



# Solubility of H<sub>2</sub>O and CO<sub>2</sub> in shoshonitic melts at 1250 °C and pressures from 50 to 400 MPa: Implications for Campi Flegrei magmatic systems

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## ABSTRACT

The solubility of H<sub>2</sub>O–CO<sub>2</sub>-bearing fluids in shoshonitic melts relevant to magmas of the Vulcanello peninsula and to mafic melts from magmas erupted at Campi Flegrei (Italy) was experimentally determined at pressures from 50 to 400 MPa and at temperature of 1250 °C. No quench crystals and less than 1 vol.% bubbles were observed in the rapid quenched glasses. H<sub>2</sub>O and CO<sub>2</sub> contents in the experimental glasses were determined via Karl–Fischer Titration (KFT) and FTIR spectroscopy. For the quantification of volatile concentrations by IR spectroscopy we have calibrated the absorption coefficients of water-related and carbon-related IR bands for the shoshonitic composition. The determined absorption coefficients are  $0.80 \pm 0.06 \text{ L mol}^{-1} \text{ cm}^{-1}$  for the band at  $\sim 4500 \text{ cm}^{-1}$  (OH groups) and  $1.02 \pm 0.03 \text{ L mol}^{-1} \text{ cm}^{-1}$  for the band at  $\sim 5200 \text{ cm}^{-1}$  (H<sub>2</sub>O molecules). CO<sub>2</sub> is bound in the shoshonitic glass as CO<sub>3</sub><sup>2-</sup> exclusively; its concentration was quantified by the peak height of the low wavenumber band of the doublet near  $1430 \text{ cm}^{-1}$  using the calibrated absorption coefficient of  $356 \pm 18 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

The H<sub>2</sub>O solubility in the shoshonitic melts is in the same range as observed for other natural aluminosilicate melts, i.e.  $5.12 \pm 0.07 \text{ wt.}\%$  at 200 MPa and  $7.92 \pm 0.07 \text{ wt.}\%$  H<sub>2</sub>O at 400 MPa. A non-linear variation of the H<sub>2</sub>O and CO<sub>2</sub> solubility in the melts with increasing mole fraction of H<sub>2</sub>O (and thus decreasing mole fraction of CO<sub>2</sub>) in the fluid was observed at each investigated pressure. At 1250 °C, the concentration of dissolved carbonate (expressed as CO<sub>2</sub> component) in melts coexisting with nearly pure CO<sub>2</sub> fluid increases from 307 to 2932 ppm ( $\pm 10\%$  relative) as the pressure increases from 50 to 400 MPa. The comparison of the dataset with available models predicting the H<sub>2</sub>O and CO<sub>2</sub> concentrations in silicate melts coexisting with H<sub>2</sub>O–CO<sub>2</sub>-bearing fluids shows that the effect of melt composition is not calibrated appropriately in the models.

The experimental data are used to re-evaluate the typical pressures of glass inclusions entrapment in phenocrysts from Minopoli2 eruption and the results indicate that the main magma chamber may have been located at a depth of  $\sim 4000 \text{ m}$ .

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## 1. Introduction

In the last two decades, it has been demonstrated that the knowledge on the solubility laws of H<sub>2</sub>O and CO<sub>2</sub> in silicate melts is crucial for understanding of many magmatic processes (e.g., saturation, exsolution, and degassing of volatiles, and magma crystallization) and, hence, it is required as an important quantitative basis for the interpretation of glass inclusion data (Kent, 2008 and reference therein). The maximum concentrations of C- and OH-bearing species that can be incorporated in aluminosilicate melts have been investigated in a range of melt compositions, temperatures, and pressures relevant to natural conditions (e.g., Blank et al., 1993; Blank and Brooker, 1994 and

references therein; Holloway and Blank, 1994; Dixon et al., 1995; Jakobsson, 1997; Tamic et al., 2001; King and Holloway, 2002; King et al., 2002; Behrens et al., 2004a, 2009; Di Matteo et al., 2004; Mysen and Cody, 2004; Botcharnikov et al., 2005a; Botcharnikov et al., 2006; Shishkina et al., 2010). Based on the experimental datasets, several models have been proposed as tools to reconstruct magma degassing conditions (e.g., Dixon et al., 1995; Papale and Polacci, 1999; Tamic et al., 2001; Newman and Lowenstern, 2002; Behrens et al., 2004a; Liu et al., 2005; Papale et al., 2006). However, except in the attempts of Newman and Lowenstern (2002) and Papale et al. (2006), the models are only valid for one or a few specific melt compositions. Although H<sub>2</sub>O and CO<sub>2</sub> solubility in MOR-basaltic and rhyolitic compositions do not differ very strongly, recent studies showed that significant variations can be observed if other natural compositions are taken into account (e.g., high CO<sub>2</sub> solubility in calc-alkaline basalt composition, Moore, 2008; high CO<sub>2</sub> solubility in phonotephrite melts, Behrens et al., 2009). Furthermore, most published datasets are restricted to pressures <200 MPa and are only useful to model shallow depths of magma degassing. The volatile

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solubility extrapolations up to pressure of 500 MPa in the recent model Papale et al. (2006) are only weakly supported by experiments, making accurate estimates of magma degassing conditions impossible. Clearly, the main problem to predict H<sub>2</sub>O and CO<sub>2</sub> solubility for a wide variety of melt compositions is the determination of the compositional parameters governing the incorporation of OH- and C-bearing species. This can only be attained if a large experimental dataset on various compositions is available. In particular, the role of alkalis and alkaline-earth elements needs to be understood for mafic melt compositions. Here we report new experimental data on the solubility of C–O–H volatiles in shoshonitic melts (which represent alkali-rich magmas) at 1250 °C and at 50 to 400 MPa.

## 2. Experimental and analytical methods

### 2.1. Starting materials

The starting material used in this work is a shoshonite from Vulcanello platform lava flow (Aeolian Island, South Italy) and is identical in composition to the material used by Vetere et al. (2007) to study the viscosity of shoshonitic melts. About 100 g of crushed bulk rock was melted in a Pt crucible in air at temperature of 1600 °C for 4 h. After quenching on a metal plate, the obtained glass was crushed and melted again in the same furnace at the same conditions to improve homogeneity. The composition of several glass fragments was analyzed by electron microprobe CAMECA SX100 (Table 1). Measurement conditions were: defocused beam of 15 μm diameter, accelerating voltage of 15 kV and a beam current of 4 nA. The glass was crushed in a mortar, sieved to the grain sizes of <100 μm and 100–200 μm and finally the two fractions were mixed together in a volume ratio 1:1.

### 2.2. Experimental strategy

In the solubility experiments, 0 to 7.5 μl of deionized water, 0 to 14.7 mg of Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and ~50 mg of glass powder were loaded in 20 mm long (inner diameter of 2.6 mm) Au<sub>80</sub>Pd<sub>20</sub> capsules. The capsules were filled using the following procedure: (1) after charging the capsule with the desired amounts of H<sub>2</sub>O and glass powder, the

capsule was fixed in a cylindrical holder fitted to the size of the capsule; (2) for further compaction the charge was compressed with a steel piston; (3) Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was added as a source for CO<sub>2</sub> (silver oxalate decomposes during heating and generates carbon dioxide); (4) the capsule was tightly squeezed on top and rolled up in a wet tissue wrapped around the capsule and frozen by placing into a bath of liquid nitrogen; and finally, (5) the upper end of the capsule was welded shut with a conventional graphite-arc welder. The amount of charged water and CO<sub>2</sub> was determined by the weight-gain of the capsule. In all our experiments the amounts of H<sub>2</sub>O and/or CO<sub>2</sub> loaded into the capsules were sufficient to ensure fluid-saturation at the investigated conditions. Four to five capsules were run simultaneously in internally heated pressure vessels (IHPV) at 1250 °C and pressures ranging from 50 to 400 MPa. The experimental duration was in the range from 16 to 48 h (Table 2).

We performed an additional set of experiments to synthesize standards necessary for the calibration of the IR molar absorption coefficients. Runs for the synthesis of standards were prepared by loading 10–15 μl of deionized water, 5 to 15 mg of silver oxalate, and 500 to 600 mg of glass powder in Au<sub>80</sub>Pd<sub>20</sub> capsules (35 mm long and 5 mm in diameter). In order to achieve homogenous initial distribution the compounds were filled in several steps into the capsules. Capsules were checked for leakage by annealing at 110 °C for at least 1 h and by subsequent weighing. Syntheses were performed at 1250 °C and 500 MPa in an IHPV for about 24 h.

For both sets of experiments, the temperature was measured by four unshielded S-type (Pt–Pt<sub>90</sub>Rh<sub>10</sub>) thermocouples. Precision of temperature determination is ± 10 °C, accounting for the temperature gradient along the sample and for fluctuation of temperature during the experiments. The pressure was monitored by calibrated digital manometer with an uncertainty of about 1 MPa. The variation of pressure during the experiments was ≤ 5 MPa. The IHPV was pressurized with argon and the experiments were performed at the intrinsic hydrogen fugacity of the vessel. The oxygen fugacity within the capsules was controlled by the fugacity of H<sub>2</sub> and H<sub>2</sub>O through the equilibrium reaction H<sub>2</sub> + ½O<sub>2</sub> ↔ H<sub>2</sub>O. Under intrinsic conditions, the oxygen fugacity within capsules containing H<sub>2</sub>O-saturated melts (pure H<sub>2</sub>O fluid) was found to be close to the *f*(O<sub>2</sub>) of the NNO buffer + 2.6 log units (Schuessler et al., 2008). In order to avoid any non-equilibrium quench effects, the samples were rapidly quenched at the end of the run by dropping the capsules down into the cold part of the vessel (Berndt et al., 2002). The cooling rate has been estimated to be about 150 °C/s (Benne and Behrens, 2003). This quench rate was sufficient to completely avoid crystallization of water-rich melts or degassing during cooling (see below).

### 2.3. Determination of fluid composition by weight-loss method

The weight-loss method was used to determine the mole fraction of CO<sub>2</sub> (*X*<sub>CO<sub>2</sub></sub><sup>f</sup>) and H<sub>2</sub>O (*X*<sub>H<sub>2</sub>O</sub><sup>f</sup>) in the fluid phase equilibrated with the silicate melt (Table 2). After the runs, the capsules were weighed, frozen by placing them into a bath of liquid nitrogen, and then punctured with a needle. After warming to room temperature, capsules were weighed again to determine the mass of CO<sub>2</sub> in the fluid, then placed in a drying oven for 3–5 min and finally weighed to measure the mass of lost H<sub>2</sub>O. The capsule weight was checked periodically until the weight remained constant. The temperature of the drying oven was 110 °C, except for samples with expected water concentration exceeding 6 wt.%. For these samples, the oven temperature was set around 60 °C.

As main source of errors of mole fractions of H<sub>2</sub>O and CO<sub>2</sub> in the fluid we considered the uncertainty in the weighing of the capsules before and after piercing. Additional uncertainty induced by atmospheric nitrogen was taken into account (0.7 mol.% for H<sub>2</sub>O and 2.0 mol.% for CO<sub>2</sub>, according to Tamic et al. (2001)). The determined molar fractions of H<sub>2</sub>O and CO<sub>2</sub> are reported in Table 2.

**Table 1**  
Electron microprobe analyses and water content of the starting material (wt.%).

	Shoshonite
n	100
SiO <sub>2</sub>	53.47 (0.29)
TiO <sub>2</sub>	0.71 (0.03)
Al <sub>2</sub> O <sub>3</sub>	15.48 (0.20)
FeO <sub>tot</sub> <sup>a)</sup>	8.39 (0.33)
MnO	0.10 (0.10)
MgO	4.88 (0.17)
CaO	8.51 (0.25)
Na <sub>2</sub> O	3.66 (0.15)
K <sub>2</sub> O	4.72 (0.16)
P <sub>2</sub> O <sub>5</sub>	–
Total	99.97 (0.63)
Fe <sup>2+</sup> /Fe <sub>tot</sub> <sup>b)</sup>	0.40
H <sub>2</sub> O (IR) <sup>c)</sup>	0.029

Notes. The starting material identical in composition to that used by Vetere et al. (2007).

Numbers in parentheses correspond to 1 σ standard deviation.

<sup>a)</sup> Total iron is given as FeO.

<sup>b)</sup> Fe<sup>2+</sup>/Fe<sub>tot</sub> was measured using the modified Wilson method (Vetere et al., 2008; Schuessler et al., 2008).

<sup>c)</sup> H<sub>2</sub>O content was measured by IR spectroscopy using the peak height of the absorption band at 3550 cm<sup>-1</sup>.

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