CO₂ Solubility and Solubility Mechanisms in Silicate Melts at High Pressures

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Abstract. CO₂ solubility has a slight negative temperature dependence in olivine melilitite at 30 kb with 9% CO₂ dissolved at 1,450 °C, 8.5% at 1,550 °C and 8.3% at 1,650 °C. CO₂ is dissolved as the carbonate molecule (CO₃⁻) only. Feldspar melts (albite-anorthite) dissolve much less CO₂ at 30 kb (around 2%) with a slight increase with increasing anorthite content. A CO₂ absorption peak in infrared spectra of albite-rich glasses disappears in favour of the CO₃⁻ peak with increasing anorthite content. It is inferred that CO₂ was present as CO₃⁻ in albite-rich melts also, but reverts to CO₂ during quenching because of bonding differences related to Ca²⁺ and Na⁺ in the melts.

Introduction

An important role for CO₂ in the upper mantle has been postulated on the basis of experiments by several groups [1–10]. It has been established that CO₂ solubility in silicate melts has a positive pressure dependence [4, 5] and that solubility increases with increasing basicity of the melt [5, 6]. However, the solubility mechanisms [5] of CO₂ in silicate melt and the temperature dependence of CO₂ solubility remain matters of speculation or disagreement. The present paper is concerned with these topics.

Experimental Methods

Experimental procedures are described by Brey and Green [3, 4]. Runs with olivine melilitite from Laughing Jack Marsh (3) ¹ + Ag₂C₂O₄ were carried out in single Pt-capsules for 7 min with procedures in which great care was taken to keep the surrounding furnace assemblage as dry as possible to avoid reduction of CO₂ to graphite (inferred to be caused by the high innate hydrogen fugacity

¹ The correct CIPW norm for this olivine melilitite is that published by Brey & Green (3, p. 95; cf. 5, p. 229)
Table 1. Accuracy of gaschromatographic determination of CO₂

<table>
<thead>
<tr>
<th>Mechanical mix of</th>
<th>CO₂ determined (%)</th>
<th>CO₂ added (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>5.2</td>
<td>5.2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>9.7</td>
<td>10.0</td>
</tr>
<tr>
<td>CO₂ determined (%)</td>
<td>15.2</td>
<td>15</td>
</tr>
</tbody>
</table>

Sample size used: ~0.5 mg each determination

of the furnace assemblage [11, 12]. It was not possible to avoid reduction in experiments with albite and anorthite (both from Tem-Pres) + Ag₂C₂O₄ with the single capsule method; therefore, these experiments were carried out under MH-buffered conditions. This has the disadvantage that hydrogen migrates into the capsule and small iron addition also occurs at the high temperatures of these experiments.

Quantitative analysis of CO₂ by gas chromatography was described previously [4]. The accuracy of the method was tested with mechanical mixtures of SiO₂ and CaCO₃ with CO₂ contents of 5, 10 and 15 wt % (Table I). A mixture of three runs on olivine melilitite + CO₂ (6,261, 6,266, 6,267) was analysed for CO₂ by a conventional gravimetric method [13]. The sample was decomposed at 950–957 °C in the presence of V₂O₅ as a flux. CO₂ was absorbed on LiOH and gravimetrically determined. This result is in good agreement with values obtained by gaschromatography of glasses from similar P, T conditions (Table 2).

Infrared Spectrometry. Infrared spectra were obtained on a Perkin-Elmer Model 457 Grating Infrared Recording Spectrophotometer in the frequency range of 4,000 cm⁻¹ to 250 cm⁻¹. Some spectra were run in nitrogen gas to avoid any atmospheric influence. The samples were ground to about 25 microns. 1–2 mg were mixed with about 200 mg KBr and pressed to a tablet. The slit program was set on N (=normal), scanning speed was set on “medium” (=400 cm⁻¹/min between 4,000–2,000 cm⁻¹ and 200 cm⁻¹/min between 2,000–250 cm⁻¹) except for the region between 2,450–2,300 cm⁻¹, where it was set on “slow” (=100 cm⁻¹/min).

Experimental Results

Experimental conditions and run products are shown in Table 2. Higher temperatures and the presence of hydrogen from the MH buffer result in increase of quench carbonates and “dusty” glasses. The colours of the feldspar glasses are probably caused by traces of Fe migrated through the capsule wall from the buffer at high temperatures.

Dependence of CO₂ Solubility on Temperature and Composition at 30 kb. The temperature dependence of CO₂ solubility in olivine melilitite is shown in figure 1a (analytical results in Table 2). The solubility of CO₂ decreases slightly with increasing temperature. The quantitative gas chromatographic determinations are confirmed qualitatively by the CO₃⁻/SiO₄²⁻ ratios from infrared spectra (Fig. 1b). The slight negative dependence of CO₂-solubility is in contrast to Mysen’s et al. [5, 6] pronounced positive temperature dependence in various silicate melts. These authors found the largest effect in an oxide mix matching the olivine melilitite used in our experiments. Their method of determining