# Compositional and pressure effects on the solubility of $H_2O$ and $CO_2$ in mafic melts

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## ARTICLE INFO

## ABSTRACT

The effect of the anhydrous composition on the solubilities of $H_2O$ and $CO_2$ in mafic melts varying from MORB to nephelinite was investigated experimentally between 50 and 500 MPa at 1200 to 1250 °C. In all compositions, $CO_2$ is only present as carbonate species in the quenched glasses. The concentrations of dissolved $H_2O$ and $CO_2$ have been analyzed by KFT (Karl–Fischer titration) and FTIR (Fourier-transform infrared spectroscopy). The Mid-Infrared (MIR) absorption coefficients for the $H_2O$ band at 3500 $cm^{-1}$ are identical within error for all investigated melt compositions and equal to $59.2 \pm 4$ L/(mol∗cm). The absorption coefficients for the carbonate bands vary in the range $306 \pm 32$ to $360 \pm 24$ L/(mol∗cm) for the 1430 $cm^{-1}$ band and in the range $349 \pm 25$ to $394 \pm 27$ L/(mol∗cm) for the 1520 $cm^{-1}$ band. However, a simple correlation with the melt composition could not be determined.

Water solubility in mafic to intermediate melts increases slightly with the total alkali content and the effect of composition is more pronounced at higher pressures. At 500 MPa, the solubility of $H_2O$ in melts coexisting with nearly pure $H_2O$ fluids varies from 8.8 to 9.5 wt.% $H_2O$. A strong effect of melt composition on the solubility of $CO_2$ is observed at all investigated pressures. For instance, at 500 MPa, mafic melts coexisting with nearly pure $CO_2$ fluids can dissolve from around 0.32 to more than 1.30 wt.% $CO_2$ as melt composition changes from tholeiite to nephelinite. The compositional effect on the solubility of $CO_2$ in melts coexisting with pure $CO_2$ fluid is best described by non-linear (exponential) correlations with compositional parameters such as the parameter $\Pi$ proposed by Dixon (1997; American Mineralogist, 82: 368–378) or structural parameters (e.g., nonbridging oxygen per tetrahedrally coordinated cation). The obtained relationships are used to propose empirically derived equations of the form $\ln(CO_2) = 1.150 \cdot \ln P + 6.71 \cdot \Pi^* - 1.345$, where $CO_2$ is the solubility of $CO_2$ in silicate melts in wt.% (at 1200 to 1250 °C), $P$ is pressure in MPa and $\Pi^*$ is a compositional parameter ($\Pi^* = Ca^{2+} + 0.8K^+ + 0.7Na^+ + 0.4Mg^{2+} + 0.4Fe^{2+}) / (Si^{4+} + Al^{3+})$ with cations expressed as cation fractions in melt.

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## 1. Introduction

The efficiency of volatile transport from depths of magma generation to shallow crustal levels is controlled by several factors and in particular by the composition of silicate melts and their ability to incorporate volatile components. Early experimental studies showed that melt composition can significantly affect solubility of $CO_2$ in mafic melts, in contrast to a weak effect on $H_2O$ solubility (e.g., Mysen, 1988; Blank and Brooker, 1994; Holloway and Blank, 1994). It was found that the solubility of $CO_2$ is positively correlated with the degree of melt depolymerization (e.g. Mysen et al., 1975; Mysen, 1976) and Brooker et al. (2001a,b) proposed

that $CO_2$ solubility can be described by a non-linear function of NBO/T (nonbridging oxygen per tetrahedrally coordinated cation).

The most commonly accepted dissolution mechanism in mafic melts is based on the reaction of $CO_2$ with non-bridging oxygens (or reaction oxygens) to form carbonate ion in the melt structure (e.g. Spera and Bergman, 1980; Fine and Stolper, 1985; Stolper and Holloway, 1988; Blank and Brooker, 1994; Kubicki and Stolper, 1995). However, a parameter such as NBO/T only cannot explain the solubility behavior of $CO_2$ and other compositional effects need to be taken into account. For example, Holloway et al. (1976) showed that in melts with the same degree of polymerization $CO_2$ solubility decreases along the CaO–MgO joint. Brooker et al. (2001a,b) reported that melt compositions with high MgO contents dissolve much less $CO_2$ than other melts with lower MgO contents but the same NBO/T value. Brooker et al. (2001a) supposed that some proportion of $Mg^{2+}$ cations can play the role of network-formers, leading to the decrease in the amount of non-bridging oxygens in the melt

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and therefore reducing $CO_2$ solubility. Moore (2008) reported a strong positive correlation of $CO_2$ solubility with CaO content in basaltic melts. Behrens et al. (2009) found that $K_2O$-rich phonotephritic melts dissolve significantly more $CO_2$ than $K_2O$-poor tholeiitic basalts and suggested that K can stabilize carbonate-bearing species in the silicate melt. Recently, Lesne et al. (2011b) and Vetere et al. (2014) also reported positive but complex effects of alkalis on the concentrations of $CO_2$ dissolved in mafic melts.

Compared to $CO_2$ (on a wt.% basis), there is no strong effect of melt composition on $H_2O$ solubility in mafic systems and in particular there is no large difference between $H_2O$ solubilities in mafic, intermediate and silicic melts at given pressure and temperature conditions. However, despite the large experimental database on $H_2O$ and $CO_2$ solubilities produced up to now (see reviews of Moore, 2008; Ni and Keppler, 2013), a successful systematic analysis of the compositional effect of mafic melts on $H_2O$ and $CO_2$ solubilities coexisting with mixed $H_2O$–$CO_2$ volatiles is still missing. Existing numerical models use different compositional parameters for calculation of $CO_2$-solubilities in silicate melts. VolatileCalc (Newman and Lowenstern, 2002) employs a linear correlation of $CO_2$ with $SiO_2$ and it is assumed that there is no effect of one dissolved component on the solubility of the other. The models of Papale et al. (2006) and Duan (2014) account for wide compositional variations from basalts to rhyolites and for more specific compositions to calculate $H_2O$–$CO_2$ solubility. However, the prediction ability of both models is limited by the available experimental data used for calibration. Iacono-Marziano et al. (2012) proposed a new semi-empirical model of $H_2O$–$CO_2$ solubility specifically focused on mafic melts as it was calibrated on a selected database consisting of 44 different mafic compositions. The model predicts a positive correlation of $CO_2$ and $H_2O$ solubilities with NBO/O (non-bridging oxygen per oxygen in the melt) and the authors mentioned that there are some limitations because of the lack of data to calibrate for example the role of alkalis or $Fe^{3+}/Fe^{2+}$ ratio.

To better understand the importance of melt composition, we present new experimental data on the solubility of mixed $H_2O$–$CO_2$ fluids in eight mafic melts with a wide compositional range including silica-undersaturated high-MgO nephelinite and basanite, alkali basalts, ferrobasalt as well as MORB and Al-rich $K_2O$-poor island-arc basalt. The new data are used to test the limitations of the models proposed so far and, together with the results from previous experimental studies, to work out the effect of melt composition on the solubility of $H_2O$ and particularly of $CO_2$ at pressures up to 500 MPa.

## 2. Experimental and analytical methods

### 2.1. Starting compositions

Eight compositions representative of different mafic magmas have been used in this study and are listed in Table 1. The investigated silicate melts represent a relatively wide range of mafic compositions with a strong variation of the alkalis, CaO, MgO and $SiO_2$ concentrations (Fig. 1). For all compositions, the starting material for the experiments was composed of a bubble-free dry glass synthesized after melting at 1 atm.

Among the eight compositions, four natural alkali-rich mafic compositions were sampled in two active quarries in Silesia (SW Poland) which belong to the Tertiary Central European Volcanic Province, extending from the Eifel Mountains in Germany through the Czech Republic to Lower Silesia: B2518 and B2507 are alkali basalts (from Męcinka quarry), A2549 is a basanite (from Rutki-Ligota) and E2624 is a nephelinite (from Gracze). All these rocks consist of olivine and clinopyroxene phenocrysts dispersed in a groundmass of olivine, clinopyroxene, plagioclase, spinel, nepheline, apatite and glass.

These four natural samples were powdered, melted for 2 h in a platinum crucible in an oven at 1600 °C and 1 atm (air conditions), and rapidly quenched to a glass by placing the crucible into a water bath. The quenched glass was crushed in a rotary mortar and remelted for 2 h to improve the homogeneity of the batch. Finally, the glass was crushed to a grain size of <200 µm.

The other mafic compositions are composed of a ferrobasalt (SC1), two alkali basalts (OB93 and Etna), a typical Mid-Oceanic Ridge basalt (169oxi). The composition SC1 is a synthetic analog of a ferrobasalt from Skaergaard intrusion and phase relations for this composition were investigated by Toplis and Carroll (1995) and Botcharnikov et al. (2005, 2008). The alkali basalt OB93 is a natural sample from Mont Crozier on the Courbet Peninsula of the Kerguelen Island. Phase relations for this sample were investigated by Freise et al. (2009). The compositions SC1 and OB93 were already used in the study on volatile solubility by Botcharnikov et al. (2005) who provided a description of the preparation of the starting material. The alkali basalt from Etna volcano is a natural trachybasalt taken at Rifugio Sapienza from a lava flow of the 2001 eruption (S-side of Mt. Etna, 1892 m above sea level). The sample was melted and prepared for experiments in a similar way as described above for the other samples (see also Stelling et al., 2008). The composition 169oxi is a fused glass of a natural MORB whole rock powder left

**Table 1**
Starting compositions and molar absorption coefficients for FTIR bands.

| Composition | Alkali basalt | Alkali basalt | Basanite | Nephelinite | Ferro-basalt | Alkali basalt | Alkali basalt | MORB | Island-arc tholeiite |
|---|---|---|---|---|---|---|---|---|---|
| Sample | B2507 | B2518 | A2549 | E2624 | SC1 | OB93 | Etna | 169oxi | N72 |
| $SiO_2$ | 47.30 | 46.21 | 43.64 | 42.32 | 48.88 | 49.03 | 48.34 | 50.69 | 50.17 |
| $TiO_2$ | 2.35 | 2.70 | 2.64 | 2.26 | 2.89 | 2.76 | 1.77 | 1.46 | 0.92 |
| $Al_2O_3$ | 14.17 | 14.65 | 12.65 | 11.80 | 14.77 | 16.20 | 16.40 | 16.95 | 18.28 |
| FeO-t | 10.82 | 11.74 | 11.54 | 11.00 | 13.05 | 11.90 | 10.48 | 8.51 | 9.37 |
| MnO | 0.17 | 0.16 | 0.19 | 0.19 | 0.00 | 0.17 | 0.20 | 0.13 | 0.17 |
| MgO | 10.36 | 8.71 | 12.07 | 13.31 | 6.47 | 5.88 | 5.97 | 7.48 | 7.00 |
| CaO | 9.94 | 10.63 | 11.82 | 13.23 | 10.99 | 9.80 | 10.83 | 12.03 | 11.37 |
| $Na_2O$ | 3.52 | 3.51 | 3.68 | 3.72 | 2.63 | 3.13 | 3.46 | 2.52 | 2.33 |
| $K_2O$ | 0.83 | 1.06 | 1.01 | 0.96 | 0.30 | 1.12 | 1.96 | 0.22 | 0.23 |
| $P_2O_5$ | 0.47 | 0.56 | 0.70 | 1.13 | 0.00 | 0.00 | 0.59 | 0.00 | 0.15 |
| $Cr_2O_3$ | 0.06 | 0.06 | 0.06 | 0.08 | n.a. | n.a. | n.a. | n.a. | n.a. |
| Total | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Density (g/L) | 2828 | 2911 | 2911 | 2889 | n.d. | n.d. | n.d. | n.d. | 2757 |
| $\Pi$ (Dixon, 1997) | 1.03 | 1.13 | 2.05 | 2.56 | 0.49 | 0.28 | 0.68 | 0.20 | −0.04 |
| $\Pi^*$ | 0.41 | 0.42 | 0.51 | 0.57 | 0.36 | 0.34 | 0.37 | 0.34 | 0.32 |

Every starting composition represents an average of about 5 to 10 electron microprobe analyses of glasses normalized to 100%. N72 — from Shishkina et al. (2010). Major elements in wt.%.
n.a. — was not analyzed, n.d. — was not determined.
$\Pi$ — compositional factor derived by Dixon (1997).
$\Pi = -6.5 * (Si^{4+} + Al^{3+}) + 20.17 * (Ca^{2+} + 0.8K^+ + 0.7Na^+ + 0.4Mg^{2+} + 0.4Fe^{2+})$.
$\Pi^*$ — compositional factor calculated as $(Ca^{2+} + 0.8K^+ + 0.7Na^+ + 0.4Mg^{2+} + 0.4Fe^{2+}) / (Si^{4+} + Al^{3+})$.