# Volatile Solubility: Experimental & Theoretical Considerations

Paul Wallace University of Oregon

# Outline

• General considerations & multicomponent vapor saturation

• H<sub>2</sub>O, CO<sub>2</sub> and mixed H<sub>2</sub>O-CO<sub>2</sub> systems

• Chlorine & sulfur

• Modeling of volatile solubility

## Some key things to remember:

- Volatiles occur as dissolved species in silicate melts & also in a separate vapor phase <u>if</u> a melt is vapor saturated.
- In laboratory experiments, melts can be saturated with a nearly pure vapor phase (e.g., H<sub>2</sub>O saturated or CO<sub>2</sub> saturated).
- In natural systems, however, multiple volatile components are always present (H<sub>2</sub>O, CO<sub>2</sub>, S, CI, F, plus noble gases, volatile metals, alkalies, etc.).
- Referring to <u>natural</u> magmas as being H<sub>2</sub>O saturated or CO<sub>2</sub> saturated is, strictly speaking, incorrect because the vapor phase always contains other volatiles.
- At pressures of a few kbar and higher, the vapor phase is dense, more like a liquid than a gas. The words 'vapor', 'fluid', or 'gas' are used to describe this phase.

# H<sub>2</sub>O and CO<sub>2</sub> solubilities measured by experiment



- Solubilities are strongly pressure dependent
- Solubilities do not vary much with composition
- CO<sub>2</sub> has very low solubility compared to H<sub>2</sub>O (~30x lower)

Solubilities with more than 1 volatile component present



- In natural systems, melts are saturated with a multicomponent vapor phase
- H<sub>2</sub>O and CO<sub>2</sub> contribute the largest partial pressures, so people often focus on these when comparing pressure & volatile solubility

#### Experimental rhyolitic melts saturated with H<sub>2</sub>O-CO<sub>2</sub> vapor



Liu et al. (2005)

# **Chlorine Solubility**



- In this simplified experimental system, basaltic melts are either saturated with H<sub>2</sub>O-Cl vapor <u>or</u> molten NaCl with dissolved H<sub>2</sub>O (hydrosaline melt)
- Natural basaltic melts typically have <0.25 wt% Cl.

## Chlorine in rhyolitic melts

Note: x and y axes have been switched from previous figure



- Cl solubility is <u>much</u> lower in rhyolitic melts compared to basaltic melts
- Some rhyolitic melts (e.g., Augustine volcano) have high enough dissolved CI for the melt to be saturated with hydrosaline melt before eruption

## Sulfur Solubility

• Sulfur solubility depends on temperature, pressure, melt composition & oxygen fugacity.

Jugo et al. (2005)

**Basalt** 

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ind a ∋compressor s picture.

Trachyandesite

Sulfide saturated

Sulfate saturated

• Changes in  $f_{O_2}$  have a strong effect on solubility because S<sup>6+</sup> is much more soluble than S<sup>2-</sup>.

# Sulfur Solubility

- S solubility is more complicated because of multiple oxidation states
- Dissolved S occurs as either S<sup>2-</sup> or S<sup>6+</sup> (S<sup>4+</sup> is negligible)
- Solubility is limited by sat'n with pyrrhotite, Fe-S melt, anhydrite, or CaSO<sub>4</sub> melt
- S in vapor phase occurs primarily as H<sub>2</sub>S and SO<sub>2</sub>

QuickTime<sup>™</sup> and a TIFF (Uncompressed) decompressor are needed to see this picture. QuickTime<sup>™</sup> and a TIFF (Uncompressed) decompressor are needed to see this picture.

Minerals

**Basaltic glasses** 

From Jugo et al. (2005)

• Fortunately we can measure the oxidation state of S in minerals & glasses by measuring the wavelength of S K $\alpha$  radiation by electron microprobe

## Effect of oxygen fugacity on S speciation in silicate melts

From Jugo et al. (2005)



QuickTime<sup>™</sup> and a TIFF (Uncompressed) decompressor are needed to see this picture.

• A rapid change from mostly S<sup>2-</sup> to mostly S<sup>6+</sup> occurs over the oxygen fugacity range that is typical for arc magmas

#### Sulfur solubility – effects of temperature, pressure & composition



S solubility at low oxygen fugacity S<sup>2-</sup> is the dominant species

Solubility of both S<sup>2-</sup> and S<sup>6+</sup> are temperature dependent

# S solubility in intermediate to silicic melts



- Because of strong temperature dependence of S solubility, low temperature magmas like dacite and rhyolite have very low dissolved S.
- This led earlier workers to erroneously conclude that eruptions of such magma would release little SO<sub>2</sub> to Earth's atmosphere

# Pressure Dependence of Sulfide Solubility

QuickTime™ and a decompressor are needed to see this picture.

Mavrogenes & O'Neill (1999)

- Sulfide-saturated melts have a negative pressure dependence for dissolved S
- Most volatiles even sulfate show a positive dependence

QuickTime™ and a decompressor are needed to see this picture.

# Modeling the solubility of H<sub>2</sub>O-CO<sub>2</sub> in natural melts

Types of models:

- <u>Regular solution</u> calibrated for a single composition (e.g., Silver and Stolper, 1985)
- 2. Empirical
- <u>Compositionally dependent</u> (includes compositionally dependent regular solution model of Papale (1997, 1999) & Papale et al (2006)

I able 3. Volatile solubility models				
Reference	Melt Composition	P - MPa	T - °C	Model Type <sup>1</sup>
H <sub>2</sub> O solubility				
Behrens & Jantos, 2001	rhyolitic	0.1-200; 500	800	comp
Carroll & Blank, 1997	phonolitic	0.1-191	850	reg sol
Di Matteo et al. 2004	trachytic	20-200	850	comp
Dixon et al. 1995	basaltic	0.1-98	1200	reg sol
Liu et al. 2005	rhyolitic	0.1-500	700-1200	emp
Moore et al. 1998b	various	0.1-300	700-1200	comp
Papale, 1997	various	0.1-1000	>730	reg sol
Yamashita, 1999	rhyolitic	0.1-100	700-1200	reg sol
Zhang, 1999	rhyolitic	0.1-800	500-1350	
CO <sub>2</sub> solubility				
Dixon et al. 1995	basaltic	0.1-98	1200	reg sol
Dixon et al. 1997	alkali basalt	0.1-500	1200	comp
Papale, 1997	various	0.1-1000	>730	reg sol
Mixed volatile solubility				
Behrens et al. 2004 <sup>2</sup>	dacitic-rhyolitic	100-500	850-1250	reg sol
Liu et al. 2005	rhyolitic	0.1-500	700-1200	emp
Newman & Lowenstern, 2002	basalt, rhyolite			various
Papale, 1999	various	<1000	>730	comp reg sol
Papale et al. 2006	various			comp reg sol
Tamic et al. 2001 <sup>3</sup>	rhyolitic	75-500	800-1100	emp

<sup>1</sup>- Model types include: comp – compositional, accounts for compositional variation, but may include an ad hoc fit equation form; comp reg sol – compositional regular solution model; emp – empirical, generally an ad hoc form of fit equation; reg sol – regular solution model, no compositional dependence; various – uses many different models for its calculations.

<sup>2</sup> - CO<sub>2</sub> solubility for H<sub>2</sub>O-CO<sub>2</sub> bearing silicic compositions.

 $^{3}$  – H<sub>2</sub>O solubility for H<sub>2</sub>O–CO<sub>2</sub> bearing rhyolite.

 Warning: do not extrapolate models beyond their calibration range!

### Extrapolation beyond calibration range



 Note good fit of Moore model to data up to 200 MPa, and instability when

extrapolated above 300 MPa.

• Extrapolation can lead to significant error

Behrens & Jantos, (2001)

### Comparison of VolatileCalc & Papale models

Calculated vapor compositions & vapor saturation pressures for rhyolite (77 wt% SiO<sub>2</sub>) and dacite (66 wt% SiO<sub>2</sub>) versus experimental values

- Good agreement for both
  VolatileCalc and Papale model for rhyolite.
- Note failure of VolatileCalc to estimate the dacite fluid compositions and pressures (no compositional dependence), while Papale model matches data quite well.

Figures from Moore (2008)



#### Comparison of Papale model to basaltic experimental data



Model of Papale et al (2006)

 Best model currently available that can account for broad melt compositional variation over magmatic P-T range.

Figure from Moore (2008)

### Modeling of sulfur solubility in silicate melts

 For low to intermediate oxygen fugacities (<~NNO), where S<sup>2-</sup> is the main S species, modeling of solubility is generally based on:

FeO (melt) + 0.5  $S_2$  (gas) = FeS (liq or solid) + 0.5  $O_2$  (gas)

• For higher oxygen fugacities, where S<sup>6+</sup> dominates, solubility is based on:

 $SO_2$  (vapor) +  $O^{2-}$  (melt) + 0.5  $O_2$  (vapor) =  $SO_4^{2-}$  (melt)

 At present, the only model (empirical) calibrated for oxidizing conditions Scaillet & Pichavant (2005).

#### Predicted S solubility in sulfide-saturated rhyolitic melt

QuickTime<sup>™</sup> and a decompressor are needed to see this picture.

Moretti & Baker (2008)

## Comparison of sulfide solubility models & experiments

Wallace & Carmichael (1992)

Scaillet & Pichavant (2005)

QuickTime™ and a decompressor are needed to see this picture.

O'Neill & Mavrogenes (2002)

Moretti & Ottonello (2005)

Evans et al. (2008)

#### Key points to remember:

- Major volatile components are H<sub>2</sub>O, CO<sub>2</sub>, S, CI, and F
- Magmas are commonly vapor saturated, meaning there is a separate, multicomponent vapor phase consisting of H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, CI, F, noble gases, etc.
- Magmas can also be saturated with sulfide and/or sulfate phases (solids or liquids) Sulfur solubility is complex because of multiple valence states.
- In some cases, magma may be saturated with both H<sub>2</sub>O-CO<sub>2</sub>-Cl vapor and a separate hydrosaline brine phase (mainly consisting of NaCl-H<sub>2</sub>O)
- When using solubility models, be careful not to extrapolate outside the range of calibration. Also think carefully about behavior & effect of volatiles <u>not</u> included in the model.

# Thermodynamics of Multi-Component Vapor Saturation

• When the sum of the partial pressures of all dissolved volatiles in a silicate melt equals the confining pressure, the melt becomes saturated with a multicomponent vapor phase.

• For each component, *i*, in the vapor phase (H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, HCl, ...):

$$f_i = \phi_i X_i P_{Total}$$

where  $f_i$  = fugacity,  $\phi_i$  = fugacity coefficient,  $X_i$  = mole frac.

Because  $X_i P_{Total}$  = the partial pressure of *i*, then:

$$\sum_{i} \frac{f_i}{\phi_i} = P_{Total}$$

if the magma is vapor saturated.