The speciation of carbon monoxide in silicate melts and glasses

TAKAHIRO YOSHIOKA1, CATHERINE MCCAMMON1, SVYATOSLAV SHCHEKA1 AND HANS KEPPLER1,*

1Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany

ABSTRACT

We have studied the speciation of carbon monoxide in both Fe-bearing and Fe-free basaltic glasses using Raman, FTIR, and Mössbauer spectroscopy. We show that a band at 2110 cm⁻¹ in the Raman spectrum and another band at 2210 cm⁻¹ in the FTIR spectrum occur both in the Fe-bearing and Fe-free samples, implying that they cannot be due to any Fe-bearing species. This observation is consistent with $^{57}$Fe Mössbauer spectra, which do not show any evidence for Fe species with zero isomer shift, as expected for carboxyls. Thermodynamic calculations show that iron carboxyl in basaltic melts under crustal and upper mantle conditions may only be a trace species. Rather than being due to distinct chemical species, the range of vibrational frequencies observed for carbon monoxide in silicate glasses appears to be due to rather subtle interactions of the CO molecule with the matrix. Similar effects are known from the extensive literature on carbon monoxide adsorption on oxides and other surfaces. In the melt at high temperature, there is likely little interaction of the CO molecule with the silicate matrix and solubility may be largely controlled by pressure, temperature, and the overall polymerization or ionic porosity of the melt.

Keywords: Silicate melt, carbon monoxide, iron, carboxyl, Raman, Mössbauer

INTRODUCTION

Carbon dioxide is an important component of volcanic gases, usually second in abundance only to water. Due to its low solubility in silicate melts at low pressure, CO₂ may drive bubble nucleation during eruptions and the melting point depression induced by CO₂ plays an important role in stabilizing low-degree partial melts in the mantle (e.g., Wylie and Huang 1976). Accordingly, carbon dioxide solubility in silicate melts has been extensively studied (Ni and Keppler 2013 and references therein). In contrast to CO₂, the solubility of carbon monoxide (CO) in silicate melts has received relatively little attention, probably because it is only a trace component in volcanic gases (Symonds et al. 1994) and because thermodynamic calculations suggest that under the oxygen fugacities prevailing in the Earth today, its abundance in crustal and upper mantle fluids is low (e.g., Frost and McCammon 2008). However, carbon monoxide could be an important species of carbon during planetary degassing under reducing conditions, e.g., on the Moon, during core formation on Earth, or perhaps even today in the reduced, deep mantle (e.g., Wetzel et al. 2013; Hirschmann 2013).

Pawley et al. (1992) suggested that carbon monoxide is much less soluble than carbon dioxide in a basaltic melt at 1200 °C and 500 to 1500 bar. A similar conclusion was reached by Morizet et al. (2010). Brooker et al. (1999) detected dissolved CO in reduced glasses prepared along the NaAlO₂-SiO₂ join by FTIR and NMR spectroscopy. In the NMR spectrum, a peak at a chemical shift of 185 ppm was assigned to CO; FTIR spectra showed a band between about 2160 and 2180 cm⁻¹, depending on the composition of the glass matrix. Notably, this absorption frequency is significantly higher than for CO in the gas phase (2143 cm⁻¹). Wetzel et al. (2013) reported a band at 2110 cm⁻¹ in the Raman spectra of reduced, carbon-bearing basalt glasses and attributed it to iron pentacarbonyl Fe(CO)₅. They inferred that Fe(CO)₅ is the main species of reduced carbon in these glasses. Stanley et al. (2014) suggested that a band at 2205 cm⁻¹ in the infrared spectrum in a graphite-saturated basalt could also be due to a carboxyl species.

The stability of carboxyl species in silicate melts and glasses could have important implications for the behavior of carbon, since carbon solubility would then be strongly coupled to the availability of iron. Carboxyls are molecules containing carbon monoxide coordinated to a transition metal. Typical examples are Ni(CO)₅ and Fe(CO)₅. Stable carboxyls are only known from the central block of the transition metals in the periodic table, where iron is the only element sufficiently abundant to be relevant for discussing the potential stability of carboxyls in natural silicate melts. The metal atom in simple carboxyls has the formal oxidation state of zero, which is related to an unusual mechanism of chemical bonding (e.g., Greenwood and Earnshaw 1984). An electron pair from the carbon atom is donated to the metal atom to form a σ bond; this bond is strengthened by a back-donation of d electrons from the metal atom into the anti-bonding orbitals of the CO molecule. Populating the anti-bonding orbitals of CO weakens the bond between carbon and oxygen and therefore usually causes the vibrational frequency of CO in a carboxyl to be shifted downward relative to the free CO molecule.

In this study, we combined Raman, FTIR, and Mössbauer spectroscopy on Fe-bearing and Fe-free basaltic glasses containing reduced carbon to investigate the dissolution mechanism of carbon monoxide in silicate melts and glasses.

EXPERIMENTAL AND ANALYTICAL METHODS

Two different synthetic glasses were used as starting materials. One was equivalent in composition to the lunar green glass used by Wetzel et al. (2013). A second glass had the same composition, with the exception that all FeO (total iron expressed as FeO) was replaced by an equimolar mixture of CaO and MgO. The glasses were