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VOLATILECALC: a silicate melt–H₂O–CO₂ solution model written in Visual Basic for excel[☆]

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Abstract

We present solution models for the rhyolite–H₂O–CO₂ and basalt–H₂O–CO₂ systems at magmatic temperatures and pressures below ~5000 bar. The models are coded as macros written in Visual Basic for Applications, for use within Microsoft[®] Excel (Office'98 and 2000). The series of macros, entitled VOLATILECALC, can calculate the following: (1) Saturation pressures for silicate melt of known dissolved H₂O and CO₂ concentrations and the corresponding equilibrium vapor composition; (2) open- and closed-system degassing paths (melt and vapor composition) for depressurizing rhyolitic and basaltic melts; (3) isobaric solubility curves for rhyolitic and basaltic melts; (4) isoplethic solubility curves (constant vapor composition) for rhyolitic and basaltic melts; (5) polybaric solubility curves for the two end members and (6) end member fugacities of H₂O and CO₂ vapors at magmatic temperatures. The basalt–H₂O–CO₂ macros in VOLATILECALC are capable of calculating melt–vapor solubility over a range of silicate–melt compositions by using the relationships provided by Dixon (American Mineralogist 82 (1997) 368). The output agrees well with the published solution models and experimental data for silicate melt–vapor systems for pressures below 5000 bar. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Dissolved volatile gases strongly affect the density and viscosity of crustal magmas, and thereby play a crucial role in magma ascent, intrusion and eruption. To evaluate the density and vesicularity of ascending magmas, one must depend on solubility models that calculate the changing melt and vapor compositions as functions of pressure and temperature. Though there exists an abundance of experimental data on the

solubility of H₂O in silicate melts (Tuttle and Bowen, 1958; Burnham and Jahns, 1962; Hamilton et al., 1964; Dingwell et al., 1984; Silver et al., 1990; Holtz et al., 1992, 1995; Yamashita, 1999), and a growing literature on CO₂ (Fogel and Rutherford, 1990; Blank et al., 1993; Dixon et al., 1995), there are no algorithms for mixed volatile (H₂O–CO₂) equilibria written in programming languages available for modern computer operating systems. Herein, we describe a computer program, VOLATILECALC, written in Visual Basic for Applications (VBA) for use with Microsoft[®] Excel. The software allows the calculation of melt solubilities for the basalt–H₂O–CO₂ and rhyolite–H₂O–CO₂ systems, as functions of pressure and temperature, and determines isobars, isopleths and closed- and open-system degassing paths. Results are automatically plotted with the Excel[®] charting tools.

[☆] Code available from server at <http://www.iamg.org/CGEditor/index.htm>.

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2. Published models and software

Holloway and Blank (1994) published a model for the solubility of H₂O and CO₂ in rhyolite melt written in Microsoft[®] Quickbasic 1.0 for the Macintosh, a program no longer available either for the Macintosh or Windows operating systems, and that has been superseded by Microsoft[®] VBA. The software must be adapted by the user to calculate isobars, isopleths, degassing paths and other potential means for assessing the melt-volatile system. Moore et al. (1998) provide an Excel[®]-based Visual Basic code (H2OSOL) to calculate H₂O solubility as a function of pressure, temperature, melt composition and activity of H₂O in the vapor phase. Intended for use at pressures <3000 bar, the model does not take into account CO₂ and thus does not calculate degassing paths, isobars, etc. for mixed volatile systems. Papale (1999) published a solubility model for the H₂O–CO₂–silicate-melt system that calculates melt–vapor equilibria as a function of melt composition, as well as pressure and temperature. The model was published solely as a manuscript and does not include the accompanying software.

VOLATILECALC calculates vapor–melt equilibria for the basalt–H₂O–CO₂ and rhyolite–H₂O–CO₂ systems. Moore et al. (1998) provided a more general code that models the system H₂O–silicate melt over a wide compositional interval. Users can therefore input their own silicate-melt composition. However, since few experiments have measured CO₂ solubility in melt compositions other than rhyolites and basalts, we opt not to model all silicate-melt compositions, and instead use algorithms that do not require input of melt composition (Silver, 1988; Dixon et al., 1995). However, using the relations between melt SiO₂ concentration and H₂O and CO₂ solubility provided by Dixon (1997), VOLATILECALC can calculate melt–vapor equilibria for the continuum of basalt compositions between tholeiite and nephelinite. As discussed below, VOLATILECALC agrees well with the model of Moore et al. (1998) for H₂O solubility in rhyolitic and basaltic melts.

VOLATILECALC is a solubility model for the system melt–H₂O–CO₂ that runs within Microsoft[®] Excel[®]. It is unique in allowing users to calculate and plot a variety of different conditions such as isobaric, isoplethic (vapor), polybaric open- and closed-system degassing.

3. Algorithms used by VOLATILECALC

VOLATILECALC is based primarily on a thermodynamic model for hydrous silicate melt initially outlined by Silver and Stolper (1985) and applied to rhyolite by Silver (1988). The silicate melt is modeled as an ideal mixture of water molecules, hydroxyl groups and oxygen atoms, as described by Stolper (1982). Equi-

librium constants describe the partitioning of water between hydroxyl (OH[−]) and molecular water (H₂O_{mol}) species dissolved within the silicate melt. The solubility of molecular water in the silicate melt is then linked to the fugacity of water in the vapor by the following equation:

$$X_{\text{H}_2\text{O}_{\text{mol}}}^{\text{m}}(P, T) = f_{\text{H}_2\text{O}}^{\circ}(P, T) \frac{X_{\text{H}_2\text{O}_{\text{mol}}}^{\circ, \text{m}}(P_0, T_0)}{f_{\text{H}_2\text{O}}^{\circ}(P_0, T_0)} \exp \left\{ \left(\frac{-\bar{V}_{\text{H}_2\text{O}}^{\circ, \text{m}}}{RT} (P - P_0) \right) + \left(\frac{\Delta \bar{H}_{\text{H}_2\text{O}}^{\circ}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right) \right\} \quad (1)$$

where $X_{\text{H}_2\text{O}_{\text{mol}}}^{\text{m}}(P, T)$ refers to the molar concentration of H₂O as molecular water (H₂O_{mol}) in the melt at pressure P and temperature T ; $X_{\text{H}_2\text{O}_{\text{mol}}}^{\circ, \text{m}}(P_0, T_0)$ is the standard state molar concentration of H₂O_{mol} in the melt at the reference P and T and in equilibrium with pure water, $f_{\text{H}_2\text{O}}^{\circ}(P, T)$ and $f_{\text{H}_2\text{O}}^{\circ}(P_0, T_0)$ are, respectively, the fugacity of water in the coexisting vapor at P and T , and the standard state fugacity of pure water vapor at the reference P and T . $\bar{V}_{\text{H}_2\text{O}}^{\circ, \text{m}}$ is the molar volume of water in the melt under standard state conditions and $\Delta \bar{H}_{\text{H}_2\text{O}}^{\circ}$ is the standard state heat of solution of one mole of water in the melt. Both the volume and enthalpy values are assumed to be constant over the pressure and temperature ranges of interest. The standard states and other parameters used by VOLATILECALC are listed in Table 1: the values for rhyolite are based on works by Silver (1988), Silver et al. (1990), Fogel and Rutherford (1990), and Blank et al. (1993); those for basalt are from Dixon et al. (1995) and Dixon (1997). Application of the Ochs and Lange (1999) algorithm for the calculation of $\bar{V}_{\text{H}_2\text{O}}^{\circ, \text{m}}$ causes VOLATILECALC to underestimate the solubility of H₂O relative to the pertinent experimental data, as discussed below. This does not necessarily imply that the values used in VOLATILECALC better represent the actual partial molar volume of H₂O than those provided by Ochs and Lange (1999), but that they allow VOLATILECALC to provide more accurate solubilities.

VOLATILECALC first calculates $X_{\text{H}_2\text{O}_{\text{mol}}}^{\text{m}}(P, T)$ and $X_{\text{CO}_2}^{\text{m}}(P, T)$ for the user-defined dissolved H₂O and CO₂ concentrations, by assigning the appropriate amount of H₂O_{mol} relative to OH[−] that should be dissolved in the melt (Stolper, 1982; Silver and Stolper, 1985), as well as the mole fraction of CO₂ dissolved in the melt. Using these values ($X_{\text{H}_2\text{O}_{\text{mol}}}^{\text{m}}(P, T)$ and $X_{\text{CO}_2}^{\text{m}}(P, T)$) and user-defined temperature, VOLATILECALC then solves a form of Eq. (1) (and a similar equation for CO₂) to determine the vapor composition. Solubility of a volatile gas in the melt is assumed to follow Henry's Law, so that dilution of H₂O in the

Table 1
Parameters for H₂O and CO₂ solubility models

Parameter	Rhyolite	Basalt	Reference
Molar Vol. H ₂ O (cm ³ /mol)	5 ^a	12	2
Solubility of H ₂ O at standard state (wt%)	3.41	0.11	1, 2
Reference <i>T</i> (°C) for H ₂ O	850	1200	1,2
Reference <i>P</i> (bar) for H ₂ O	799	1	1,2
Molar Vol. CO ₂ (cm ³ /mol)	28	23	3, 2, 4
Solubility of CO ₂ at standard state (ppm)	537	0.5	3,2
Reference <i>T</i> °C for CO ₂	850	1200	3,2
Reference <i>P</i> bars for CO ₂	750	1	3,2
Weight of melt: anhydrous single-O basis (g/mol)	32.5	36.6	5,2

^aThis work, (1) Silver (1988); (2) Dixon et al. (1995); (3) Blank et al. (1993); (4) Pan et al. (1991); (5) Silver et al. (1990).

vapor phase linearly decreases its concentration in the melt. Increasing the computed pressure, while holding the dissolved volatiles fixed, results in lower calculated mole fractions in the vapor. Pressure is iterated using Newton's Method until a condition is found where the mole fractions of CO₂ and H₂O in the vapor phase sum up to unity. The solubility of H₂O in silicate melt is assumed to be independent of CO₂ concentration, and vice versa. Though this assumption may not be valid at pressures over ~4000 bars (Mysen et al., 1976; Jakobson, 1997), it holds at lower pressures (Blank et al., 1993).

The basalt–H₂O–CO₂ code within VOLATILECALC is similar to that for rhyolite, but it does not include a term for the heat of solution of the volatile components in the melt and thus assumes a negligible temperature dependence on volatile solubility. This should be valid for temperatures within 200° of the reference temperature (1200°C) and the assumption was used in the model of Dixon et al. (1995). Using the model of Dixon (1997), VOLATILECALC accounts for the strong control of melt SiO₂ concentration on the solubility of carbonate, and the lesser but important effect on the solubility of molecular H₂O. The following equations are used from Dixon (1997):

$$X_{\text{CO}_2}^m(P_0T_0) = 8.70 \times 10^{-6} - 1.70 \times 10^{-7}\text{SiO}_2 \text{ (in wt\%)}, \quad (2)$$

$$X_{\text{H}_2\text{O,mol}}^m(P_0T_0) = -3.04 \times 10^{-5} + 1.29 \times 10^{-6}\text{SiO}_2 \text{ (in wt\%)}. \quad (3)$$

As a result, the user can calculate melt–vapor equilibria for the range of basaltic compositions from tholeiite to nephelinite.

Vapor fugacities are calculated according to the modified Redlich–Kwong equations outlined by Holloway (1977) and modified by Flowers (1979). H₂O and CO₂ are assumed to mix ideally within the vapor phase.

4. Application of VOLATILECALC

4.1. Operation of the macros

The macros can be utilized from the *input* worksheet and by clicking on the relevant button. Five yellow buttons correspond to the SATURATION PRESSURE, DEGASSING, ISOBAR, ISOPLETH, and SOLUBILITY VERSUS PRESSURE macros for rhyolitic–melt compositions. Five orange buttons correspond to the same macros for basaltic–melt compositions. When running basalt–vapor calculations, VOLATILECALC requires the user to input a silica concentration (default = 49 wt%). A gray button allows independent calculations of H₂O and CO₂ fugacities as functions of temperature and pressure (temperature > 450°C and pressure > 100 bar).

Results are tabulated in the *output* worksheet. After the calculations are completed for the isobar, isopleth and degassing macros, the user is asked whether to plot the data. If desired, the VBA code then uses the Excel[®] charting tools to create a plot of dissolved H₂O versus CO₂. Results and plots within the output worksheet are deleted during subsequent runs of VOLATILECALC. In order to save the corresponding data and/or plot, they must be copied to a new worksheet within VOLATILECALC or another Excel[®] workbook.

4.2. Saturation pressures

The SATURATION PRESSURE macro calculates the pressure at which a silicate melt of known dissolved H₂O and CO₂ concentrations would be saturated with a vapor phase. At lower pressure, the melt would be vapor-supersaturated. At higher pressure, the melt would be vapor-undersaturated and no vapor would exsolve. The SATURATION PRESSURE macro also calculates the composition of the vapor in equilibrium with that melt.

Required input: wt% H₂O in the melt and ppm CO₂ by weight in the melt (both relative to melt + dissolved volatiles, but not including crystals), temperature in °C. *Output:* Pressure, H₂O speciation (H₂O_{mol} and OH⁻) and vapor composition (in mol% H₂O and CO₂).

4.3. Isobaric calculations

The ISOBARS macro calculates the locus of all melt compositions in equilibrium with CO₂-H₂O vapor for a given temperature and pressure (Fig. 1a). Each point on the curve yields a different melt composition (in terms of dissolved volatiles) and a different corresponding vapor. Such a curve is useful for modeling isobaric processes (e.g., crystallization) or simply to demarcate isobaric conditions for comparison with polybaric degassing paths.

Required input: Pressure in bars, temperature in °C, number of points desired along the isobar. *Output:* wt% H₂O dissolved in the melt, ppm CO₂ dissolved in the melt, melt H₂O speciation (H₂O_{mol} and OH⁻) and vapor composition (in mol% H₂O and CO₂).

4.4. Isopleth calculations

The ISOPLETH macro provides a curve for all melt compositions in equilibrium with a fixed vapor composition at a set temperature (Fig. 1b). The polybaric curve displays the varying melt compositions in equilibrium with a vapor of fixed composition. Such conditions are probably not realistic in nature, but isoplethic contours on saturation plots (Fig. 1) are useful for interpretive purposes.

Required input: Temperature in °C, vapor composition in mol% H₂O, amount to increment CO₂ (in ppm by weight: default = 50), number of points along the isopleth (default = 25)

Output: wt% H₂O dissolved in melt, ppm CO₂ dissolved in melt, H₂O speciation (H₂O_{mol} and OH⁻) and pressure for each point along the curve.

4.5. Degassing path

The DEGASSING PATH macro calculates the series of compositions (both melt and vapor) that a magma would follow during depressurization (Fig. 1c). It can calculate one of two options: *Open-system degassing*—the magma is depressurized along a series of steps. At each step, the melt composition and vapor compositions are re-calculated until they are in equilibrium with the vapor exsolved during that step; *Closed-system degassing*—the magma is depressurized along a series of steps. At each step, the melt composition and vapor compositions are re-calculated until they are in equilibrium with the total vapor exsolved from the melt along all previous steps. Closed-system runs allow the user to specify the

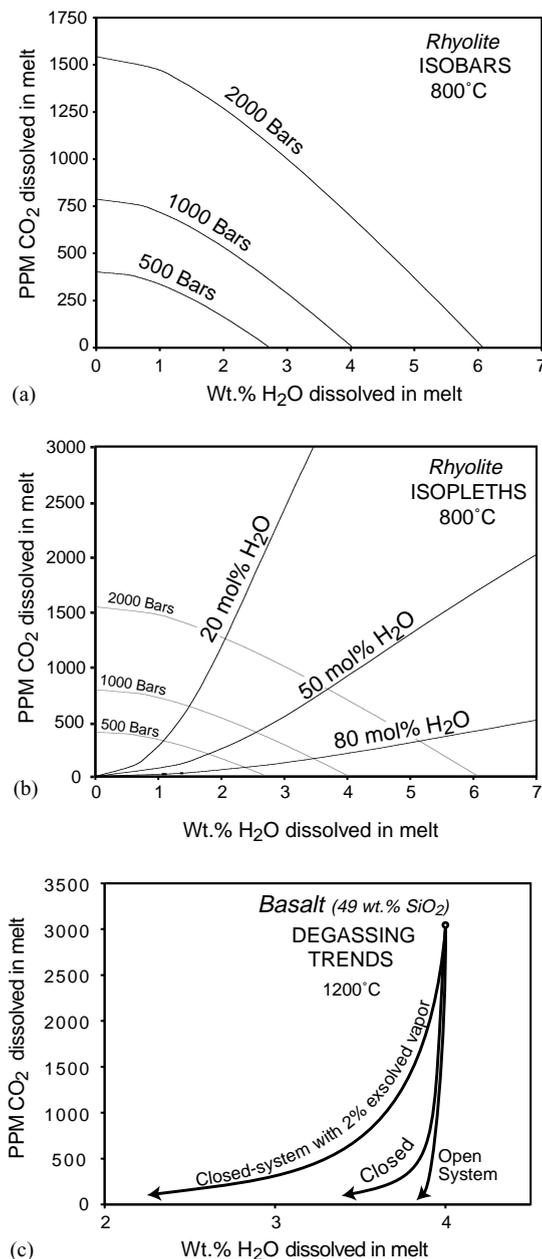


Fig. 1. Examples of output from VOLATILECALC. (a) Isobars represent locus of values for dissolved H₂O and CO₂ in rhyolitic melt in equilibrium with H₂O-CO₂ vapor at 800°C and selected pressures. (b) Similarly, isopleths represent locus of rhyolitic melt compositions in equilibrium with the given vapor compositions (20, 50 and 80 mol% H₂O shown here) at 800°C. Overlaid in gray are isobars from Fig. 1a. (c) Degassing trends are shown for 1200°C and demonstrate paths taken by basaltic (49wt% SiO₂) melt with 4wt% H₂O and 3000ppm CO₂ under open- and closed-system conditions. One path demonstrates closed-system trend where melt ascends with 2wt% exsolved vapor present at initial pressure (relative to total system of melt plus vapor).

initial presence of exsolved vapor that is in equilibrium with the melt composition given as input. For example, if input was provided for 3 wt% dissolved H₂O and 1000 ppm dissolved CO₂ at 800°C, VOLATILECALC would determine that the melt would be vapor saturated at ~2000 bar in equilibrium with a vapor phase containing ~37 mol% H₂O. The melt could be equilibrating with a trifling amount of vapor or an abundance. The closed-system degassing path of this melt would differ, depending on the amount of vapor present at this initial pressure. By varying the amount of exsolved vapor, the user can model the buffering capacity of exsolved vapor on the dissolved volatiles remaining within an ascending magma. After initial input, VOLATILECALC determines the initial pressure and vapor composition, and then queries the user on whether to calculate a closed- or open-system path.

Required input: wt% H₂O in the melt and ppm CO₂ in the melt as above, temperature in °C, open- or closed-system degassing (if closed: wt% exsolved vapor is equal to 100 multiplied by mass fraction of exsolved vapor relative to melt + dissolved volatiles + exsolved vapor), number of steps along degassing path (default = 25).

Output: wt% H₂O dissolved in melt, ppm CO₂ dissolved in melt, H₂O speciation (H₂O_{mol} and OH⁻), vapor composition (in mol% H₂O and CO₂) and pressure at each step along the path.

4.6. Solubility versus pressure calculations

The SOLUBILITY VERSUS PRESSURE macro demonstrates the effect of pressure on the solubility of pure end member H₂O or CO₂ in silicate melt (Fig. 2).

Required input: H₂O or CO₂ (enter 1 or 2), temperature in °C, amount to increment pressure (default is 200 bar)

Output: wt% H₂O dissolved in melt, ppm CO₂ dissolved in melt, H₂O speciation (H₂O_{mol} and OH⁻) and pressure for each point along the curve.

4.7. Vapor fugacities

This macro calculates the fugacity of H₂O and CO₂ vapor for a given temperature and pressure, based on a modified Redlich–Kwong equation of state by Holloway (1977) as modified by Flowers (1979). Melt composition is irrelevant. This macro is not recommended for temperatures below about 450°C and pressures below 200 bar.

Required input: Pressure in bars, temperature in °C

Output: The fugacity (in bars) of end member CO₂ and H₂O vapors.

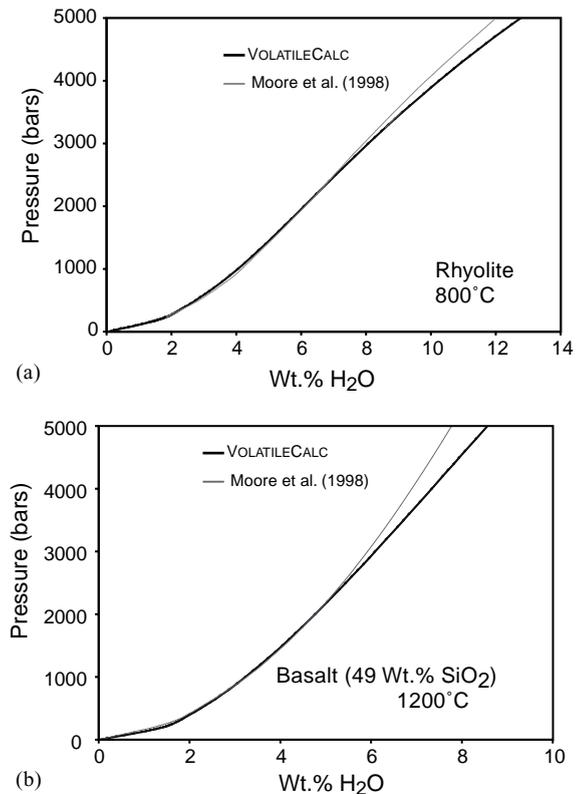


Fig. 2. H₂O solubility as function of pressure as calculated by VOLATILECALC, compared with model of Moore et al. (1998). (a) Comparison of rhyolite SOLUBILITY VERSUS PRESSURE macro in VOLATILECALC at 800°C as compared with model of Moore et al. (1998) using composition of rhyolite “CAM-73” listed in that paper. (b) Comparison of basalt (SiO₂ = 49 wt%) SOLUBILITY VERSUS PRESSURE macro in VOLATILECALC at 1200°C as compared with model of Moore et al. (1998) using composition of “Kilauea Tholeiite” listed in Table 1 of Dixon (1997).

5. Recommendations for use

VOLATILECALC is designed to model volatile solubility relationships for rhyolitic and basaltic melt compositions. The code may not apply to strongly peralkaline or peraluminous rhyolites. However, because many andesites and dacites contain rhyolitic interstitial melt, VOLATILECALC may also be applicable to these intermediate compositions. The basalt algorithms can be used for all basalt compositions that fall between the continuum tholeiite to nephelinite covered by Dixon (1997), which includes alkali olivine basalt and basanite. It is anticipated that results for a basalt with 49 wt% SiO₂ would be generally applicable for other basaltic rocks with <52 wt% SiO₂. For example, the model of

Moore et al. (1998), estimates the solubility of H_2O to be 3.26 wt% for a tholeiitic basalt at 1 kbar and 1200°C (sample 1 with 49.1 wt% SiO_2 , from Dixon, 1997). The same model estimates a solubility of 3.11 wt% H_2O at the same conditions for a high-Al, arc basalt with 51.4 wt% SiO_2 from Fuego, Guatemala (glass composition 8-1 from Sisson and Layne, 1993). Nor would the solubility for CO_2 be expected to change substantially over this compositional range (King, 1999).

VOLATILECALC accepts input values of H_2O < 11 wt%, CO_2 < 10,000 ppm by weight, and temperatures between 600°C and 1500°C. The isobar macro accepts values < 5000 bar. Though VOLATILECALC will allow input of dissolved H_2O and CO_2 concentrations that correspond to saturation pressures greater than 5000 bar, the user is alerted that calculated pressures may not be highly accurate.

As noted above, other solubility models for rhyolites and basalts exist (Moore et al., 1998; Papale, 1999). The results obtained with VOLATILECALC, even below 5000 bar, may differ significantly from these other models, but will most typically be within 10% relative for pressure calculations. Because the basalt macros are based on the work of Dixon et al. (1995) and Dixon (1997), VOLATILECALC will exactly match the results of the solubility model presented therein. As shown in Fig. 2, agreement between VOLATILECALC and the model of Moore et al. (1998) is excellent for rhyolite and basaltic compositions, especially at pressures below about 3000 bar.

6. Comparison with experimental data

In Fig. 3a, an isobar calculated by VOLATILECALC is compared with the experiments from Blank et al. (1993), where rhyolitic melt was equilibrated with vapors of varying H_2O/CO_2 at 750 bar and 850°C. The correspondence between experimental data and the calculated isobar is close. Fig. 2b documents the ability of VOLATILECALC to model the experimental data from Dixon et al. (1995) and Hamilton et al. (1964) for basaltic (non-alkalic) melt compositions. Here, the dissolved volatile concentrations of experimental run products were input into VOLATILECALC to predict the equilibration pressure. The diagonal line would indicate an exact correspondence between the pressures calculated and the actual experimental pressure.

Fig. 4 displays data from a variety of experimental investigations, primarily for the system rhyolite- H_2O . Again, VOLATILECALC estimates equilibration pressures with input of the measured dissolved H_2O and CO_2 concentrations in the experimental run products. At pressures above 2000 bar, there is considerable disagreement in the published literature as to the solubility of

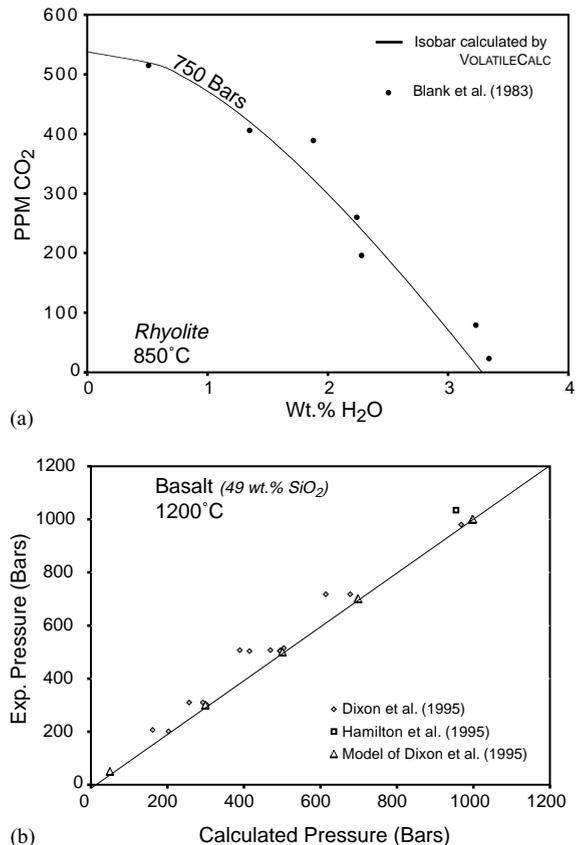


Fig. 3. Comparison of output from VOLATILECALC with experimental data on H_2O - CO_2 -silicate-melt system. (a) Calculated 750-bar isobar at 850°C for H_2O - CO_2 -rhyolite system as compared with compositions of silicate glasses produced under same conditions (Blank et al., 1993). (b) Comparison of pressure calculations by VOLATILECALC with pressures of equilibration for solubility experiments in H_2O -basalt system. Line represents perfect coincidence between calculated and experimental pressures. Small gray diamonds are compositions of experimental run products listed in table 1 of Dixon et al. (1995). Unfilled triangles are calculated with solubility model of Dixon et al. (1995) and are listed in table 5 of that paper. Because basalt macros in VOLATILECALC are based entirely on model of Dixon et al. (1995), perfect correspondence between that model and calculations by VOLATILECALC is expected.

H_2O , resulting in variations in the predicted experimental pressure (by VOLATILECALC). The parameters in VOLATILECALC are defined such that the macros calculate solubilities intermediate between the various studies. The solubility of H_2O in silicate melts at pressures > 3000 bar is not known with great precision, and users of this and other solubility models should exercise caution when interpreting their numerical results.

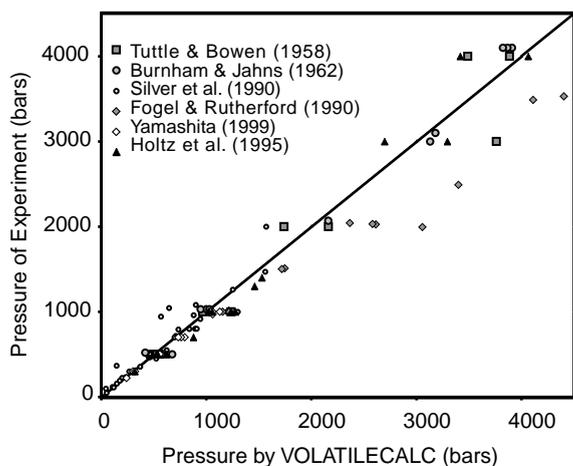


Fig. 4. Comparison of pressure calculations by VOLATILECALC with pressures of equilibration for solubility experiments in H₂O–rhyolite system. Diagonal line represents perfect coincidence between calculated and experimental pressures. Pressures calculated with VOLATILECALC use input from reported dissolved H₂O concentrations of run products, and run temperature. Fogel and Rutherford (1990) experiments were on H₂O–CO₂–rhyolite system; all other experiments were CO₂-free.

7. Summary

VOLATILECALC is a series of macros written in Visual Basic for Applications (VBA) for Microsoft[®] Excel that allows modeling of melt-volatile equilibrium within the basalt–H₂O–CO₂ or rhyolite–H₂O–CO₂ systems. It calculates open- and closed-system depressurization (degassing) paths, curves of constant pressure or vapor composition, and plots of solubility versus pressure within melt–H₂O–CO₂ systems. The code provides good agreement with pertinent experimental data.

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