

## 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<sub>2</sub>O and CO<sub>2</sub> 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<sub>2</sub>O and CO<sub>2</sub> 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<sub>2</sub> in alkalic magmas causes vapor saturation in CO<sub>2</sub>-bearing alkalic magmas to be reached at lower pressures than in CO<sub>2</sub>-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<sub>2</sub>O and CO<sub>2</sub> into the vapor during volatile exsolution is controlled by the difference between H<sub>2</sub>O and CO<sub>2</sub> solubilities. As melts become more alkalic, the relative difference between H<sub>2</sub>O and CO<sub>2</sub> solubilities decreases, thus diminishing the preferential partitioning of CO<sub>2</sub> into the vapor. Exsolution of volatiles from tholeiites is characterized by strong partitioning of CO<sub>2</sub> into the vapor such that most or all CO<sub>2</sub> is lost before any significant loss of H<sub>2</sub>O. In contrast, the combination of higher CO<sub>2</sub> solubility and higher volatile contents (and perhaps higher CO<sub>2</sub>/H<sub>2</sub>O ratio) in alkalic melts results in less fractionation between CO<sub>2</sub> and H<sub>2</sub>O 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<sub>2</sub>O and CO<sub>2</sub> solubil-

ities and incorporate them into mixed H<sub>2</sub>O-CO<sub>2</sub> vapor saturation and degassing models for alkalic basaltic melts.

### SOLUBILITY MODELS

#### Review of H<sub>2</sub>O and CO<sub>2</sub> solubilities in tholeiitic melts

Calculation of H<sub>2</sub>O and CO<sub>2</sub> solubilities in tholeiitic melts using the Stolper thermodynamic model (i.e., the activity of H<sub>2</sub>O is taken to be the activity of molecular H<sub>2</sub>O in the melt; Holloway and Blank 1994) involves (1) calculation of H<sub>2</sub>O or CO<sub>2</sub> fugacities at the *P* and *T* of interest; (2) calculation of the mole fractions of molecular H<sub>2</sub>O or carbonate ions in the melt in equilibrium with pure H<sub>2</sub>O or CO<sub>2</sub> vapor; and (3) calculation of total H<sub>2</sub>O 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<sub>2</sub>O 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<sub>2</sub>O and CO<sub>2</sub> in mixed volatile systems.

Fugacities are calculated using a modified Redlich-Kwong (MRK) equation of state (Holloway 1977). At the

high  $T$  ( $\sim 1200$  °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  $\sim 4$  kbar, however, the Saxena and Fei (1987) equation of state should be used to calculate fugacities, particularly for  $\text{CO}_2$  (Holloway and Blank 1994).

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

$$X_{\text{CO}_3^{2-}}^m(P, T_0) = X_{\text{CO}_3^{2-}}^m(P_0, T_0) \frac{f_{\text{CO}_2}(P, T_0)}{f_{\text{CO}_2}(P_0, T_0)} \cdot \exp\left\{\frac{-\Delta V_r^{o,m}(P - P_0)}{RT_0}\right\} \quad (1)$$

and

$$X_{\text{H}_2\text{O,mol}}^m(P, T_0) = X_{\text{H}_2\text{O,mol}}^m(P_0, T_0) \frac{f_{\text{H}_2\text{O}}(P, T_0)}{f_{\text{H}_2\text{O}}(P_0, T_0)} \cdot \exp\left\{\frac{(-V_{\text{H}_2\text{O}}^{o,m})(P - P_0)}{RT_0}\right\} \quad (2)$$

where  $X_i^m(P, T_0)$  is the mole fraction of carbonate or molecular  $\text{H}_2\text{O}$  in melt saturated with vapor with a fugacity of carbon dioxide or  $\text{H}_2\text{O}$  of  $f_i(P, T_0)$  at pressure,  $P$ , and temperature,  $T_0$  ( $1473.15$  K);  $X_i^m(P_0, T_0)$  is the mole fraction of carbonate or molecular  $\text{H}_2\text{O}$  in melt in equilibrium with vapor with a fugacity of carbon dioxide or  $\text{H}_2\text{O}$  of  $f_i(P_0, T_0)$  at  $P_0$  (1 bar) and  $T_0$ ;  $f_{\text{CO}_2}(P_0, T_0)$  and  $f_{\text{H}_2\text{O}}(P_0, T_0) = 1$  bar;  $X_{\text{CO}_3^{2-}}^m(P_0, T_0) = 3.8 \times 10^{-7}$ ;  $X_{\text{H}_2\text{O,mol}}^m(P_0, T_0) = 3.28 \times 10^{-5}$ ;  $V_{\text{H}_2\text{O}}^{o,m}$  is the molar volume of  $\text{H}_2\text{O}$  the melt in its standard state and is assumed to be constant and equal to the partial molar volume of  $\text{H}_2\text{O}$  in the melt ( $12 \text{ cm}^3/\text{mol}$ ; Dixon et al. 1995);  $\Delta V_r^{o,m} = (V_{\text{CO}_3^{2-}}^{o,m}) - (V_{\text{O}^{2-}}^{o,m})$  and  $(V_{\text{CO}_3^{2-}}^{o,m})$  and  $(V_{\text{O}^{2-}}^{o,m})$  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) ( $23 \text{ cm}^3/\text{mole}$ ; Pan et al. 1991); and  $R$  is the gas constant ( $83.15 \text{ cm}^3/\text{bar}/\text{mol}\cdot\text{K}$ ).

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

$$\text{CO}_2 \text{ (ppm)} = 10^4 [4400 X_{\text{CO}_3^{2-}}^m / (36.6 - 44 X_{\text{CO}_3^{2-}}^m)] \quad (3)$$

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

$$-\ln\left(\frac{(X_{\text{OH}}^m)^2}{(X_{\text{H}_2\text{O,mol}}^m)(1 - X_{\text{H}_2\text{O,mol}}^m)}\right) = A' + B'X_{\text{OH}}^m + CX_{\text{H}_2\text{O,mol}}^m \quad (4)$$

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

$$X_B = X_{\text{H}_2\text{O,mol}}^m + X_{\text{OH}}^m/2. \quad (5)$$

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

$$\text{wt}\% \text{H}_2\text{O}_{\text{tot}} = 1801.5 X_B / (36.6 - 18.6 X_B). \quad (6)$$

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

$\text{CO}_2$  solubility depends strongly on melt composition though the details of this compositional dependence are poorly known (Blank and Brooker 1994; Holloway and Blank 1994).  $\text{CO}_2$  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), basaltic (Holloway and Blank 1994), and leucitic (Thibault and Holloway 1994) compositions (Fig. 1). Compositions of these liquids are listed in Table 1. The  $\text{CO}_2$  contents for these solubility studies were measured by infrared spectroscopy or a combination of bulk carbon analysis (LECO<sup>®</sup> carbon analysis) and infrared spectroscopy, thereby minimizing discrepancies between different analytical techniques (Blank and Brooker 1994).

The temperature dependence of  $\text{CO}_2$  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 leucitic melts (Thibault and Holloway 1994). For example, at 10 kbar the  $\text{CO}_2$  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  $\text{CO}_2$  solubility over this compositional

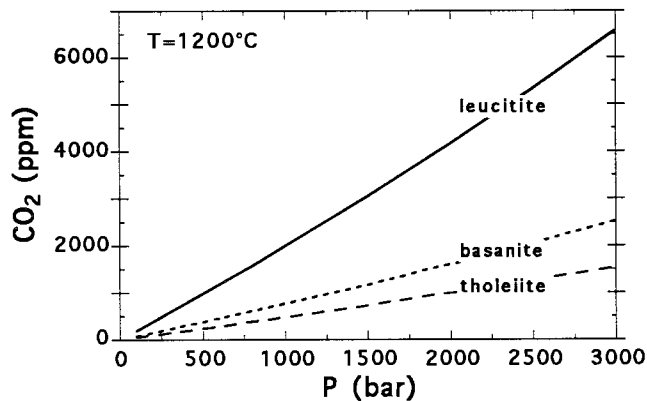


FIGURE 1. Solubility of CO<sub>2</sub> in mafic melts at 1200 °C using the parameters and compositions given in Holloway and Blank (1994) for tholeiite (Dixon et al. 1995), basanite (Pan and Holloway unpublished data), and leucitite (Thibault and Holloway 1994). CO<sub>2</sub> fugacities are calculated using an MRK equation of state (Holloway 1981, 1987).

range is required. Previous work has shown that CO<sub>2</sub> solubility increases as melt depolymerization increases, e.g., decreasing SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> 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 SiO<sub>2</sub> content, CO<sub>2</sub> 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 ( $\Delta G_r$ , Spera and Bergman 1980) suggest that the

order of increasing ability of a cation to increase CO<sub>2</sub> solubility is Ca<sup>+2</sup> > K<sup>+1</sup> > Na<sup>+1</sup>  $\gg$  Mg<sup>+2</sup>  $\approx$  Fe<sup>+2</sup>. Thus the compositional dependence of CO<sub>2</sub> 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 Si<sup>+4</sup> and Al<sup>+3</sup>. The second term sums the molar proportions of cations (Ca<sup>+2</sup> + 0.8K<sup>+1</sup> + 0.7Na<sup>+1</sup> + 0.4Mg<sup>+2</sup> + 0.4Fe<sup>+2</sup>), 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 Ca<sup>+2</sup> ( $\Delta G_r^{Ca}/\Delta G_r^i$ ).

These two terms are combined into a compositional parameter ( $\Pi$ ). Linearity between  $\Pi$  and CO<sub>2</sub> 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  $A = (\text{Si}^{+4} + \text{Al}^{+3})$ ,  $B = (\text{Ca}^{+2} + 0.8\text{K}^{+1} + 0.7\text{Na}^{+1} + 0.4\text{Mg}^{+2} + 0.4\text{Fe}^{+2})$ , 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  $\Pi$  is:

$$\Pi = -6.50(\text{Si}^{+4} + \text{Al}^{+3}) + 20.17(\text{Ca}^{+2} + 0.8\text{K}^{+1} + 0.7\text{Na}^{+1} + 0.4\text{Mg}^{+2} + 0.4\text{Fe}^{+2}). \quad (7)$$

Figure 2a shows the best-fit correlation between CO<sub>2</sub> solubility and  $\Pi$  at 1 kbar and 1200 °C ( $r^2 = 0.984$ , standard error in predicting CO<sub>2</sub> solubility = 122 ppm). Under these  $P$ - $T$  conditions, the CO<sub>2</sub> solubility increases  $\sim 4$ - $5\times$  from tholeiitic ( $\Pi = 0.4$ ) to leucititic ( $\Pi = 2.2$ ) compo-

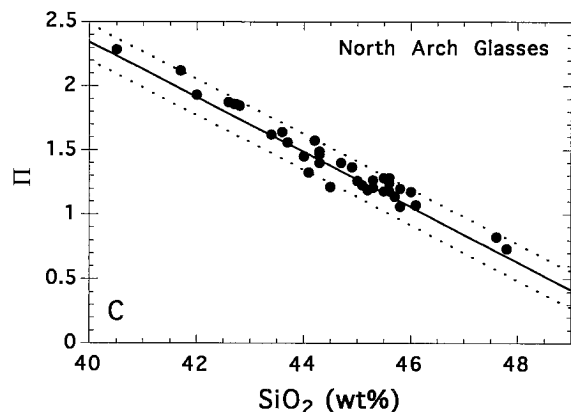
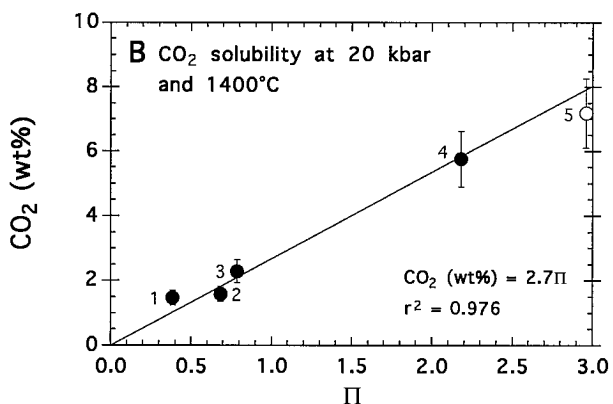
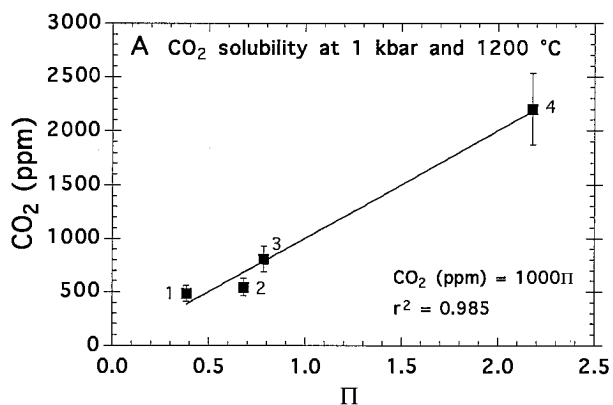
TABLE 1. Major element compositions of glasses used in compositional parameterization of CO<sub>2</sub> solubility

	MORB Thol (1)	Kilauea Thol (2)	Basanite (3)	Leucitite (4)	Sodame- lilite (5)
Oxide (wt%)					
SiO <sub>2</sub>	49.1	49.2	46.0	44.1	46.5
Al <sub>2</sub> O <sub>3</sub>	16.4	13.3	15.2	12.8	19.7
Fe <sub>2</sub> O <sub>3</sub>	n.r.	1.72	n.r.	2.69	0.0
FeO	8.86*	9.68	12.0*	6.62	0.0
MgO	10.2	10.4	9.06	9.14	0.0
CaO	11.7	10.9	8.22	14.3	21.7
Na <sub>2</sub> O	2.13	2.15	4.33	3.20	12.0
K <sub>2</sub> O	0.07	0.51	1.32	3.45	0.0
TiO <sub>2</sub>	0.74	2.29	3.17	2.69	0.0
P <sub>2</sub> O <sub>5</sub>	n.r.	n.r.	0.27	0.77	0.0
Total	99.2	99.7	99.6	99.8	100.0
CO <sub>2</sub> solubility					
1200 °C, 1 kbar (ppm)	484	543	807	2200	n.d.
1400 °C, 20 kbar (wt%)	1.48	1.60	2.30	5.77	7.19
Cation Proportions					
Si <sup>+4</sup>	0.477	0.455	0.422	0.405	0.400
Al <sup>+3</sup>	0.152	0.145	0.164	0.138	0.200
Fe <sup>+2</sup>	0.082*	0.075	0.078	0.051*	0
Mg <sup>+2</sup>	0.093	0.144	0.124	0.125	0
Ca <sup>+2</sup>	0.116	0.108	0.081	0.141	0.200
Na <sup>+1</sup>	0.049	0.039	0.077	0.057	0.200
K <sup>+1</sup>	0.002	0.006	0.0155	0.040	0
$\Pi^*$	0.41	0.70	0.81	2.19	2.96

Notes: 1: Dixon et al. (1995). 2: Pan et al. (1992). 3: Composition from Dixon and Pan 1995. CO<sub>2</sub> solubility data from Holloway and Blank (1994). 4: Thibault and Holloway (1994). 5: Matthey et al. (1990). n.r. means not reported. n.d. means not determined.

\*  $\Pi = -6.50(\text{Si}^{+4} + \text{Al}^{+3}) + 20.17(\text{Ca}^{+2} + 0.8\text{K}^{+1} + 0.7\text{Na}^{+1} + 0.4\text{Mg}^{+2} + 0.4\text{Fe}^{+2})$ .

**FIGURE 2.** (A) Linear correlation between CO<sub>2</sub> solubility data (1 kbar and 1200 °C) and  $\Pi$ , an empirically derived compositional parameter (see text). Sources of data listed in caption to Table 1. Error bars for CO<sub>2</sub> solubility data are  $\pm 15\%$  (relative). (B) CO<sub>2</sub> solubility data (20 kbar, 1400 °C) plotted against  $\Pi$  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  $\Pi$ , but agrees within errors with the projected linear correlation between CO<sub>2</sub> solubility and  $\Pi$  at constant  $P$  and  $T$ . (C) Values of  $\Pi$  plotted against SiO<sub>2</sub> for glasses from the North Arch volcanic field (Dixon et al. 1997). Solid line is best fit line ( $\Pi = 10.9 - 0.214 \cdot \text{SiO}_2$ ). Dotted lines are  $\pm 2$  standard error in calculation of  $\Pi$ .



sitions. It is important to emphasize that this compositional parameterization for CO<sub>2</sub> 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 CO<sub>2</sub>.

Figure 2b shows the linear correlation between CO<sub>2</sub> solubility and  $\Pi$  at 20 kbar and 1400 °C. As an independent check of the calibration, the CO<sub>2</sub> 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 CO<sub>2</sub> solubility vs.  $\Pi$  for tholeiitic, basanitic, and leucititic compositions.

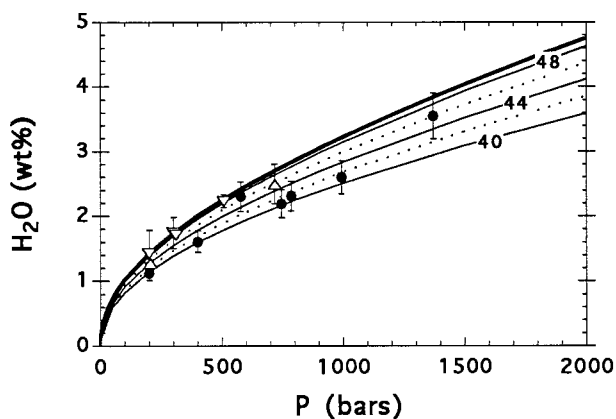
Given this compositional parameterization for CO<sub>2</sub> solubility in mafic liquids, I can now evaluate the effect of composition on CO<sub>2</sub> solubility in oceanic alkalic series magmas. Glasses from the North Arch volcanic field, a suite of alkalic to strongly alkalic lavas erupted on the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

This compositional parameterization can be integrated into the thermodynamic expression for CO<sub>2</sub> solubility. Because the values of  $\Pi$  in the North Arch glasses vary linearly with SiO<sub>2</sub> and because no a priori information is available on the compositional dependence of  $\Delta V_r^{o,m}$ , I allow  $X_{\text{CO}_3^{m-}}^m(P_0, T_0)$  to vary as a linear function of SiO<sub>2</sub> and assume that  $\Delta V_r^{o,m}$  is constant. The desired  $5\times$  range of solubilities for a SiO<sub>2</sub> range of 40–49 wt% is produced by substituting the following expression for  $X_{\text{CO}_3^{m-}}^m(P_0, T_0)$  into Equation 1:

$$X_{\text{CO}_3^{m-}}^m(P_0, T_0) = 8.70 \times 10^{-6} - 1.70 \times 10^{-7} \text{SiO}_2 \quad (8)$$

(where SiO<sub>2</sub> is in wt%) followed by calculation of concentration using Equation 3. The compositional dependence of the molecular weight on a single oxygen basis of mafic melts is small ( $\sim \pm 3\%$ ) and therefore the value for tholeiitic liquid (36.6 g/mol) is used throughout the compositional range.

In contrast to CO<sub>2</sub>, H<sub>2</sub>O solubility is not a strong function of composition for tholeiitic through nephelinitic



**FIGURE 3.** Comparison of H<sub>2</sub>O solubilities at 1200 °C measured in tholeiitic basaltic glasses having SiO<sub>2</sub> of 49–50 wt% (open triangles; Dixon et al. 1995) and basanitic glasses having SiO<sub>2</sub> of 45 wt% (filled circles—error bars are plotted as 10% of the amount present representing ~2σ; Cocheo and Holloway 1993). Heavy curve is solubility model of Dixon et al. (1995). Light solid curves and dashed curves are H<sub>2</sub>O solubilities as a function of SiO<sub>2</sub> content (labeled on curves) as presented in this study showing a 30% decrease in H<sub>2</sub>O solubility as SiO<sub>2</sub> decreases from 49% (tholeiite) to 40% (nephelinite).

compositions (McMillan 1994; Holloway and Blank 1994). In consideration of a wide range of silicate melt compositions, H<sub>2</sub>O solubility is more dependent on melt composition at low *P* than at high *P* (McMillan and Holloway 1987). However, existing models (Burnham 1994; Holloway and Blank 1994; Moore et al. 1995) predict the magnitude of the variation over the limited compositional range of tholeiitic to nephelinitic melts is small (<10% relative). These models, however, are not optimized for mafic compositions.

Recent low *P* experimental determinations of H<sub>2</sub>O 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 H<sub>2</sub>O solubility in a basanitic melt is about 20% lower than that in tholeiitic melt (Fig. 3) and that the speciation of H<sub>2</sub>O 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 H<sub>2</sub>O 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 H<sub>2</sub>O solubility to be constant over the composition range of interest will also be discussed. The important point is that the compositional dependence of H<sub>2</sub>O solubility is small compared with that

of CO<sub>2</sub> solubility; therefore, the compositional dependence of the volatile exsolution process is controlled dominantly by CO<sub>2</sub>.

Analogous to the treatment of CO<sub>2</sub> solubility, I use a simple linear extrapolation for the compositional dependence of H<sub>2</sub>O solubility as a function of SiO<sub>2</sub> content in wt%. Thus,  $X_{\text{H}_2\text{O},\text{mol}}^m(P_0, T_0)$  is allowed to vary as a linear function of SiO<sub>2</sub>, while  $V_{\text{H}_2\text{O}}^{o,m}$  is assumed to be independent of *P*, *T*, and melt composition. The appropriate range of solubilities over a SiO<sub>2</sub> range of 40–49 wt% are produced using the following expression for the mole fraction of molecular H<sub>2</sub>O dissolved in the melt at standard state:

$$X_{\text{H}_2\text{O},\text{mol}}^m(P_0, T_0) = -3.04 \times 10^{-5} + 1.29 \times 10^{-6} \text{ SiO}_2 \quad (9)$$

Total H<sub>2</sub>O contents are calculated from  $X_{\text{H}_2\text{O},\text{mol}}^m(P_0, T_0)$  using equations (4)–(6). The experimentally determined H<sub>2</sub>O solubility data for basanite (SiO<sub>2</sub> = 45 wt%; Cocheo and Holloway 1993) agree with the predicted solubility model to better than 15% relative (Fig. 3).

### VAPOR SATURATION MODELS

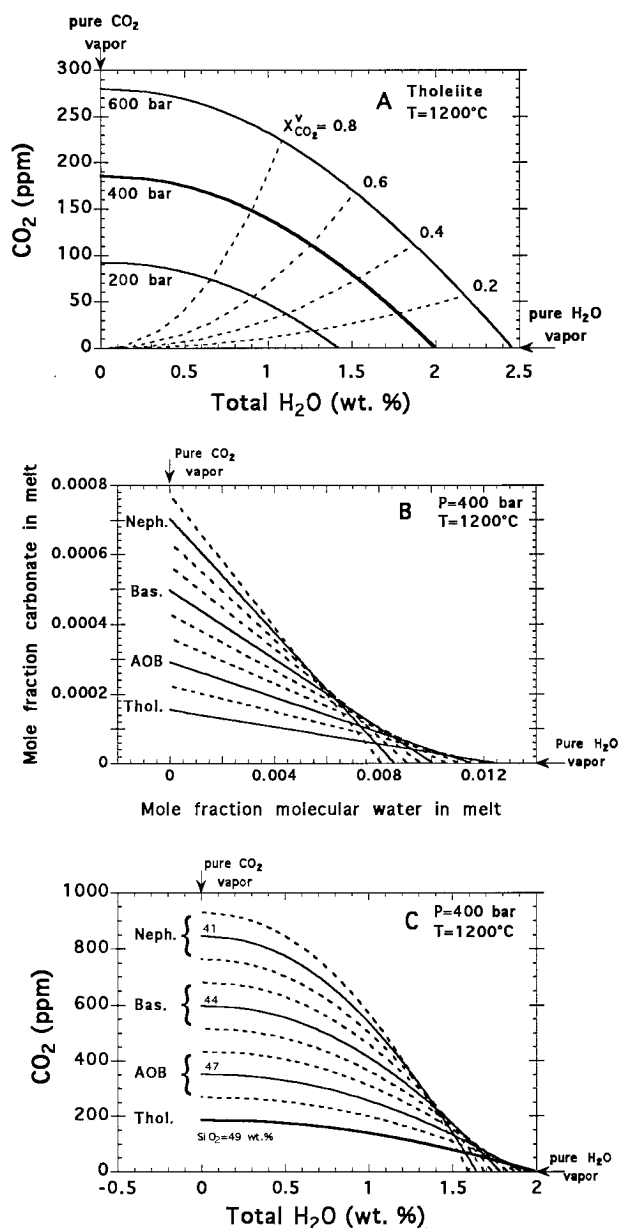
#### Evaluation of vapor saturation and calculation of H<sub>2</sub>O-CO<sub>2</sub> vapor-phase composition

CO<sub>2</sub> and H<sub>2</sub>O 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 H<sub>2</sub>O and CO<sub>2</sub> 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 H<sub>2</sub>O and CO<sub>2</sub> dissolved in a vapor-saturated tholeiitic melt at constant *P* (isobars) and 1200 °C as the vapor composition varies from pure CO<sub>2</sub> to pure H<sub>2</sub>O. Dashed curves show the change in saturation values of H<sub>2</sub>O and CO<sub>2</sub> 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 CO<sub>2</sub> and H<sub>2</sub>O concentrations of volcanic glasses. For example, a melt containing 0.9 wt% H<sub>2</sub>O and 150 ppm CO<sub>2</sub> is saturated at a *P* of 400 bars (4 km H<sub>2</sub>O 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 CO<sub>2</sub> and H<sub>2</sub>O solubility must be incorporated into the equations describing vapor saturation. Vapor-saturation diagrams are constructed with the assumption that the vapor contains only CO<sub>2</sub> and H<sub>2</sub>O and that the vapor mixes ideally (i.e.,  $f_i = X_i f_i^o$ ). If these conditions are satisfied, then the following must be true at vapor saturation:

$$\frac{a_{\text{H}_2\text{O}}^m}{a_{\text{H}_2\text{O}}^{o,m}} + \frac{a_{\text{CO}_2}^m}{a_{\text{CO}_2}^{o,m}} = 1 \quad (10)$$

where the  $a_i^m$  is the activity of H<sub>2</sub>O or carbonate in the melt and  $a_i^{o,m}$  is the corresponding activity in melt in equilibrium with pure H<sub>2</sub>O or carbon dioxide. Given that the vapor mixes ideally, it can be shown that the mole frac-



tions of H<sub>2</sub>O and CO<sub>2</sub> in the vapor can be determined using  $a_{\text{H}_2\text{O}}^m/a_{\text{H}_2\text{O}}^v = X_{\text{H}_2\text{O}}^v$  and  $a_{\text{CO}_3^{2-}}^m/a_{\text{CO}_3^{2-}}^v = X_{\text{CO}_2}^v$ . 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:

$$\frac{X_{\text{H}_2\text{O},\text{mol}}^m}{X_{\text{H}_2\text{O},\text{mol}}^{o,m}} + \frac{X_{\text{CO}_3^{2-}}^m}{X_{\text{CO}_3^{2-}}^{o,m}} = 1 \quad (11)$$

where  $X_i^m$  is the mole fraction of molecular H<sub>2</sub>O or carbonate in the melt and  $X_i^{o,m}$  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 de-

**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 tholeiitic liquids at constant  $P$  (isobars) and a range in vapor compositions. 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 tholeiitic 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  $X_{\text{CO}_3^{2-}}^m$  and  $X_{\text{H}_2\text{O},\text{mol}}^m$  as a function of vapor composition in vapor-saturated mafic liquids at 400 bars and 1200 °C. Solid and dashed lines are lines of constant  $P$  (isobars) and melt composition for nephelinitic (SiO<sub>2</sub> = 40 wt%) through tholeiitic (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 contents as a function of vapor composition in vapor-saturated mafic liquids at 400 bars and 1200 °C. Solid and dashed curves show the compositional dependence of vapor saturation at constant  $P$  (isobars) as presented in this study. The lowermost solid curve for tholeiitic liquids is identical to the 400 bars isobar in Figure 4a.

nominators 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  $X_{\text{CO}_3^{2-}}^m$  and  $X_{\text{H}_2\text{O},\text{mol}}^m$  as a function of vapor composition in vapor-saturated melts. To show the effect of melt composition on the saturation surface, isobars for  $X_{\text{CO}_3^{2-}}^m$  vs.  $X_{\text{H}_2\text{O},\text{mol}}^m$  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 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

North Arch lavas were all dredged at H<sub>2</sub>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<sub>2</sub>O and CO<sub>2</sub> 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  $1.09 \pm 0.15$ ). This agreement is within the estimated uncertainty of the model [ $1\sigma$  uncertainties in the H<sub>2</sub>O analyses ( $\sim \pm 5\%$ ), CO<sub>2</sub> analyses ( $\sim \pm 20\%$ ), and compositional dependence of H<sub>2</sub>O and CO<sub>2</sub> solubilities ( $\sim \pm 15\%$ ) combine to give a total uncertainty of  $\sim 30\%$  in the value of the saturation index] and suggests that most of the North Arch glasses were vapor saturated with a H<sub>2</sub>O-CO<sub>2</sub> vapor upon quenching on the seafloor at 400 bar.

#### Calculation of equilibrium saturation pressure

As described above, given measurements of the H<sub>2</sub>O and CO<sub>2</sub> 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<sub>2</sub> undersaturated (more alkalic) as a consequence of increasing CO<sub>2</sub> solubility. For example, a nephelinite with 2.0 wt% H<sub>2</sub>O and 2.0 wt% CO<sub>2</sub> reaches saturation at  $\sim 7$  kbar, whereas a tholeiite with identical volatile contents reaches saturation at  $\sim 18$  kbar. Figure 6a shows the effect of changing the CO<sub>2</sub> content at constant H<sub>2</sub>O. Figure 6b shows the effect of changing H<sub>2</sub>O content at constant CO<sub>2</sub>/H<sub>2</sub>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

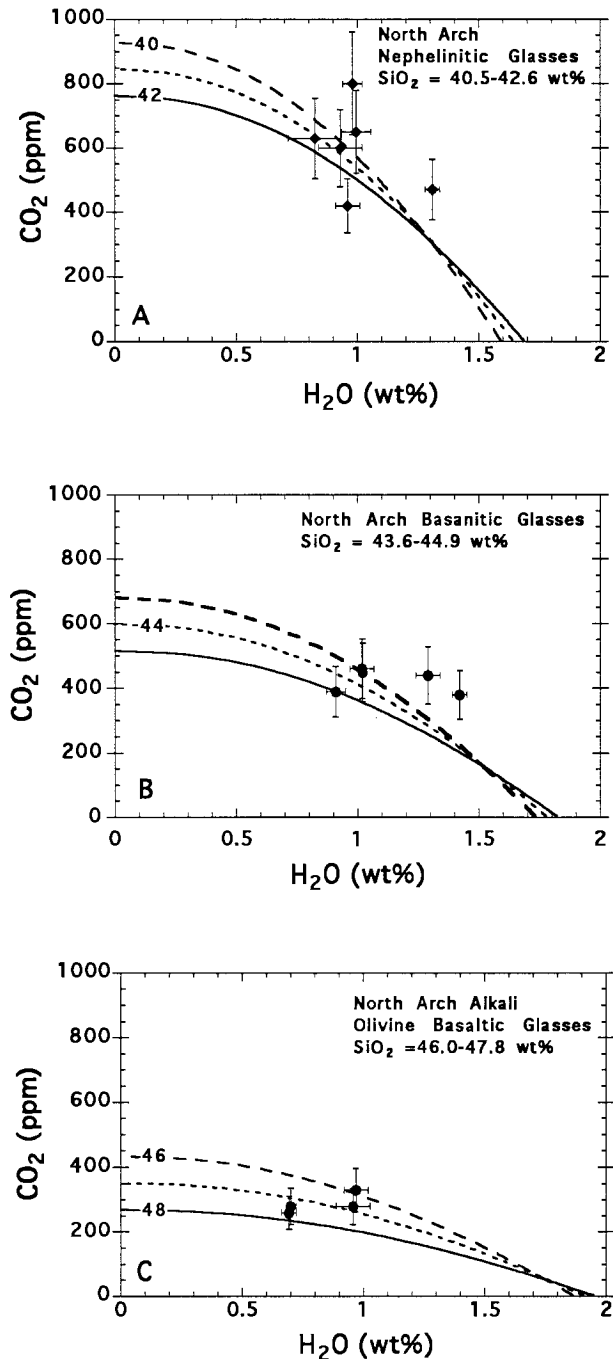
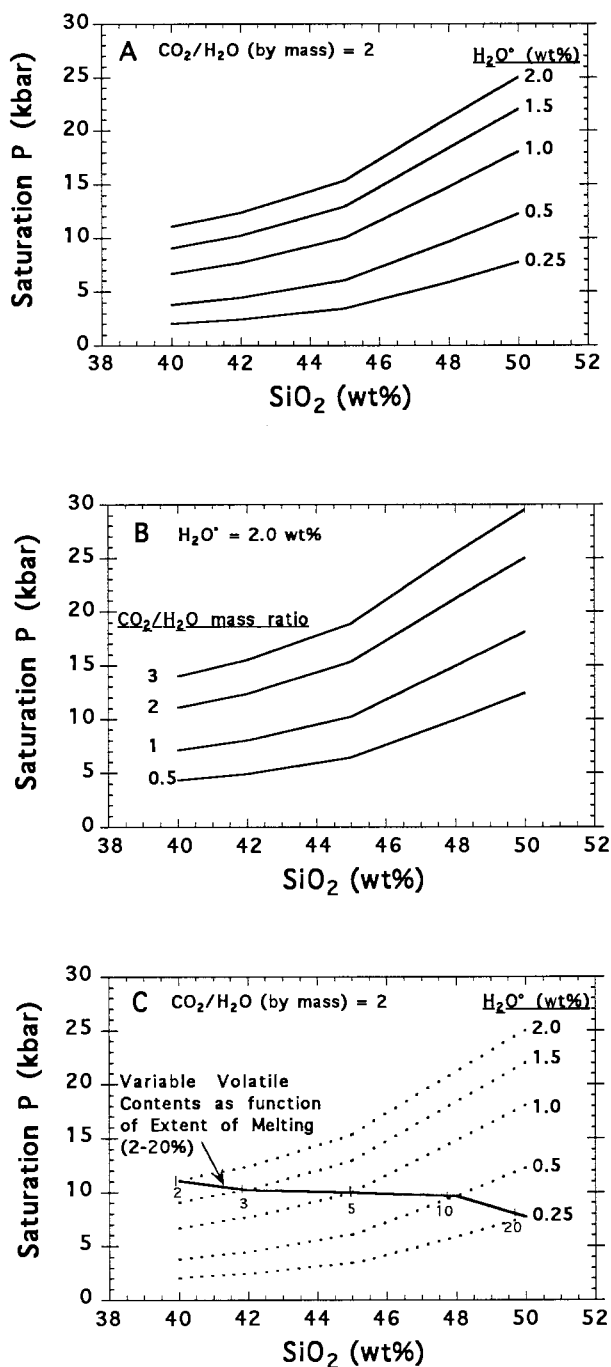


FIGURE 5. CO<sub>2</sub> and H<sub>2</sub>O contents determined by FTIR in glasses from the submarine North Arch Volcanic Field erupted at 3900–4390 m H<sub>2</sub>O depth (Clague et al. 1990; Dixon et al. 1997) plotted against the compositionally appropriate 400 bars isobars. (A) Nephelinitic glasses, SiO<sub>2</sub> = 40–42 wt%. (B) Basanitic glasses, SiO<sub>2</sub> = 43–45 wt%. (C) Alkali olivine basaltic glasses, SiO<sub>2</sub> = 46–48 wt%.



initial volatile concentration to vary with silicate melt composition. In this example,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are modeled as incompatible elements, the mantle  $\text{CO}_2/\text{H}_2\text{O}$  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%  $\text{H}_2\text{O}$  and 40 wt%  $\text{SiO}_2$ , and a tholeiitic melt has 0.25 wt%  $\text{H}_2\text{O}$  and 50 wt%  $\text{SiO}_2$ . Using these boundary conditions, the saturation  $P$  remains nearly constant at ~8–11 kbar, and a nephelinitic melt reaches

**FIGURE 6.** Plot of  $P$  at which an ascending magma would reach vapor-saturation as a function of initial volatile content and melt composition. (A) Curves of saturation  $P$  as a function of melt composition for melts having a range in initial  $\text{H}_2\text{O}$  contents at  $\text{CO}_2/\text{H}_2\text{O} = 2$ . (B) Curves of saturation  $P$  as a function of melt composition for melts having an initial  $\text{H}_2\text{O}$  content of 2.0 wt% and a range of  $\text{CO}_2/\text{H}_2\text{O}$  of 3–0.5. (C) Dashed curves are reproduced from A. Solid curve represents pressure of initial vapor saturation for mafic melts whose major element compositions and initial volatile contents are controlled by variable extents of melting. Parameters used:  $\text{H}_2\text{O}$  content in mantle source region of 600 ppm, bulk distribution content for  $\text{H}_2\text{O}$  ( $D_{\text{H}_2\text{O}}^0$ ) of 0.010, and batch melting equation:  $\text{H}_2\text{O}^{\text{m}} = \text{H}_2\text{O}^{\text{source}}/[D_{\text{H}_2\text{O}}^0 + F(1 - D_{\text{H}_2\text{O}}^0)]$ . Tick marks show  $\text{H}_2\text{O}$  contents (2.0, 1.5, 1.0, 0.55, and 0.29 wt%  $\text{H}_2\text{O}$ ) generated by variable extents of melting (2, 3, 5, 10, and 20%, respectively).

←

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  $\text{CO}_2$  solubility and volatile contents are similar in magnitude but opposite in sign and nearly cancel. Similar trends are observed at different  $\text{CO}_2/\text{H}_2\text{O}$  ratios (for  $\text{CO}_2/\text{H}_2\text{O} = 1$ ,  $P_{\text{sat}} = 4\text{--}7$  kbar; for  $\text{CO}_2/\text{H}_2\text{O} = 3$ ,  $P_{\text{sat}} = 10\text{--}14$  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 $\text{H}_2\text{O}$ and $\text{CO}_2$ between vapor and melt

Whereas absolute solubilities control  $\text{H}_2\text{O}$  and  $\text{CO}_2$  concentrations at vapor saturation, the relative differences in solubility control partitioning of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  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  $\text{H}_2\text{O}$  and  $\text{CO}_2$  and applied the theory to fractionation of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  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  $\text{CO}_2\text{--H}_2\text{O}$  fractionation factor ( $\beta$ ) between vapor and melt as:

$$\beta_{\text{CO}_2\text{--H}_2\text{O,mol}} = \frac{\left(\frac{N_{\text{CO}_2}}{N_{\text{H}_2\text{O}}}\right)^{\text{vapor}}}{\left(\frac{N_{\text{CO}_2}}{N_{\text{H}_2\text{O}}}\right)^{\text{melt}}} \quad (12)$$



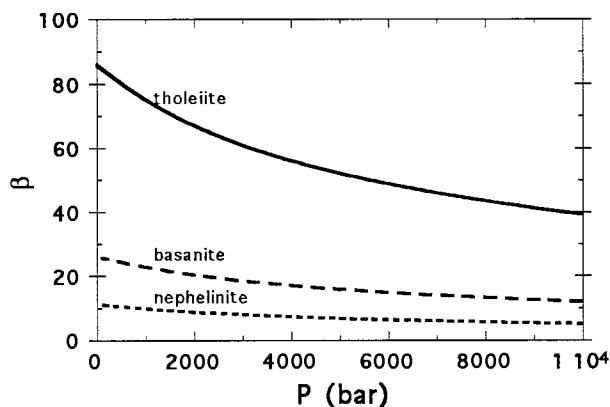


FIGURE 7. Plot of  $\beta$  as a function of  $P$  and composition for tholeiite ( $\text{SiO}_2 = 49$  wt%), basanite ( $\text{SiO}_2 = 45$  wt%), and nephelinite ( $\text{SiO}_2 = 40$  wt%). Values of  $\beta$  calculated assuming  $\text{H}_2\text{O}$  solubility decreases with  $\text{SiO}_2$  undersaturation according to Equation 13. The combination of increasing  $\text{CO}_2$  solubility and decreasing  $\text{H}_2\text{O}$  solubility cause a sharp decrease in the value of  $\beta$  as melt composition varies from tholeiitic to nephelinitic.

where  $N_i$  is the number of moles of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the vapor or number of moles of carbonate and molecular  $\text{H}_2\text{O}$  in the melt. The value of  $\beta$  is a function of  $P$  and melt composition. The pressure dependence (exponential terms) of the activity of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  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  $\text{H}_2\text{O}$  and carbonate in the melt are given in Equations 8 and 9. Following Dixon and Stolper (1995) it can be shown that:

$$\beta_{\text{CO}_2-\text{H}_2\text{O,mol}} = \frac{\left(\frac{f_{\text{H}_2\text{O}}^o}{f_{\text{CO}_2}^o}\right) \left[\frac{\left(\frac{f_{\text{CO}_2}}{f_{\text{H}_2\text{O}}}\right)}{\left(\frac{X_{\text{CO}_3^{2-}}^m}{X_{\text{H}_2\text{O,mol}}^m}\right)}\right]}{\left(\frac{f_{\text{H}_2\text{O}}^o}{f_{\text{CO}_2}^o}\right) \left[\frac{X_{\text{H}_2\text{O,mol}}^{o,m}(1 \text{ bar}, 1473 \text{ K})}{X_{\text{CO}_3^{2-}}^{o,m}(1 \text{ bar}, 1473 \text{ K})}\right]} \cdot \left(\frac{\exp\{-12(P-1)/[(83.15)(1473.15)]\}}{\exp\{-23(P-1)/[(83.15)(1473.15)]\}}\right) \quad (13)$$

Note that the fractionation factor must be expressed in terms of mole fractions of carbonate and molecular  $\text{H}_2\text{O}$  species that behave Henrian with respect to fugacities of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  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  $\text{CO}_2$  is fractionated preferentially into the vapor with respect to  $\text{H}_2\text{O}$ . 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  $\text{CO}_2$  is strongly partitioned into the vapor phase relative to  $\text{H}_2\text{O}$ . Thus, for a tholeiite with concentrations of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  typical of oceanic basalts, almost all  $\text{CO}_2$  would be lost before significant quantities of  $\text{H}_2\text{O}$  begin to exsolve. Using logic based on our experience with degassing of tholeiitic melts, significant exsolution of  $\text{H}_2\text{O}$  would seem to be precluded in lavas having high  $\text{CO}_2$  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  $\text{H}_2\text{O}$  and  $\text{CO}_2$  solubilities decreases, and the strength of fractionation of  $\text{CO}_2$  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  $\text{CO}_2$  into the vapor relative to  $\text{H}_2\text{O}$ ) to 10 in nephelinitic melts (indicative of weak preferential partitioning of  $\text{CO}_2$  into the vapor). Thus, if tholeiitic and nephelinitic melts with identical volatile contents degas under identical conditions, less  $\text{CO}_2$  will degas from the nephelinitic melt than from the tholeiitic melt for a given amount of  $\text{H}_2\text{O}$  loss. Figure 7 also illustrates that  $\beta$  decreases with increasing  $P$  as a result of  $\text{CO}_2$  fugacity increasing more rapidly with  $P$  than  $\text{H}_2\text{O}$  fugacity. Thus,  $\text{CO}_2$  would not be as strongly fractionated into the vapor in melts at high pressures.

The values of  $\beta$  are relatively insensitive to the specific  $\text{H}_2\text{O}$  solubility model selected. The value of  $\beta$  for basanitic and nephelinitic liquids calculated assuming constant  $\text{H}_2\text{O}$  solubility are only slightly higher (~15–50%) than those calculated assuming that  $\text{H}_2\text{O}$  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  $\text{H}_2\text{O}$  and  $\text{CO}_2$  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  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (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 H<sub>2</sub>O and CO<sub>2</sub> contents,  $P$ , and the style of degassing (open or closed).

(2) Calculate H<sub>2</sub>O and CO<sub>2</sub> solubilities and fractionation factor ( $\beta$ ) as a function of SiO<sub>2</sub> content.

(3) Degas magma at a given  $P$  by incrementally transferring H<sub>2</sub>O and CO<sub>2</sub> 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 H<sub>2</sub>O in melt (Dixon and Stolper 1995). Saturation is evaluated using equation (11) after each increment.

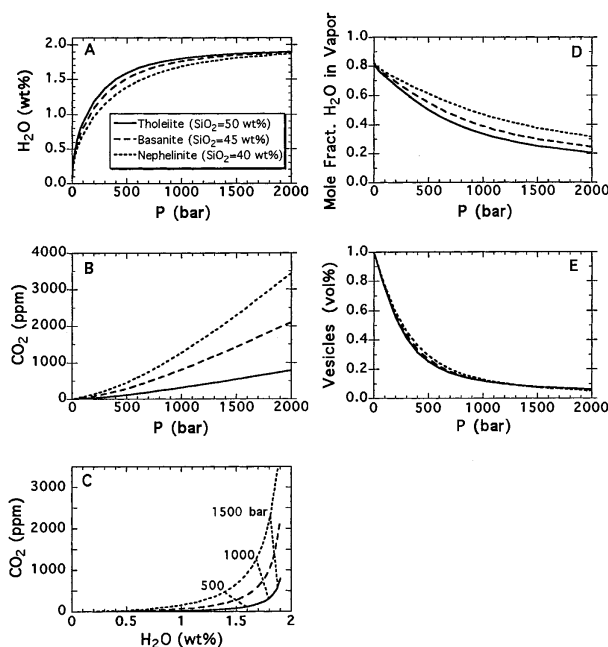
(4) Output final H<sub>2</sub>O and CO<sub>2</sub> contents in degassed melt, composition of vapor phase, and volume proportion vapor phase (percent vesicles).

Closed system degassing paths calculated using initial H<sub>2</sub>O content of 2.0 wt%, CO<sub>2</sub> 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 CO<sub>2</sub>-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 CO<sub>2</sub> lost in a shallow crustal environment. For simplification, the following SiO<sub>2</sub> contents will be used to represent the following magma compositions—alkali olivine basalt (48% SiO<sub>2</sub>), basanite (45% SiO<sub>2</sub>), and nephelinite (42% SiO<sub>2</sub>).

Figures 8a–c show that closed-system degassing of alkalic melts results in lower H<sub>2</sub>O and higher CO<sub>2</sub> contents in comparison with tholeiitic melts. For example, if a nephelinite and tholeiite had degassed at 400 bars, the tholeiitic liquid would have a H<sub>2</sub>O content of 1.5 wt% (25% loss) and a CO<sub>2</sub> content of 80 ppm (99.2% loss), whereas the nephelinitic liquid would have a H<sub>2</sub>O content of 1.3 wt% (35% loss) and a CO<sub>2</sub> content of 340 ppm (96.6% loss). The extra H<sub>2</sub>O loss contributes to greater proportion of H<sub>2</sub>O in the vapor (Fig. 8d).

For completeness, additional degassing calculations were performed assuming constant H<sub>2</sub>O solubility. In the constant H<sub>2</sub>O solubility case, constant H<sub>2</sub>O contents, vapor composition, and vesiculation are essentially the same for all compositions as  $P$  decreases (less degassing of H<sub>2</sub>O than in the variable H<sub>2</sub>O solubility case). CO<sub>2</sub> contents at a given  $P$  are slightly higher than in the variable H<sub>2</sub>O solubility case for alkalic compositions, reflecting the slightly higher proportion of CO<sub>2</sub> in the vapor. Thus, the amount of H<sub>2</sub>O loss during exsolution of a vapor phase is sensitive to the assumed H<sub>2</sub>O solubility model. However, for both cases the vapor-saturated alkalic basalts have higher CO<sub>2</sub> contents than tholeiitic basalts degassed under identical conditions.

In summary, I have estimated the compositional dependence of H<sub>2</sub>O and CO<sub>2</sub> solubility in tholeiitic through nephelinitic liquids and have generated vapor saturation



**FIGURE 8.** Example results of forward degassing model using the compositional dependence of CO<sub>2</sub> and H<sub>2</sub>O solubility at 1200 °C on SiO<sub>2</sub> as presented in this study. Closed system degassing paths are shown for melts initially containing 2.0 wt% H<sub>2</sub>O and 1.0 wt% CO<sub>2</sub>. Results are shown for  $P < 2000$  bar, though vapor saturation was reached at ~12 kbar for the tholeiite (SiO<sub>2</sub> = 49 wt%), ~6.5 kbar for basanite (SiO<sub>2</sub> = 45 wt%), and ~4 kbar for nephelinite (SiO<sub>2</sub> = 40 wt%). Progressive, closed system degassing was modeled as described in the text. (A) H<sub>2</sub>O content as a function of  $P$ . (B) CO<sub>2</sub> content as a function of  $P$ . These values are lower than those shown in Figure 1 because the vapor contains significant amounts of H<sub>2</sub>O. (C) Degassing path showing covariation of CO<sub>2</sub> and H<sub>2</sub>O during progressive volatile exsolution. (D) Mole fraction of H<sub>2</sub>O in vapor as a function of  $P$ . (E) Volume percent exsolved gas as a function of  $P$ .

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 H<sub>2</sub>O and CO<sub>2</sub> contents in glasses, the depth of initial vapor saturation based on estimates of initial H<sub>2</sub>O and CO<sub>2</sub> contents, and fractionation of various volatile species during progressive depressurization. Specifically, partitioning of CO<sub>2</sub> into the vapor phase relative to H<sub>2</sub>O 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 CO<sub>2</sub> and more H<sub>2</sub>O than tholeiitic magmas.

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## REFERENCES CITED

- Blank, J.G., and Brooker, R.A. (1994) Experimental studies of carbon dioxide in silicate melts: Solubility, speciation, and stable carbon isotope behavior. In *Mineralogical Society of America Reviews in Mineralogy*, 30, 157–186.
- Bottinga, Y., and Javoy, M. (1990) MORB degassing: Bubble growth and ascent. *Chemical Geology*, 81, 255–270.
- Burnham, C.W. (1994) Development of the Burnham model for prediction of H<sub>2</sub>O solubility in magmas. In *Mineralogical Society of America Reviews in Mineralogy*, 30, 123–129.
- Clague, D.A., and Dalrymple, G.B. (1988) Age and petrology of alkalic postshield and rejuvenated stage lava from Kauai, Hawaii. *Contributions to Mineralogy and Petrology*, 99, 202–218.
- Clague, D.A., and Frey, F.A. (1982) Petrology and trace element geochemistry of the Honolulu Volcanics, Implications for the oceanic mantle beneath Hawaii. *Journal of Petrology*, 23, 447–504.
- Clague, D.A., Holcomb, R.T., Sinton, J.M., Detrick, R.S., and Torresan, M.R. (1990) Pliocene and Pleistocene alkalic flood basalts on the seafloor north of the Hawaiian islands. *Earth and Planetary Science Letters*, 98, 175–191.
- Cocheo, P.A., and Holloway, J.R. (1993) The solubility of H<sub>2</sub>O in basaltic melts at low pressures. *EOS Transactions of the American Geophysical Union* 74, Spring Meeting Supplemental, 350.
- Dixon, J.E., and Pan, V. (1995) Determination of the molar absorptivity of dissolved carbonate in basaltic glass. *American Mineralogist*, 80, 1339–1342.
- Dixon, J.E., and Stolper, E.M. (1995) An experimental study of H<sub>2</sub>O and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. Part II: Application to degassing of basaltic liquids. *Journal of Petrology*, 36, 1633–1646.
- Dixon, J.E., Stolper, E.M., and Holloway, J.R. (1995) An experimental study of H<sub>2</sub>O and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. Part I: Calibration and solubility results. *Journal of Petrology*, 36, 1607–1631.
- Dixon, J.E., Clague, D.A., Wallace, P., and Poreda, R. (1997) Volatiles in alkalic basalts from the North Arch Volcanic Field, Hawaii: Extensive degassing of deep submarine-erupted alkalic series lavas. *Journal of Petrology*, in press.
- Eggler, D.H. (1974) Effect of CO<sub>2</sub> on the melting of peridotite. *Carnegie Institute of Washington Yearbook*, 72, 215–224.
- Eitel, W., and Weyl, W. (1932) Residuals in the melting of commercial glasses. *Journal of the American Ceramic Society*, 15, 159–166.
- Gerlach, T.M. (1986) Exsolution of H<sub>2</sub>O, CO<sub>2</sub>, and S during eruptive episodes at Kilauea Volcano, Hawaii. *Journal of Geophysical Research*, 91, 12177–12185.
- Holloway, J.R. (1977) Fugacity and activity of molecular species in supercritical fluids. In *Fraser, D., (Ed.), Thermodynamics in Geology*, p. 161–181. Reidel, Boston.
- Holloway, J.R., and Blank, J.G. (1994) Application of experimental results to C-O-H species in natural melts. In *Mineralogical Society of America Reviews in Mineralogy*, 30, 187–230.
- Holloway, J.R., Mysen, B.O., and Eggler, D.H. (1976) The solubility of CO<sub>2</sub> in liquids on the join CaO-MgO-SiO<sub>2</sub>-CO<sub>2</sub>. *Carnegie Institute of Washington Yearbook*, 75, 626–631.
- Jambon, A., Weber, H., and Braun, O. (1986) Solubility of He, Ne, Ar, Kr and Xe in a basalt melt in the range 1250–1600 °C. *Geochemical implications*. *Geochimica et Cosmochimica Acta*, 50, 401–408.
- Mattey, D.P., Taylor, W.R., Green, D.H., and Pillinger, C.T. (1990) Carbon isotopic fractionation between CO<sub>2</sub> vapour, silicate and carbonate melts: An experimental study to 30 kbar. *Contributions to Mineralogy and Petrology*, 104, 492–505.
- McMillan, P. (1994) H<sub>2</sub>O solubility and speciation models. In *Mineralogical Society of America Reviews in Mineralogy*, 30, 131–156.
- McMillan, P., and Holloway, J.R. (1987) H<sub>2</sub>O solubility in aluminosilicate melts. *Contributions to Mineralogy and Petrology*, 97, 320–332.
- Mysen, B.O. (1976) The role of volatiles in silicate melts: Solubility of CO<sub>2</sub> and H<sub>2</sub>O in feldspar, pyroxene, and feldspathoid melts to 30 kb and 1625 °C. *American Journal of Science*, 276, 969–996.
- Mysen, B.O., Eggler, D.H., Setiz, M.G., Holloway, J.R. (1976) Carbon dioxide in silicate melts and crystals: Part I. Solubility measurements. *American Journal of Science*, 276, 455–579.
- Moore, G.M., Vennemann, T., and Carmichael, I.S.E. (1995) Solubility of H<sub>2</sub>O in magmas to 2 kbar. *Geology*, 23, 1099–1102.
- Pan, V., Holloway, J.R., and Hervig, R.L. (1991) The pressure and temperature dependence of carbon dioxide solubility in tholeiitic basalt melts. *Geochimica et Cosmochimica Acta*, 55, 1587–1595.
- Saxena, S.K., and Fei, Y. (1987) High pressure and high temperature fluid fugacities. *Geochimica et Cosmochimica Acta*, 51, 783–791.
- Silver, L.A. and Stolper, E.M. (1989) H<sub>2</sub>O in albitic glasses. *Journal of Petrology*, 30, 667–709.
- Spera, F.J. and Bergman, S.C. (1980) Carbon dioxide in igneous petrogenesis: I. *Contributions to Mineralogy and Petrology*, 74, 55–66.
- Thibault, Y., and Holloway, J.R. (1994) Solubility of CO<sub>2</sub> in a Ca-rich leucite: Effects of pressure, temperature, and oxygen fugacity. *Contributions to Mineralogy and Petrology*, 116, 216–224, 1994.
- Zhang, Y., and Zindler, A. (1989) Noble gas constraints on the evolution of the Earth's atmosphere. *Journal of Geophysical Research*, 94, 13719–13737.

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