples, that crystals (minerals) and melt (volcanic rocks) were not kept in equilibrium with respect to the noble gas phase, and that the calculated distribution
coefficients were not real.

The first systematic approach of measuring crystal-melt distribution coefficients in a laboratory was made by HIYAGON and OZIMA (1982, 1986). They did the experiments by growing crystals in silicate melt. Two methods of crystal growth were used; one was to grow crystals under high pressure (1.5 GPa) using a piston-cylinder-type apparatus, and the other was to grow crystals under flowing Ar at atmospheric pressure. The separation of the crystals from the melt was done by hand under microscopic observation. The obtained distribution coefficients were 0.2–0.5 for Ar and Kr at high pressure and 0.08–0.18 for Ar at atmospheric pressure. The distribution coefficients obtained by HIYAGON and OZIMA (1982, 1986) were likely to be upper limits, since in their experiments there was a possibility that the separated crystals contained submicroscopic melt or fluid inclusions which contained noble gases.

To avoid glass contamination of crystal separates, BROADHURST et al. (1990, 1992) developed an alternative experimental technique. Silicate melts and natural minerals were held in separate platinum capsules in a 1 bar flowing noble gas atmosphere. The samples were then quenched, and the gas concentrations were measured with a mass spectrometer. The obtained distribution coefficients were surprisingly high; 0.013–0.37 for Ne, 0.15–0.84 for Ar, 0.31–2.4 for Kr, and 3.2–47 for Xe. These results suggest that noble gases are compatible in crystals and the solubility of the noble gases increases with increasing noble gas atomic number. BROADHURST et al. (1990, 1992) concluded that noble gas solubilities in crystals were controlled by point defect abundances.

The results by HIYAGON and OZIMA (1982, 1986) and by BROADHURST et al. (1990, 1992) are very important in interpreting mantle degassing processes, since the results are contrary to the common assumption that noble gases solve more easily into melt than into crystal. It is very important to re-examine this problem, and therefore we performed experiments to measure noble gas solubilities in basaltic melt and olivine crystals at high pressures.

Surface tension is one of the most important parameters in discussing magma generation. Magma is formed by partial melting of mantle materials. The partially molten material migrates through grain boundaries and forms magma. The flow of melt through grain boundaries is primarily controlled by the surface tension of the melt. The surface tensions of silicate melts at atmospheric pressure were measured by MURASE and McBRIN (1973). They used two experimental methods to measure surface tension: the sessile-drop technique and the pin method. The estimated values of surface tensions were about 250–450 dyn/cm at 1000–1400°C. However, the estimated values were those at atmospheric pressure, but not at high pressures which are relevant to the condition in the Earth’s interior. Surface tension data at high pressure are extremely scarce owing to experimental difficulty. We, therefore, attempted to estimate surface tension of basaltic melt at high pressure through the measurement of noble gas solubility.
2. Experimental Procedures

2.1 Starting samples

We used basalt powder and olivine crystals in the experiments. Chemical analyses and sample source data for the basalt powder and olivine crystals are given in Table 1. Olivine crystals were crushed, and washed in ethanol. They were ground to powders in several steps, and their final size was a few microns. In the case of basalt powder, its size was about 250 μ.

2.2 High pressure experiments

Basalt powder and olivine crystals were contained in platinum capsules (2 mm in diameter and 5 mm in depth). Since one end of the platinum capsule was only

<table>
<thead>
<tr>
<th>sample</th>
<th>basalt (%)</th>
<th>olivine (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>53.20</td>
<td>39.64</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.19</td>
<td>0.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14.67</td>
<td>0.03</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.13</td>
<td>-</td>
</tr>
<tr>
<td>FeO</td>
<td>10.09</td>
<td>10.52</td>
</tr>
<tr>
<td>MnO</td>
<td>0.20</td>
<td>0.16</td>
</tr>
<tr>
<td>MgO</td>
<td>4.66</td>
<td>48.25</td>
</tr>
<tr>
<td>CaO</td>
<td>9.89</td>
<td>0.08</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.03</td>
<td>0.01</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.42</td>
<td>0.00</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>H₂O⁺</td>
<td>0.31</td>
<td>-</td>
</tr>
<tr>
<td>H₂O⁻</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>Cr₂O₅</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>NiO</td>
<td>-</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Total 99.96  99.09

*: Tholeiitic basalt from O-shima volcano in Japan. Chemical analyses are after Ando et al. (1989).

**: Olivine from peridotite KLB-1 (Kilborne Hole crater in New Mexico). Chemical analyses are after Takahashi (1986).
loosely pinched, the noble gas mixture \((^4\text{He};^20\text{Ne};^36\text{Ar};^84\text{Kr} = 1:0.905:0.326:0.570)\)
used as a pressure medium could freely enter into the capsule. The samples were then
loaded in a pressure vessel, and kept for 1, 2, 5, and more than ten hours at 1250°C,
1300°C, and 1600°C and at 0.5, 1, and 2 Kbars pressures of the noble gas mixture.
At these temperatures, the basalt was melted, but olivine did not melt. The samples
were then quenched to 100°C in about 5 seconds. No visible alteration of the samples
was noticed.

2.3 Gas analyses
Samples used for noble gas analyses were weighed, wrapped in clean Al foil,
and preheated to 150°C for several hours in a high vacuum gas extraction line to
remove adsorbed atmospheric gases. Gases were extracted from the samples in one
step (at 1400°C for basalt, and 1800°C for olivine) heating. Active gases were
removed by Ti-Zr getters. After removal of active gases, He and Ne were separated
from Ar, Kr, and Xe by adsorption of the latter on a charcoal trap at liquid nitrogen
boiling temperature. The Ar, Kr, and Xe fractions were later desorbed from the
charcoal trap at 100°C.

A BALZERS QMG421 quadru-pole mass spectrometer (QMS) was used for
quantitative analyses of noble gases. The QMS had a crossbeam ion source, where
emission current was 1 mA, and was fitted with two collectors: a Faraday collector
with on-axis and a 17-stage secondary electron multiplier with 90° off-axis. In the
experiments we used the secondary electron multiplier (SEM) with an ion counting
 collector.

We calibrated the instrument before and after every two or three sample
analyses, and the average values of the before and after calibrations were used for the
analyses. The reproducibility of the calibrations was less than 5% for all noble gases.
We tried to keep the pressures of the samples close to the pressures at which the
sensitivity measurements were carried out, since sensitivity of the QMS might
depend on sample pressure.

3. Results

3.1 Solubility equilibrium of noble gases
To confirm whether or not solubility equilibrium was attained, we measured the
time variation of noble gas contents. In Fig. 1 we show concentrations of noble gases
in basaltic melt and olivine crystal normalized to the concentrations obtained after
2 hours. For the basaltic melt (Fig. 1(a)), there was little change in the concentrations
of noble gases after 2 hours. Therefore, we concluded that 2 hours were enough to
attain solubility equilibrium of noble gases in the basaltic melt. In the case of olivine
crystal (Fig. 1(b)), we needed at least 5 hours to attain solubility equilibrium.

3.2 Noble gases solubilities and distribution coefficients
The results of solubility measurements are listed in Table 2. We plotted noble
gas solubilities measured at various pressure and temperature conditions in Fig. 2.
The He solubilities obtained in these experiments should be discarded because of
Fig. 1. (a) Noble gas concentration in basaltic melt is plotted against time duration during which basaltic melt samples were equilibrated with noble gases. The results show that there is little change in the concentration after 2 hours. Hence, we conclude that 2 hours are enough to attain solubility equilibrium. (b) Noble gas concentration in olivine is plotted against time duration during which the olivine crystal samples were equilibrated with noble gases. The results show that we need at least 5 hours to attain solubility equilibrium.
Table 2. Noble gas solubilities in basaltic melt and olivine crystal.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure (Kbars)</th>
<th>Temperature (°C)</th>
<th>Time Duration (hours)</th>
<th>$^4$He (x 10^-4 cm^3 STP/g/bar)</th>
<th>$^{20}$Ne</th>
<th>$^{36}$Ar</th>
<th>$^{84}$Kr</th>
</tr>
</thead>
<tbody>
<tr>
<td>basaltic melt</td>
<td>0.5</td>
<td>1300</td>
<td>13</td>
<td>(2.90)</td>
<td>3.53</td>
<td>1.47</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1300</td>
<td>12</td>
<td>(2.14)</td>
<td>3.65</td>
<td>1.77</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1300</td>
<td>14</td>
<td>(4.12)</td>
<td>3.76</td>
<td>1.58</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1250</td>
<td>10.5</td>
<td>(2.32)</td>
<td>2.55</td>
<td>0.896</td>
<td>0.421</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1600</td>
<td>1</td>
<td>(2.81)</td>
<td>5.00</td>
<td>2.34</td>
<td>1.64</td>
</tr>
<tr>
<td>olivine crystal</td>
<td>0.5</td>
<td>1300</td>
<td>13</td>
<td>(1.89)</td>
<td>2.54</td>
<td>3.93</td>
<td>3.57</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1300</td>
<td>12</td>
<td>(1.28)</td>
<td>1.67</td>
<td>2.25</td>
<td>2.32</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1300</td>
<td>14</td>
<td>(0.953)</td>
<td>1.02</td>
<td>1.39</td>
<td>1.41</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1600</td>
<td>1</td>
<td>(19.6)</td>
<td>30.4</td>
<td>47.1</td>
<td>50.5</td>
</tr>
</tbody>
</table>

The solubilities of He in two materials can not be trusted because of possible He loss from the sample.

Possible He loss from the samples. The possibility of He loss was inferred from hot blank of He that was much higher than usual. It seems that the higher hot blank of He was due to He leaked from samples. Therefore, the obtained solubility data of He could not be trusted. Noble gas solubilities in basaltic melts obtained in the present study are almost the same as other published values (Lux, 1987).
Fig. 2. (a) Noble gas solubilities in basaltic melts obtained by the present study and by Lux at 1350°C (1987): Helium data in the present study may not be trusted because of possible helium loss. (b) Noble gas solubilities in olivine: Helium data may not be trusted because of possible helium loss.

The results of distribution coefficients between basaltic melt and olivine crystal are shown in Fig. 3, that includes distribution coefficients obtained in a laboratory by Hiyagon and Ozima (1982, 1986) and Broadhurst et al. (1990, 1992), and on natural samples by Marty and Lussiez (1993) and Trull and Kurt (1993). In Fig. 3, we see that our results agree with the laboratory experiments, but not with the
natural sample result by Marty and Lussiez (see comments on Marty and Lussiez by Hiyagon (1994)).

4. Discussions

4.1 Equilibrium condition

We evaluated the equilibrium condition by comparing the typical diffusive length of a noble gas atom with the typical grain size of the basalt powder. We can write the equilibrium condition as

$$\sqrt{D_t t} > r,$$

where $D_t$ is the diffusion coefficient for noble gas “i” in the basaltic melt, $t$ is the time duration of the solubility experiment, and $r$ is the radius of the basalt powder. We examined the equilibrium condition only for Kr, because it has the lowest diffusivity in the four noble gases (Lux, 1987). Taking value of $4.0 \times 10^{-6}$ cm$^2$/s at 1350°C for Kr (Lux, 1987) for basaltic melt, we obtained a typical diffusive length of 1200 µ for one hour. This value is much larger than the typical grain size ($r \approx 250$ µ). Therefore, we believe that the equilibrium condition is safely satisfied for basaltic melt.
In principle we can apply the same method for an olivine crystal as applied for the basaltic melt. However, we examined the equilibrium condition of the olivine crystal for He, because diffusion coefficients of noble gases in olivine are scarce except for He. Therefore, we take a value of $1.97 \times 10^{-8} \text{ cm}^2/\text{s}$ at $1360^\circ\text{C}$ for He (HART, 1984), and we obtain typical diffusive length of $84 \mu$ for one hour. This value is far beyond the typical grain size ($r \approx 1 \mu$). In the case of basaltic melt, the diffusion coefficient of Kr is 10 times smaller than that of He (LUX, 1987). If we assume that diffusion coefficients of the other noble gases are at most 10 times smaller than that of He, we obtain the typical diffusive length of $27 \mu$. This value is lower limit, but still larger than a typical grain size. Therefore, we believe that the equilibrium condition is also attained in the olivine crystal for the noble gases.

4.2 Solubilities and distribution coefficients

Noble gas solubilities in basaltic melt measured at various conditions are shown in Fig. 2(a). In Fig. 2(a), we can see that there is little change of the solubilities with pressure, but there is significant change of the solubilities with noble gas radius; the greater the noble gas radius, the smaller the solubilities. Also there is change of the solubilities with temperature between $1250^\circ\text{C}$ and $1600^\circ\text{C}$; the higher the temperature, the larger the solubilities.

In the case of olivine crystal (Fig. 2(b)), the trend of solubility is different from the case in the basaltic melt. Figure 2(b) shows that the solubility slightly increases with increasing noble gas atomic number, and there is significant pressure and temperature dependences of the solubilities. As pressure increases, the solubility decreases, and the solubility is higher for higher temperature. These trends are contrary to what one would generally expect for solubility. Also, the observed values of the solubility are unexpectedly high. In accordance with the high solubility in olivine, the distribution coefficients between basaltic melt and olivine crystal are also high. Furthermore, the distribution coefficients are higher for heavier noble gases.

We examined carefully olivine crystals before and after the solubility experiments with a scanning electron microscope, and found that in the sample used for the solubility experiments, there developed submicroscopic crystals ranging from $1 \mu$ to $10 \mu$. No such microscopic crystals were observed before the solubility experiments. Consequently, we cannot totally rule out a possibility that some fractions of the ambient noble gases used as a pressure medium might be trapped in the grain boundaries of the crystals to give the rather unexpected results such as the unusually high solubility values and the negative pressure coefficient of the solubility. However, we should also emphasize that the present experimental results are in accordance with the previous experimental results by HIYAGON and OZIMA (1982, 1986) and by BROADHURST et al. (1990, 1992), which were obtained with quite different experimental arrangements from the present one. We are currently working to answer the question whether the unexpected results truly represent solubility of olivine crystal or it is merely an artifact resulted from the trapped noble gas or from some other unknown causes.
5. Application for Estimation of Surface Tension

5.1 Thermodynamic theory

We follow FOWLER and GUGGENHEIM (1939) for a thermodynamic treatment of solution. A simple relation can be obtained from statistical thermodynamics:

\[
\ln H = - \frac{\omega - \Lambda + kT \ln \frac{\nu}{kT}}{kT},
\]

where \( H \) is Henry’s law constant, \( k \) is Boltzmann constant, \( T \) is absolute temperature, \( \omega \) is the reversible work of adding a solute molecule to the solution, \( \Lambda \) is the molecular heat of evaporation, \( \nu \) is free volume per molecule.

We then derive a relation between surface tension and solubility by using the assumption proposed by UHLIG (1937). Uhlig assumed that the reversible work of adding a solute molecule into a solution (\( \omega \)) is done by producing a cavity of essentially the same size as the solute molecule in the solvent and therefore the reversible work is given by the increase in a surface area of the cavity multiplied by the surface tension of the solvent. Using above assumption, if the solute molecule is a spherical gas molecule of radius \( r \), the reversible work is equal to \( 4\pi r^2 \sigma \), where \( \sigma \) is the surface tension of the solvent. Since \( \Lambda + kT \ln(\nu/kT) \) is only dependent on the solute molecule, it is set as \( E \) at the equilibrium condition. We can then rewrite Eq. (1) as

\[
\ln H = - \frac{4\pi r^2 \sigma - E}{kT}.
\]

Hence, we have a relation between the surface tension of the solvent and the noble gas solubility.

5.2 Estimation of surface tension

If we know noble gas solubility, we can estimate surface tension from Eq. (2). It is easy to see from Eq. (2) that if we plot the logarithm of Henry’s law constants against the square of noble gas radii, a straight line should be obtained. The slope of the line then should be proportional to surface tension. Therefore, we plotted the logarithm of the Henry’s law constants in basaltic melts against the square of the noble gas radii in Fig. 4. For noble gas radii, we used Van der Waals radii (BONDI, 1964). As we can see in Fig. 4, the data lie nearly on straight lines for various conditions. From the slopes of the lines, we calculated the surface tensions between basaltic melt and noble gases. The surface tensions are almost independent of temperature and pressure with value of 130 ± 10 dyne/cm. The values are significantly smaller than the surface tensions (about 350 dyne/cm) at atmospheric pressure estimated between silicate melt and coexisting gas by MURASE and McBRINEY (1973) and by WALKER and MULLINS (1981). One of the possibilities for the differ-
ence is that the effective radius of noble gases in the liquid is different from that of Van der Waals. The crude approximation of Eq. (2) may also be suspected for the discrepancy. It is also possible that disagreement is due to the difference in the chemical composition of silicate melt between Murase and Mc Birney or Walker and Mullins and the present study. The present result must be considered to be preliminary, and more experimental and theoretical studies are needed. Nevertheless, we would like to emphasize that the proposed noble gas method is the first experimental approach for estimation of surface tension at high pressures, and its possibility should be exploited further.

6. Summary

(i) Solubilities of noble gases were determined for basaltic melt and olivine crystals for various temperature and pressure conditions, i.e., $T = 1250^\circ C$, $1300^\circ C$, and $1600^\circ C$ and $P = 0.5$ Kbars, 1 Kbar, and 2 Kbars.

(ii) Solubilities were dependent on temperature; the higher the temperature, the larger the solubility.

(iii) Solubilities in basaltic melt were independent of pressure up to 2 Kbars, but the solubilities in olivine were dependent on pressure; the higher the pressure become, the smaller the solubilities.

(iv) Distribution coefficients of noble gases between olivine crystals and basaltic melt were determined for four pairs of olivine crystals and basaltic melt at the same conditions as in (i). The distribution coefficients $(D_i)$ of noble gases thus
obtained are \( 0.02 < D_{\text{He}} < 0.7, 0.03 < D_{\text{Ne}} < 0.6, 0.087 < D_{\text{Ar}} < 2.0, 0.1 < D_{\text{Kr}} < 3.0 \).

(v) The distribution coefficients were dependent on temperature and pressure; the distribution coefficients increased with increasing temperature. In contrast to the temperature dependence, the distribution coefficients decreased with increasing pressure.

(vi) Surface tensions were calculated from the noble gas solubilities. The surface tensions were approximately independent of temperature and of pressure up to 2 Kbars. The value is \( 130 \pm 10 \) dyne/cm.

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