Degassing of alkalic basalts

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ABSTRACT

In order to model quantitatively exsolution of volatiles over the range of basaltic melt compositions found on oceanic islands, I present compositional parameterizations of $H_2O$ and $CO_2$ solubilities and use these parameterizations to develop vapor saturation and degassing models for alkalic basaltic liquids. Vapor-saturation diagrams generated as a function of melt composition are used to determine the pressure at which the melt was last in equilibrium with a vapor and the composition of the vapor phase based on measured $H_2O$ and $CO_2$ contents in basaltic glasses. These models allow the calculation of the pressure at which a magma of known initial volatile content reaches vapor saturation and begins to exsolve a vapor phase. The higher solubility of $CO_2$ in alkalic magmas causes vapor saturation in $CO_2$-bearing alkalic magmas to be reached at lower pressures than in $CO_2$-bearing tholeiitic magmas having identical volatile contents. However, if variations in major element and volatile concentrations were linked by variations in the extent of melting, then volatile-rich, strongly alkalic magmas would begin to exsolve a vapor at slightly higher pressures than volatile-poor alkali olivine basalts or tholeiites.

Partitioning of $H_2O$ and $CO_2$ into the vapor during volatile exsolution is controlled by the difference between $H_2O$ and $CO_2$ solubilities. As melts become more alkalic, the relative difference between $H_2O$ and $CO_2$ solubilities decreases, thus diminishing the preferential partitioning of $CO_2$ into the vapor. Exsolution of volatiles from tholeiites is characterized by strong partitioning of $CO_2$ into the vapor such that most or all $CO_2$ is lost before any significant loss of $H_2O$. In contrast, the combination of higher $CO_2$ solubility and higher volatile contents (and perhaps higher $CO_2/H_2O$ ratio) in alkalic melts results in less fractionation between $CO_2$ and $H_2O$ during volatile exsolution.

INTRODUCTION

Volatiles play an important role in the generation and evolution of mantle-derived melts, affecting the extent of mantle melting, liquidus phase relationships, physical properties of melts, and explosivity of volcanic eruptions. Alkalic lavas from oceanic islands provide a wealth of information on mantle heterogeneities with respect to major and trace elements and radiogenic isotopes, but heterogeneities in mantle volatiles remain poorly known. Determining heterogeneities in mantle volatiles is important to characterize mantle reservoirs fully, to understand the role of volatiles in igneous processes in different tectonic environments, and to constrain global cycling of these elements. However, to investigate the underlying mantle volatile concentrations, it is first necessary to see through the window of shallow level processes such as degassing and assimilation.

Recently, Dixon and Stolper (1995) presented a quantitative degassing model for tholeiitic basaltic melts and used this model to gain insight into exsolution of volatiles from oceanic tholeiitic magmas. This study extends their model to alkalic basaltic compositions. I present new compositional parameterizations of $H_2O$ and $CO_2$ solubilities and incorporate them into mixed $H_2O-CO_2$ vapor saturation and degassing models for alkalic basaltic melts.

SOLUBILITY MODELS

Review of $H_2O$ and $CO_2$ solubilities in tholeiitic melts

Calculation of $H_2O$ and $CO_2$ solubilities in tholeiitic melts using the Stolper thermodynamic model (i.e., the activity of $H_2O$ is taken to be the activity of molecular $H_2O$ in the melt; Holloway and Blank 1994) involves (1) calculation of $H_2O$ or $CO_2$ fugacities at the $P$ and $T$ of interest; (2) calculation of the mole fractions of molecular $H_2O$ or carbonate ions in the melt in equilibrium with pure $H_2O$ or $CO_2$ vapor; and (3) calculation of total $H_2O$ or carbon dioxide concentrations in the melt. The advantage of Stolper-type solubility models for degassing calculations is that the activities of both molecular $H_2O$ and carbonate in basaltic melt follow Henry’s law at the low pressures of degassing. Also, the thermodynamic properties determined in the end-member systems can be used to calculate saturation concentrations of $H_2O$ and $CO_2$ in mixed volatile systems.

Fugacities are calculated using a modified Redlich-Kwong (MRK) equation of state (Holloway 1977). At the
high $T$ (~1200 °C) and low $P$ (<4 kbar) relevant to degassing of basaltic melts, differences between fugacities calculated using various equations of state, including even the ideal gas law, are not significant. If this model were to be used at pressures greater than ~4 kbar, however, the Saxena and Fei (1987) equation of state should be used to calculate fugacities, particularly for CO$_2$ (Holloway and Blank 1994).

The amounts of carbonate and molecular H$_2$O dissolved in tholeiitic melts coexisting with pure carbon dioxide or H$_2$O vapor at 1200 °C can be calculated from the following equations (Dixon et al. 1995):

$$X_{\text{CO}_2}(P, T_\text{m}) = X_{\text{CO}_2}(P_\text{o}, T_\text{m}) + \sum_{i} \left( \frac{f_{\text{CO}_2}(P, T_\text{m})}{f_{\text{CO}_2}(P_\text{o}, T_\text{m})} \right) \cdot \exp \left( \frac{-\Delta V_{\text{CO}_2}^\text{m} (P - P_\text{o})}{RT_\text{m}} \right)$$

(1)

and

$$X_{\text{H}_2\text{O}_{\text{mol}}}(P, T_\text{m}) = X_{\text{H}_2\text{O}_{\text{mol}}}(P_\text{o}, T_\text{m}) + \sum_{i} \left( \frac{f_{\text{H}_2\text{O}_{\text{mol}}}(P, T_\text{m})}{f_{\text{H}_2\text{O}_{\text{mol}}}(P_\text{o}, T_\text{m})} \right) \cdot \exp \left( \frac{(-\Delta V_{\text{H}_2\text{O}_{\text{mol}}}^{m})(P - P_\text{o})}{RT_\text{m}} \right)$$

(2)

where $X_i$ $(P, T_\text{m})$ is the mole fraction of carbonate or molecular H$_2$O in melt saturated with vapor with a fugacity of carbon dioxide or H$_2$O of $f_i(P, T_\text{m})$ at pressure $P$ and temperature $T_\text{m}$ (1473.15 K); $X_i$ $(P_\text{o}, T_\text{m})$ is the mole fraction of carbonate or molecular H$_2$O in melt in equilibrium with vapor with a fugacity of carbon dioxide or H$_2$O of $f_i(P_\text{o}, T_\text{m})$ at $P_\text{o}$ (1 bar) and $T_\text{m}$; $f_{\text{CO}_2}(P, T_\text{m})$ and $f_{\text{H}_2\text{O}_{\text{mol}}}(P_\text{o}, T_\text{m}) = 1$ bar; $X_{\text{CO}_2}(P_\text{o}, T_\text{m}) = 3.8 \times 10^{-2}$; $X_{\text{H}_2\text{O}_{\text{mol}}}(P_\text{o}, T_\text{m}) = 3.28 \times 10^{-2}$; $V_{\text{CO}_2}^\text{m}$ is the molar volume of CO$_2$ in the melt in its standard state and is assumed to be constant and equal to the partial molar volume of H$_2$O in the melt (12 cm$^3$/mol; Dixon et al. 1995); $\Delta V_{\text{CO}_2}^\text{m} = (V_{\text{CO}_2}^\text{m} - V_{\text{CO}_2}^\text{L})$ and $\Delta V_{\text{H}_2\text{O}_{\text{mol}}}^\text{m}$ are the molar volumes of the melt species in their standard states and have been taken to be independent of $P$ and $T$ in deriving equation (1) (23 cm$^3$/mole; Pan et al. 1991); and R is the gas constant (83.15 cm$^3$bar/mol-K).

Concentration of CO$_2$ (ppm) is calculated from mole fraction of carbonate in the melt using:

$$\text{CO}_2 \text{ (ppm)} = 10^4 \left[ 4400 X_{\text{CO}_2}^\text{m} / (36.6 - 44 X_{\text{CO}_2}^\text{m}) \right]$$

(3)

where 36.6 is the molecular weight for anhydrous tholeiitic basalt on a single-O basis. Calculation of H$_2$O concentration based on mole fraction of molecular H$_2$O involves three steps. First, the mole fraction of hydroxyl groups ($X_{\text{OH}}$) must be calculated as a function of the mole fraction of molecular H$_2$O using a regular solution model (Silver and Stolper 1989):

$$\ln \left( \frac{(X_{\text{OH}})^2}{X_{\text{H}_2\text{O}_{\text{mol}}}(1 - X_{\text{H}_2\text{O}_{\text{mol}}})} \right) = A' + B' X_{\text{OH}} + C X_{\text{H}_2\text{O}_{\text{mol}}}$$

(4)

where $A' = 0.403$, $B' = 15.333$, and $C' = 10.894$. Second, the mole fraction of total H$_2$O dissolved in the melt ($X_\text{H}_2\text{O}$) must be calculated from the mole fractions of the individual H$_2$O species using:

$$X_\text{H}_2\text{O} = X_{\text{OH}} + X_{\text{H}_2\text{O}_{\text{mol}}} / 2.$$  

(5)

Finally, the concentration of total H$_2$O dissolved in the melt (wt%$\text{H}_2\text{O}_{\text{tot}}$) is calculated from the total number of moles of H$_2$O using:

$$\text{wt%H}_2\text{O}_{\text{tot}} = 1801.5X_\text{H}_2\text{O} / (36.6 - 18.6X_\text{H}_2\text{O}).$$  

(6)

This method of determining H$_2$O solubility assumes a single regular solution model for H$_2$O speciation is valid over the conditions of glass formation. Determination of the $T$ dependence (and consequently quench rate dependence) of H$_2$O speciation in silicate glasses is currently an area of active research (McMillan 1994). The quench rate dependence of H$_2$O speciation is not considered a significant source of error in this study because (1) no difference is detected in H$_2$O speciation in experimentally quenched basaltic glasses produced by quench rates differing by two orders of magnitude (Dixon et al. 1995) and (2) H$_2$O speciation in most oceanic basaltic glasses is within errors of the predicted speciation curve (Dixon et al. 1995; Dixon et al. 1997).

**Compositional dependence of H$_2$O and CO$_2$ solubility in alkalic basaltic melts**

CO$_2$ solubility depends strongly on melt composition though the details of this compositional dependence are poorly known (Blank and Brooker 1994; Holloway and Blank 1994). CO$_2$ solubility in mafic liquids recently has been determined as a function of $P$ and $T$ for tholeiitic (Pan et al. 1991; Dixon et al. 1995), basanitic (Holloway and Blank 1994), and leucititic (Thibault and Holloway 1994) compositions (Fig. 1). Compositions of these liquids are listed in Table 1. The CO$_2$ contents for these solubility studies were measured by infrared spectroscopy or a combination of bulk carbon analysis (LECO® carbon analysis) and infrared spectroscopy, thereby minimizing discrepancies between different analytical techniques (Blank and Brooker 1994).

The temperature dependence of CO$_2$ solubility is also a function of melt composition, with negligible temperature dependence for tholeiitic melts (Pan et al. 1991) and strong negative temperature dependence for leucititic melts (Thibault and Holloway 1994). For example, at 10 kbar the CO$_2$ solubility in leucitic melt decreases from about 5 wt% at 1300 °C to about 3.2 wt% at 1600 °C (Holloway and Blank 1994). For the model presented here, $T$ is assumed to be constant at 1200 °C, representing slightly to moderately fractionated liquids erupting on the Earth’s surface.

The main purpose of this study is to provide a framework for modeling the exsolution of volatiles from alkali olivine basaltic through nephelinitic liquids erupted in submarine environments. Therefore, a compositional parameterization of CO$_2$ solubility over this compositional...
range is required. Previous work has shown that CO₂ solubility increases as melt depolymerization increases, e.g., decreasing SiO₂ and Al₂O₃ contents or increasing proportion of non-bridging O atoms to tetrahedral cations (NBO/T) (Eitel and Weyl 1932; Mysen et al. 1976; Mysen 1976; Spera and Bergman 1980). For a given SiO₂ content, CO₂ solubility varies as a function of the proportions of metal cations (Holloway et al. 1976; Spera and Bergman 1980). Gibbs free energies of carbonation reactions (ΔG, Spera and Bergman 1980) suggest that the order of increasing ability of a cation to increase CO₂ solubility is Ca²⁺ > K⁺⁺ > Na⁺⁺ ≫ Mg²⁺ ≈ Fe²⁺. Thus the compositional dependence of CO₂ solubility in mafic liquids should be able to be parameterized with two terms representing (1) melt depolymerization and (2) potential of cations to react with carbonate. I have derived an empirical relation reflecting this dependence. The first term is just the sum of the molar proportions of Si⁴⁺ and Al³⁺. The second term sums the molar proportions of cations (Ca²⁺ + 0.8K⁺⁺ + 0.7Na⁺⁺ + 0.4Mg²⁺ + 0.4Fe²⁺), where the coefficient for each cation is calculated from the magnitude of the Gibbs free energy of the carbonation reaction (Spera and Bergman 1980) for each cation relative to Ca²⁺ (ΔG°C/ΔG°C).

These two terms are combined into a compositional parameter (II). Linearity between II and CO₂ solubility in tholeiitic (no. 1 and no. 2), basanitic (no. 3), and leucititic (no. 4) compositions was achieved by multiple regression of \(aA + bB = C = \Pi \times 10^3\), where \(A = (\text{Si}^{4+} + \text{Al}^{3+})\), \(B = (\text{Ca}^{2+} + 0.8\text{K}^{+2} + 0.7\text{Na}^{+2} + 0.4\text{Mg}^{+2} + 0.4\text{Fe}^{+2})\), and \(C = \text{CO}_2\) solubility at 1 kbar and 1200 °C. Coefficients \(a\) and \(b\) were determined to be −6.50 and 20.17, respectively. Thus, the best fit value determined for II is:

\[\Pi = -6.50(\text{Si}^{4+} + \text{Al}^{3+}) + 20.17(\text{Ca}^{2+} + 0.8\text{K}^{+2} + 0.7\text{Na}^{+2} + 0.4\text{Mg}^{+2} + 0.4\text{Fe}^{+2}).\]  

Figure 2a shows the best-fit correlation between CO₂ solubility and P at 1 kbar and 1200 °C (r² = 0.984, standard error in predicting CO₂ solubility = 122 ppm). Under these P-T conditions, the CO₂ solubility increases ~4.5× from tholeiitic (II = 0.4) to leucitic (II = 2.2) compo-

### Table 1. Major element compositions of glasses used in compositional parameterization of CO₂ solubility

<table>
<thead>
<tr>
<th>Oxide (wt%)</th>
<th>MORB Thol (1)</th>
<th>Kilauea Thol (2)</th>
<th>Basanite (3)</th>
<th>Leucite (4)</th>
<th>Sodamite (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>49.1</td>
<td>49.2</td>
<td>46.0</td>
<td>44.1</td>
<td>46.5</td>
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<tr>
<td>Al₂O₃</td>
<td>16.4</td>
<td>13.3</td>
<td>15.2</td>
<td>12.8</td>
<td>19.7</td>
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<tr>
<td>Fe₂O₃</td>
<td>n.r.</td>
<td>1.72</td>
<td>n.r.</td>
<td>2.69</td>
<td>0.0</td>
</tr>
<tr>
<td>FeO</td>
<td>8.86*</td>
<td>9.68</td>
<td>12.0*</td>
<td>6.62</td>
<td>0.0</td>
</tr>
<tr>
<td>MgO</td>
<td>10.2</td>
<td>10.4</td>
<td>9.06</td>
<td>9.14</td>
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<tr>
<td>CaO</td>
<td>11.7</td>
<td>10.9</td>
<td>8.22</td>
<td>14.3</td>
<td>21.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.13</td>
<td>2.15</td>
<td>4.33</td>
<td>3.20</td>
<td>12.0</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.07</td>
<td>0.51</td>
<td>1.32</td>
<td>3.45</td>
<td>0.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.74</td>
<td>2.29</td>
<td>3.17</td>
<td>2.69</td>
<td>0.0</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>n.r.</td>
<td>n.r.</td>
<td>0.27</td>
<td>0.77</td>
<td>0.0</td>
</tr>
<tr>
<td>Total</td>
<td>99.2</td>
<td>99.7</td>
<td>99.6</td>
<td>99.8</td>
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CO₂ solubility

<table>
<thead>
<tr>
<th>1200 °C, 1 kbar (ppm)</th>
<th>MORB Thol (1)</th>
<th>Kilauea Thol (2)</th>
<th>Basanite (3)</th>
<th>Leucite (4)</th>
<th>Sodamite (5)</th>
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<tbody>
<tr>
<td>484</td>
<td>1.48</td>
<td>543</td>
<td>807</td>
<td>2200</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Cation Proportions

<table>
<thead>
<tr>
<th>Cation</th>
<th>MORB Thol (1)</th>
<th>Kilauea Thol (2)</th>
<th>Basanite (3)</th>
<th>Leucite (4)</th>
<th>Sodamite (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si⁺⁴</td>
<td>0.477</td>
<td>0.455</td>
<td>0.422</td>
<td>0.405</td>
<td>0.400</td>
</tr>
<tr>
<td>Al⁺³</td>
<td>0.152</td>
<td>0.145</td>
<td>0.164</td>
<td>0.138</td>
<td>0.200</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.085*</td>
<td>0.075</td>
<td>0.078</td>
<td>0.051*</td>
<td>0</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.093</td>
<td>0.144</td>
<td>0.124</td>
<td>0.125</td>
<td>0</td>
</tr>
<tr>
<td>Ca⁺²</td>
<td>0.116</td>
<td>0.108</td>
<td>0.081</td>
<td>0.141</td>
<td>0.200</td>
</tr>
<tr>
<td>Na⁺⁺</td>
<td>0.049</td>
<td>0.039</td>
<td>0.077</td>
<td>0.057</td>
<td>0.200</td>
</tr>
<tr>
<td>K⁺⁺</td>
<td>0.002</td>
<td>0.006</td>
<td>0.0155</td>
<td>0.040</td>
<td>0</td>
</tr>
<tr>
<td>Fe⁺⁺</td>
<td>0.41</td>
<td>0.70</td>
<td>0.81</td>
<td>2.19</td>
<td>2.96</td>
</tr>
</tbody>
</table>


* II = −6.50(\text{Si}^{4+} + \text{Al}^{3+}) + 20.17(\text{Ca}^{2+} + 0.8\text{K}^{+2} + 0.7\text{Na}^{+2} + 0.4\text{Mg}^{+2} + 0.4\text{Fe}^{+2}).
FIGURE 2. (A) Linear correlation between CO₂ solubility data (1 kbar and 1200 °C) and Π, an empirically derived compositional parameter (see text). Sources of data listed in caption to Table 1. Error bars for CO₂ solubility data are ±15% (relative). (B) CO₂ solubility data (20 kbar, 1400 °C) plotted against Π showing validity of parameterization at higher P and T. Data sources and errors are the same as (A). Sodamelilite (no. 5) composition was not used in the calibration to determine Π, but agrees within errors with the projected linear correlation between CO₂ solubility and P at constant P and T. (C) Values of Π plotted against SiO₂ for glasses from the North Arch volcanic field (Dixon et al. 1997). Solid line is best fit line (Π = 10.9–0.214×SiO₂). Dotted lines are ±2 standard error in calculation of Π.

It is important to emphasize that this compositional parameterization for CO₂ solubility at constant P and T is valid only for liquids in which carbon dissolves totally as carbonate ions and should not be used for intermediate or silicic liquids in which carbon dissolves as both carbonate ions and molecular CO₂.

Figure 2b shows the linear correlation between CO₂ solubility and Π at 20 kbar and 1400 °C. As an independent check of the calibration, the CO₂ solubility data for sodamelilite (Mattey et al.1990) is also plotted. Although this composition was not used in the calibration, it plots within errors of the best-fit line of CO₂ solubility vs. Π for tholeiitic, basanitic, and leucititic compositions.

Given this compositional parameterization for CO₂ solubility in mafic liquids, I can now evaluate the effect of composition on CO₂ solubility in oceanic alkalic series magmas. Glasses from the North Arch volcanic field, a suite of alkalic to strongly alkalic lavas erupted on the seafloor north of Oahu (Clague et al. 1990; Dixon et al.1997) provide a useful example. These glasses have values of Π ranging from 0.7 to 2.3. Furthermore, values of Π vary linearly with SiO₂ in these glasses (Fig. 2c; r² = 0.944, twice standard error in predicting Π is 0.14), allowing SiO₂ to be used as a proxy for Π for this suite of lavas and enabling a single parameter to be used to predict the compositional dependence of both CO₂ and H₂O solubility (see below). On the basis of the 1200 °C, 1 kbar data, CO₂ solubility in a volatile exsolution model designed to encompass compositions ranging from tholeiite (49 wt% SiO₂, Π = 0.45) to nephelinite (40 wt% SiO₂, Π = 2.3) would increase from ~5×. Given the scatter in the SiO₂–Π correlation (Fig. 2c), I can infer that my prediction of CO₂ solubility is good to ~15%.

This compositional parameterization can be integrated into the thermodynamic expression for CO₂ solubility. Because the values of Π in the North Arch glasses vary linearly with SiO₂ and because no apriori information is available on the compositional dependence of ΔVw,v, I allow XCO₂ (P₀,T₀) to vary as a linear function of SiO₂ and assume that ΔVw,v is constant. The desired 5× range of solubilities for a SiO₂ range of 40–49 wt% is produced by substituting the following expression for XCO₂ (P₀,T₀) into Equation 1:

$$X_{CO_2}^{v} = 8.70 \times 10^{-5} - 1.70 \times 10^{-7} \text{SiO}_2$$ (8)
The dependence of H₂O solubility is small compared with that discussed. The important point is that the compositional variation over the composition range of interest will also be significant because they were determined using identical experimental and analytical techniques. Cocheo and Holloway (1993) determined that the H₂O solubility in a tholeiitic melt (Fig. 3) and that the speciation of H₂O in basanitic melt is about 20% lower than that in tholeiitic melts. These models, however, are not optimized for mafic compositions.

Recent low P experimental determinations of H₂O solubility in tholeiitic (Dixon et al. 1995) and basanitic (Cocheo and Holloway 1993) melts are directly comparable because they were determined using identical experimental and analytical techniques. Cocheo and Holloway (1993) determined that the H₂O solubility in a basanitic melt is about 20% lower than that in tholeiitic melt (Fig. 3) and that the speciation of H₂O in basanitic glass was essentially identical to that in tholeiitic glass. I have selected these results as the basis for my models because both experiments were optimized for the low pressures relevant to exsolution of volatiles from basalts and the two compositions are specifically suited to this application. For these reasons, in the models presented below I assume that H₂O solubility decreases by ~30% as melt composition changes from tholeiitic to nephelinitic and that the speciation model for tholeiitic glass (Dixon et al. 1995) is valid over the range of compositions of interest here. For completeness, the effect on the volatile exsolution models of assuming H₂O solubility to be constant over the composition range of interest will also be discussed. The important point is that the compositional dependence of H₂O solubility is small compared with that of CO₂ solubility; therefore, the compositional dependence of the volatile exsolution process is controlled dominantly by CO₂.

Analogous to the treatment of CO₂ solubility, I use a simple linear extrapolation for the compositional dependence of H₂O solubility as a function of SiO₂ content in wt%. Thus, \( X_{\text{H}_2\text{O},\text{mol}}(P, T) \) is allowed to vary as a linear function of SiO₂, while \( V_{\text{H}_2\text{O}} \) is assumed to be independent of \( P, T \), and melt composition. The appropriate range of solubilities over a SiO₂ range of 40–49 wt% are produced using the following expression for the mole fraction of molecular H₂O dissolved in the melt at standard state:

\[
X_{\text{H}_2\text{O},\text{mol}}(P, T) = -3.04 \times 10^{-5} + 1.29 \times 10^{-6} \text{SiO}_2 \quad (9)
\]

Total H₂O contents are calculated from \( X_{\text{H}_2\text{O},\text{mol}}(P, T) \) using equations (4)–(6). The experimentally determined H₂O solubility data for basanite (SiO₂ = 45 wt% ; Cocheo and Holloway 1993) agree with the predicted solubility model to better than 15% relative (Fig. 3).

**Vapor saturation models**

**Evaluation of vapor saturation and calculation of H₂O-CO₂ vapor-phase composition**

CO₂ and H₂O concentrations in vapor-saturated melts vary as a function of P and vapor composition. Dixon and Stolper (1995) presented a model for calculating the equilibrium pressure and vapor composition of vapor-saturated tholeiitic melts based on measured H₂O and CO₂ concentrations in the glass. An example of a vapor-saturation diagram is shown for tholeiitic melts in Figure 4a. Solid curves show the change in the amount of H₂O and CO₂ dissolved in a vapor-saturated tholeiitic melt at constant P (isobars) and 1200 °C as the vapor composition varies from pure CO₂ to pure H₂O. Dashed curves show the change in saturation values of H₂O and CO₂ as P is reduced while holding vapor composition constant (isopleths). This model provides a valuable tool for determining the pressures of vapor–melt equilibration based on measured CO₂ and H₂O concentrations of volcanic glasses. For example, a melt containing 0.9 wt% H₂O and 150 ppm CO₂ is saturated at a P of 400 bars (4 km H₂O depth) with a vapor phase having \( X_{\text{CO}_2} = 0.8 \).

To extend this type of diagram to a range in melt compositions, the equations for the compositional dependence of CO₂ and H₂O solubility must be incorporated into the equations describing vapor saturation. Vapor-saturation diagrams are constructed with the assumption that the vapor contains only CO₂ and H₂O and that the vapor mixes ideally (i.e., \( f_i = X_i f' \)). If these conditions are satisfied, then the following must be true at vapor saturation:

\[
\frac{a_{\text{H}_2\text{O}}^{\text{vol}}}{a_{\text{H}_2\text{O}}^{\text{mol}}} + \frac{a_{\text{CO}_2}^{\text{vol}}}{a_{\text{CO}_2}^{\text{mol}}} = 1 \quad (10)
\]

where the \( a_i^{\text{vol}} \) is the activity of H₂O or carbonate in the melt and \( a_i^{\text{mol}} \) is the corresponding activity in melt in equilibrium with pure H₂O or carbon dioxide. Given that the vapor mixes ideally, it can be shown that the mole frac-
Figure 4. (A) Vapor saturation diagram for tholeiite at 1200 °C. Solid curves represent the H<sub>2</sub>O and CO<sub>2</sub> contents in vapor saturated tholeitic liquids at constant P (isosbars) and a range in vapor composition. Dashed curves are saturation values at constant vapor composition (isopleths) over a range in P. As an example at 400 bars and 1200 °C, a tholeitic liquid in equilibrium with a vapor having 80 mol% CO<sub>2</sub> contains 150 ppm CO<sub>2</sub> and 0.9 wt% H<sub>2</sub>O. (B) Compositional dependence of the inverse correlation between X<sub>CO<sub>2</sub></sub> and X<sub>H<sub>2</sub>O</sub> in vapor-saturated mafic liquids at 400 bars and 1200 °C. Solid and dashed lines are lines of constant P (isosbars) and melt composition for nephelinitic (SiO<sub>2</sub> = 40 wt%) through tholeitic (SiO<sub>2</sub> = 49 wt%) melts plotted at increments of 1 wt% SiO<sub>2</sub>. Vapor compositions range from pure CO<sub>2</sub> along the y-axis to pure H<sub>2</sub>O along the x-axis. (C) Compositional dependence of the inverse correlation between CO<sub>2</sub> and H<sub>2</sub>O in vapor-saturated melts. To show the effect of melt composition on the saturation surface, isobars for X<sub>CO<sub>2</sub></sub> vs. X<sub>H<sub>2</sub>O</sub> for tholeiitic through nephelinitic compositions are shown at constant P (400 bar) on Figure 4b.

The relationship between total dissolved H<sub>2</sub>O and dissolved carbonate in vapor-saturated melts at a constant total P is nonlinear, however, because of the nonlinear relationship between the concentration of molecular H<sub>2</sub>O and total H<sub>2</sub>O in basalts. The compositional dependence of the 400 bar isobar for total H<sub>2</sub>O and carbonate in tholeiitic through nephelinitic melts is shown in Figure 4c. Note the 5-fold increase in CO<sub>2</sub> concentration and the small decrease in H<sub>2</sub>O concentration at saturation with pure CO<sub>2</sub> and H<sub>2</sub>O, respectively. Figure 4c can be used to evaluate graphically whether a basaltic liquid (tholeiitic through nephelinitic) with known concentrations of H<sub>2</sub>O and carbon dioxide would be vapor saturated at 1200 °C and at the P plotted. Alternatively, a figure comprising of a set of isobars over a range of pressures can be constructed for a single-melt composition (analogous to Fig. 4a) to evaluate the P at which that melt composition would be vapor saturated.

Basaltic lavas that erupted deep on the seafloor may have some of their magmatic volatiles preserved in quenched glassy rinds. As an example of the application of vapor saturation diagrams, I again use data from the North Arch volcanic field glasses (Dixon et al. 1997). The

tions of H<sub>2</sub>O and CO<sub>2</sub> in the vapor can be determined using a<sub>H<sub>2</sub>O</sub>/a<sub>CO<sub>2</sub></sub> = X<sub>H<sub>2</sub>O</sub>/X<sub>CO<sub>2</sub></sub> and a<sub>CO<sub>2</sub></sub>/a<sub>CO<sub>2</sub></sub> = X<sub>CO<sub>2</sub></sub>. Dixon et al. (1995) showed that it is valid to adopt the Henrian approximations for both molecular H<sub>2</sub>O and carbonate activities, so the activities in Equation 10 are just the mole fractions of molecular H<sub>2</sub>O and carbonate in the melt. Equation 10 thus becomes:

$$\frac{X_{H_2O, mol}}{X_{H_2O, mol}} + \frac{X_{CO_2, mol}}{X_{CO_2, mol}} = 1$$

(11)

where X<sub>H<sub>2</sub>O</sub> is the mole fraction of molecular H<sub>2</sub>O or carbonate in the melt and X<sub>CO<sub>2</sub></sub> is the corresponding mole fraction in melt in equilibrium with pure H<sub>2</sub>O or carbon dioxide. At constant P, T, and melt composition the denominators in Equation 11 (i.e., the amounts of molecular H<sub>2</sub>O and carbon dioxide dissolved in melts that coexist with pure H<sub>2</sub>O vapor or carbon dioxide vapor) are constants (i.e., independent of vapor composition) and can be calculated from the equations describing solubilities and the compositional dependence for CO<sub>2</sub> (Eq. 1 and Eq. 8) and H<sub>2</sub>O (Eq. 2 and Eq. 9). Thus, at constant P, T, and melt composition, Equation 11 describes a linear relationship between X<sub>CO<sub>2</sub></sub> and X<sub>H<sub>2</sub>O</sub> as a function of vapor composition in vapor-saturated melts. To show the effect of melt composition on the saturation surface, isobars for X<sub>CO<sub>2</sub></sub> vs. X<sub>H<sub>2</sub>O</sub> for tholeiitic through nephelinitic compositions are shown at constant P (400 bar) on Figure 4b.
North Arch lavas were all dredged at H$_2$O depths of 3900–4380 m and so are directly comparable to the 400 bar calculations summarized in Figure 4. Figure 5 compares the models given in Figure 4c to three suites of North Arch lavas, representing respectively nephelinitic (5a), basanitic (5b), and alkali olivine basaltic (5c) compositions. Good agreement exists between the measured H$_2$O and CO$_2$ contents of the North Arch glasses and the predicted vapor saturation curves. The calculated vapor-saturation indices at 400 bar for each sample [Eq. 11, where a value of 1.00 is perfect saturation (on the curve), <1.0 is undersaturated (below the curve), and >1.0 is supersaturated (above the curve)] are all within 40% of 1.0 and all but one sample are within 30% of 1.0 (mean of 1.09 ± 0.15). This agreement is within the estimated uncertainty of the model [1σ uncertainties in the H$_2$O analyses (~±5%), CO$_2$ analyses (~±20%), and compositional dependence of H$_2$O and CO$_2$ solubilities (~±15%) combine to give a total uncertainty of ~30% in the value of the saturation index] and suggests that most of the North Arch glasses were vapor saturated with a H$_2$O-CO$_2$ vapor upon quenching on the seafloor at 400 bar.

**Calculation of equilibrium saturation pressure**

As described above, given measurements of the H$_2$O and CO$_2$ contents of natural basaltic glasses, the P at which a liquid of a given composition would be vapor saturated can be determined either graphically or by substituting Equations 1 and 2 into Equation 11 and then iteratively solving for P. For purposes of illustration, the P at which an ascending melt first reaches saturation as a function of melt composition and initial volatile concentrations is shown in Figures 6a–c. Upon continued depressurization, a vapor phase begins to exsolve. Figure 6a shows the dramatic decrease in saturation P as the melt composition becomes more SiO$_2$ undersaturated (more alkalic) as a consequence of increasing CO$_2$ solubility. For example, a nephelinite with 2.0 wt% H$_2$O and 2.0 wt% CO$_2$ reaches saturation at ~7 kbar, whereas a tholeiite with identical volatile contents reaches saturation at ~18 kbar. Figure 6a shows the effect of changing the CO$_2$ content at constant H$_2$O. Figure 6b shows the effect of changing H$_2$O content at constant CO$_2$/H$_2$O. For a given melt composition, both figures show the expected trend that melts with higher volatile contents reach saturation at greater depths.

In many alkalic lava series, however, trends in trace element concentrations suggest that the lavas can be related by variable extents of melting of a homogeneous source region (Clague and Frey 1982; Clague and Dalrymple 1988). Therefore, it is probably not realistic to assume that various melt compositions in an alkalic magma series were generated with identical initial volatile contents. Though the behavior of volatiles during melting is not yet well understood, this model provides a tool for investigating the consequences of various assumptions. For example, Figure 6c shows the effect of allowing the
initial volatile concentration to vary with silicate melt composition. In this example, CO₂ and H₂O are modeled as incompatible elements, the mantle CO₂/H₂O is assumed to be constant and equal to 2 (by mass), and the extent of melting varies from 2–20%, such that a nephelinitic melt has 2.0 wt% H₂O and 40 wt% SiO₂, and a tholeiitic melt has 0.25 wt% H₂O and 50 wt% SiO₂. Using these boundary conditions, the saturation P remains nearly constant at ~8–11 kbar, and a nephelinitic melt reaches saturation at a slightly greater P than a tholeiite. The depth range over which vapor saturation is reached narrows because the relative effects of changes in CO₂ solubility and volatile contents are similar in magnitude but opposite in sign and nearly cancel. Similar trends are observed at different CO₂/H₂O ratios (for CO₂/H₂O = 1, P_{sat} = 4–7 kbar; for CO₂/H₂O = 3, P_{sat} = 10–14 kbar). Thus, in a region where the mantle is melting by variable amounts, all melts may reach saturation and begin vesiculating over a narrow range of pressures. This may have important consequences for initiation of melt segregation and transport. In addition, it suggests that the depth of vesiculation alone is not a good indicator of initial magmatic volatile contents.

**Fractionation of H₂O and CO₂ between vapor and melt**

Whereas absolute solubilities control H₂O and CO₂ concentrations at vapor saturation, the relative differences in solubility control partitioning of H₂O and CO₂ into the vapor phase during volatile exsolution. According to the principle of vapor-melt fractionation, often applied to the study of rare gases (Jambon et al. 1986; Zhang and Zindler 1989) and volatile exsolution from tholeiitic melts (Gerlach 1986; Bottinga and Javoy 1990; Dixon et al. 1995), a vapor-saturated melt is enriched in the most soluble component whereas the vapor is enriched in the least soluble component. Eggler (1974) was one of the first to consider the effect of basaltic melt composition on vapor fractionation of H₂O and CO₂ and applied the theory to fractionation of H₂O and CO₂ during generation of mafic melts.

This concept can be expressed in terms of a fractionation factor, analogous to the fractionation factor in stable isotopic studies. Dixon and Stolper (1995) defined the CO₂-H₂O fractionation factor (β) between vapor and melt as:

\[
\beta_{\text{CO}_2-\text{H}_2\text{O}} = \frac{N_{\text{CO}_2}^{\text{vapor}}}{N_{\text{H}_2\text{O}}^{\text{vapor}}} \frac{N_{\text{CO}_2}^{\text{melt}}}{N_{\text{H}_2\text{O}}^{\text{melt}}} \tag{12}
\]
where \( N_i \) is the number of moles of CO\(_2\) and H\(_2\)O in the vapor or number of moles of carbonate and molecular H\(_2\)O in the melt. The value of \( \beta \) is a function of \( P \) and melt composition. The pressure dependence (exponential terms) of the activity of H\(_2\)O and CO\(_2\) in tholeiitic basaltic melts at \( T = 1200 \) °C are given in Equations 1 and 2 and are assumed to be independent of composition. The compositional dependence of solubility is modeled by varying the standard state activities of H\(_2\)O and carbonate in the melt are given in Equations 8 and 9. Following Dixon and Stolper (1995) it can be shown that:

\[
\beta_{\text{CO}_2 - \text{H}_2\text{O, mol}} = \frac{f_{\text{H}_2\text{O}}}{f_{\text{CO}_2}} \left( \frac{\frac{X_{\text{CO}_2}}{X_{\text{H}_2\text{O}}(1 \text{ bar}, 1473 K)}}{\frac{X_{\text{H}_2\text{O}}}{X_{\text{CO}_2}(1 \text{ bar}, 1473 K)}} \right) \exp\left\{ \frac{-12(P - 1)/[(83.15)(1473.15)]}{\exp\left\{ \frac{-23(P - 1)/[(83.15)(1473.15)]}{(13)} \right\}} \right. \]

Note that the fractionation factor must be expressed in terms of mole fractions of carbonate and molecular H\(_2\)O species that behave Henrian with respect to fugacities of CO\(_2\) and H\(_2\)O in the vapor at constant \( P \) and \( T \). The value of \( \beta \) is constant for a given melt composition at constant \( P \) and \( T \) (Dixon and Stolper 1995).

Values of \( \beta \) for tholeiitic, basanitic, and nephelinitic liquids are plotted against \( P \) in Figure 7. Any value of \( \beta \) greater than 1 indicates that CO\(_2\) is fractionated preferentially into the vapor with respect to H\(_2\)O. The magnitude of \( \beta \) is related to the strength of this preferential partitioning. During depressurization and progressive exsolution of volatiles from tholeiitic melts, \( \beta \) is large and CO\(_2\) is strongly partitioned into the vapor phase relative to H\(_2\)O. Thus, for a tholeiite with concentrations of H\(_2\)O and CO\(_2\) typical of oceanic basalts, almost all CO\(_2\) would be lost before significant quantities of H\(_2\)O begin to exsolve. Using logic based on our experience with degassing of tholeiitic melts, significant exsolution of H\(_2\)O would seem to be precluded in lavas having high CO\(_2\) concentrations.

This logic is not valid for alkalic basalts, however, as illustrated by the strong compositional dependence of \( \beta \). In general, as the melt composition changes from tholeiitic to nephelinitic, the difference between H\(_2\)O and CO\(_2\) solubilities decreases, and the strength of fractionation of CO\(_2\) into the vapor phase also decreases. For example, at 400 bars, the value of \( \beta \) ranges from 81 in tholeiitic melts (indicative of strong preferential partitioning of CO\(_2\) into the vapor relative to H\(_2\)O) to 10 in nephelinitic melts (indicative of weak preferential partitioning of CO\(_2\) into the vapor). Thus, if tholeiitic and nephelinitic melts with identical volatile contents degas under identical conditions, less CO\(_2\) will degas from the nephelinitic melt than from the tholeiitic melt for a given amount of H\(_2\)O loss. Figure 7 also illustrates that \( \beta \) decreases with increasing \( P \) as a result of CO\(_2\) fugacity increasing more rapidly with \( P \) than H\(_2\)O fugacity. Thus, CO\(_2\) would not be as strongly fractionated into the vapor in melts at high pressures.

The values of \( \beta \) are relatively insensitive to the specific H\(_2\)O solubility model selected. The value of \( \beta \) for basanitic and nephelinitic liquids calculated assuming constant H\(_2\)O solubility are only slightly higher (~15–50%) than those calculated assuming that H\(_2\)O solubility decreases 30% over the tholeiitic to nephelinitic melt composition range, but this variation is small compared with the factor of 5–8 variation in \( \beta \) as a function of melt composition.

**Degassing Models**

The degassing model presented here is a modification of the one presented in Dixon and Stolper (1995). The compositional dependence of H\(_2\)O and CO\(_2\) solubility has been incorporated in order to predict the volatile contents in alkalic magmas during depressurization and progressive volatile exsolution. [These models are the basis for interpreting the volatile exsolution history of the alkalic lavas from the North Arch volcanic field in a subsequent paper (Dixon et al. 1997)].

Degassing of tholeiitic through nephelinitic magmas can be modeled as either closed or open system. In closed system degassing, the evolved vapor stays in contact and in equilibrium with the melt throughout the entire degassing process. In open system degassing, each increment of vapor is removed immediately after exsolution resulting in accentuation of fractionation between CO\(_2\) and H\(_2\)O (Dixon and Stolper 1995). In this paper, I focus on the closed-system case in which the effect of melt composition on degassing paths is maximized.
The models are implemented in a computer program through the following steps:

1. Input initial H₂O and CO₂ contents, P, and the style of degassing (open or closed).
2. Calculate H₂O and CO₂ solubilities and fractionation factor (β) as a function of SiO₂ content.
3. Degas magma at a given P by incrementally transferring H₂O and CO₂ from the supersaturated melt into the vapor phase until saturation is reached. Each increment of volatiles partitioned into the vapor must satisfy equations for mass balance, vapor-melt fractionation, and speciation of H₂O in melt (Dixon and Stolper 1995). Saturation is evaluated using equation (11) after each increment.
4. Output final H₂O and CO₂ contents in degassed melt, composition of vapor phase, and volume proportion vapor phase (percent vesicles).

Closed system degassing paths calculated using initial H₂O content of 2.0 wt%, CO₂ content of 1.0 wt%, and initial degassing P of 400 bars are shown on Figures 8a–d. The starting compositions are more volatile-rich, in particular more CO₂-rich, than the tholeiitic compositions modeled in Dixon and Stolper (1995) because alkalic basalts typically have higher total volatile contents and may be more likely to erupt in a single stage, which would limit the amount of CO₂ lost in a shallow crustal environment. For simplification, the following SiO₂ contents will be used to represent the following magma compositions: alkali olivine basalt (48% SiO₂), basanite (45% SiO₂), and nephelinite (42% SiO₂).

Figures 8a–c show that closed-system degassing of alkali melts results in lower H₂O and higher CO₂ contents in comparison with tholeiitic melts. For example, if a nephelinite and tholeiite had degassed at 400 bars, the tholeiitic liquid would have a H₂O content of 1.5 wt% (25% loss) and a CO₂ content of 80 ppm (99.2% loss), whereas the nephelinitic liquid would have a H₂O content of 1.3 wt% (35% loss) and a CO₂ content of 340 ppm (96.6% loss). The extra H₂O loss contributes to greater proportion of H₂O in the vapor (Fig. 8d).

For completeness, additional degassing calculations were performed assuming constant H₂O solubility. In the constant H₂O solubility case, constant H₂O contents, vapor composition, and vesiculation are essentially the same for all compositions as P decreases (less degassing of H₂O than in the variable H₂O solubility case). CO₂ contents at a given P are slightly higher than in the variable H₂O solubility case for alkalic compositions, reflecting the slightly higher proportion of CO₂ in the vapor. Thus, the amount of H₂O loss during exsolution of a vapor phase is sensitive to the assumed H₂O solubility model. However, for both cases the vapor-saturated alkalic basalts have higher CO₂ contents than tholeiitic basalts degassed under identical conditions.

In summary, I have estimated the compositional dependence of H₂O and CO₂ solubility in tholeiitic through nephelinitic liquids and have generated vapor saturation and degassing models for alkalic basaltic liquids. These models provide the means to begin unraveling the exsolution of volatiles from alkalic magmas, including the pressure of last vapor saturation based on measured H₂O and CO₂ contents in glasses, the depth of initial vapor saturation based on estimates of initial H₂O and CO₂ contents, and fractionation of various volatile species during progressive depressurization. Specifically, partitioning of CO₂ into the vapor phase relative to H₂O during closed system degassing is stronger in tholeiites than in more alkalic melt compositions. During progressive exsolution of volatiles, strongly alkalic magmas will lose less CO₂ and more H₂O than tholeiitic magmas.

ACKNOWLEDGMENTS

This work has benefited from continued interactions with David Clague, John Holloway, and Edward Stolper. Gordon Moore and Paul Wallace provided thoughtful reviews. Support was provided by NSF OCE-9302574.
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MANUSCRIPT RECEIVED FEBRUARY 2, 1996
MANUSCRIPT ACCEPTED DECEMBER 11, 1996