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Determination of the molar absorptivity of dissolved carbonate in basanitic glass

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ABSTRACT

Basanitic glasses with known dissolved C concentrations have been analyzed using infrared spectroscopy to calibrate the molar absorptivity of carbonate. C is dissolved as carbonate complexes in the glass resulting in absorption bands at 1525 and 1425 cm^{-1}. Molar absorptivities of 283 ± 8 L/(mol·cm) were determined for both 1525 and 1425 cm^{-1} absorption bands. An integrated molar absorptivity of 60000 ± 1700 L/($mol \cdot cm^2$) was determined using the integrated area under the doublet. These values are about 20–25% lower than those determined for tholeiitic and leucititic glasses and are intermediate between values characteristic of Na- and Ca-rich silicate glasses. Carbonate molar absorptivities for a range of basaltic glass compositions correlate with the molar ratio of Na/(Na + Ca).

INTRODUCTION

Infrared spectroscopy, when accurately calibrated for the composition of interest, can be used as a quantitative tool for measuring the dissolved CO_2 and H_2O contents in silicate glasses (see recent reviews by Ihinger et al., 1994; Blank and Brooker, 1994). To use the intensities of infrared absorptions to determine concentrations, the molar absorptivity, ϵ, which is the proportionality constant between the measured absorbance and the concentration for the absorbance band of interest, must be determined (Stolper, 1982; Fine and Stolper, 1985, 1986; Newman et al., 1986; Stolper et al., 1987). Infrared spectroscopic data have been used successfully to model degassing of H_2O and CO_2 from tholeiitic basaltic and rhyolitic melts (Fine and Stolper, 1986; Newman et al., 1988; Dixon et al., 1988, 1991; Anderson et al., 1989; Bacon et al., 1992; Anderson and Brown, 1993; Stolper and Newman, 1994; Dixon and Stolper, 1995). Study of the behavior of volatiles in more alkalic compositions has been hampered by the lack of calibration of molar absorptivities for these compositions. This study presents new molar absorptivity determinations for C dissolved as carbonate ion complexes in basanitic glass and presents a method for the prediction of molar absorptivities in other mafic silicate liquids.

INFRARED SPECTROSCOPIC ANALYSIS OF C IN ALUMINOSILICATE GLASSES

C can dissolve in silicate liquids as molecules of CO_2 or as carbonate groups [$(CO_3)^{2-}$] (see Blank and Brooker, 1994, and references therein). Quantitative infrared spectroscopic studies of C-bearing aluminosilicate glasses have focused on the asymmetric stretching vibration of molecular CO_2 near 2350 cm^{-1} and the ν_3 vibrations of carbonate species in the 1350–1600 cm^{-1} region (e.g., Fine and Stolper, 1985, 1986; Blank et al., 1993). Undistorted carbonate molecules have a doubly degenerate vibrational mode (single band) at 1415 cm^{-1}. Distortion of the carbonate groups through interaction with various metal cations or with the Si or Al framework cations in the glass results in removal of the degeneracy of the ν_3 vibration and splitting of the 1415 cm^{-1} band into a doublet with one band at 1500–1700 cm^{-1} and the other at 1350–1430 cm^{-1} (Brey and Green, 1975; Sharma, 1979; Sharma et al., 1979; Mysen and Virgo, 1980a; Fine and Stolper, 1986). The degree of splitting of the ν_3 doublet bands ($\Delta\nu_3$) provides information on the environment around the carbonate group (Fine and Stolper, 1985, 1986; Blank and Brooker, 1994; Ihinger et al., 1994).

Previous studies have found that the character of the carbonate bands in silicate glasses strongly depends on composition. In NaAl-rich silicate glasses (e.g., albitic, jadeitic, and nephelinitic compositions), C dissolves both as molecular CO_2 and as carbonate groups (Brey, 1976; Mysen et al., 1976; Mysen and Virgo, 1980a, 1980b; Fine and Stolper, 1985; Stolper et al., 1987; Taylor, 1990; Kubicki and Stolper, 1995). The carbonate bands in these NaAl-rich glasses are split by about 200 cm^{-1} and have molar absorptivities of 199–235 L/(mol·cm) (Fine and Stolper, 1985; Stolper et al., 1987; Taylor, 1990; Brooker, in preparation). Detailed study of the carbonate bands shows that they contain at least two unresolved components corresponding to carbonate groups in different chemical environments within the glass (Stolper et al., 1987; Brooker, personal communication).

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TABLE 1. Composition of mafic silicate glasses

	Tholeiite*	Leucitite**	Basanite† (this study)
SiO_2	49.1	44.1	46.0
TiO_2	0.74	2.69	3.17
Al_2O_3	16.44	12.8	15.2
FeO	8.86	9.0	12.0
MnO	0.16	0.19	0.23
MgO	10.15	9.14	9.06
CaO	11.65	14.34	8.22
Na_2O	2.13	3.20	4.33
K_2O	0.07	3.45	1.32
P_2O_5	n.r.	0.77	0.27
Total	99.3	99.7	100.0
Molar Na/(Na + Ca)	0.25	0.29	0.49
ρ(g/L)‡	2830	2940	2950
ϵ_{1525}[L/(mol·cm)]	375 ± 20	340 ± 20§	283 ± 8

Note: Total Fe reported as FeO; n.r. = not reported.

* Fine and Stolper (1986).

** Thibault and Holloway (1994).

† Pan and Holloway, in preparation.

‡ Glass density calculated according to Silver et al. (1990).

§ Thibault and Holloway (1994) reported a value (without estimate of error) of 355 for ϵ_{1525}. However, in their calibration they used an estimate of liquid density of ~2700 g/L based on Lange and Carmichael (1987). A better estimate of glass density is 2950 g/L calculated using the Gladstone-Dale rule and the Church-Johnson equation (Silver et al., 1990). We refit their data to yield a value of 330 L/(mol·cm); a value of 340 ± 20 L/(mol·cm) incorporates the uncertainty in density.

TABLE 2. Infrared data

Sample	CO_2 (wt%)	No.	Band (cm^{-1})	Intensity* (abs)	Band (cm^{-1})	Intensity* (abs)	Area* (cm^{-1})
3048-7	0.0807	1	1523	0.171	1424	0.160	35.62
		2	1522	0.141	1420	0.139	27.91
		3	1528	0.170	1426	0.162	34.41
		4	1521	0.153	1424	0.147	30.05
3048-11	2.427	1	1530	4.778	1424	4.778	1035.63
		2	1529	4.466	1423	4.447	957.50
		3	1529	4.597	1420	4.490	950.33
3048-13	2.178	1	1524	4.114	1431	4.116	890.82
		2	1526	4.323	1425	4.325	926.82
		3	1526	4.121	1423	4.079	887.87
3048-15	1.727	1	1524	3.240	1426	3.213	680.67
		2	1526	3.303	1425	3.287	696.00
		3	1524	3.004	1424	2.936	606.43
3048-16	1.177	1	1523	2.210	1425	2.253	467.33
		2	1523	2.191	1426	2.139	444.55
		3	1524	2.170	1428	2.119	437.87

* Normalized to a sample thickness of 100 μm.

In contrast, C dissolves only as carbonate groups in Ca- and CaMg-rich silicate glasses (e.g., diopsidic, sodamelilitic, and akermanitic compositions). The carbonate bands are split by about 90 ± 10 cm^{-1}, and the molar absorptivity determined for diopsidic glass is 375 ± 20 L/(mol·cm) (Fine and Stolper, 1986; Mattey et al., 1990; Sharma et al., 1979). IR spectra of CO_2-bearing glasses on the $NaAlSi_3O_8$-$CaAl_2Si_2O_8$ join exhibit characteristics transitional between those of the Na- and Ca-rich end-member compositions; the ratio of carbonate to molecular CO_2 increases as the composition changes from albite to anorthite, and all C dissolves as carbonate at a composition of Ab:An of 1:1 (Blank and Brooker, 1994).

Quantitative infrared spectroscopic studies of natural basaltic glasses have been conducted on tholeiitic (Fine and Stolper, 1986) and leucititic (Thibault and Holloway, 1994) compositions (Table 1). Reported molar absorptivities of 375 ± 20 L/(mol·cm) for tholeiitic and 355 L/(mol·cm) for leucititic glasses (see caption to Table 1) and values of $\Delta\nu_3$ are similar to those determined for other Ca-rich silicate glasses. Though quite different in their silica contents, the tholeiitic and leucititic glasses have similar ratios of Na/(Na + Ca) of 0.25 and 0.29, respectively. The basanitic glass used in this study is more alkali-rich, with Na/(Na + Ca) of 0.49, and allows us to extend the infrared spectroscopic calibration to alkali-rich basaltic compositions.

ANALYTICAL TECHNIQUE

Transmission infrared spectra in the 4000–1200 cm^{-1} (2.5–8.3 μm) range were collected on a Nicolet 60SX FTIR spectrometer using a globar source, KBr beamsplitter, HgCdTe detector, 4 cm^{-1} resolution, and mirror velocity of 1.57 cm/s. Analyses were performed in the main sample compartment using 200 μm apertures. Bubble-free glass chips were doubly polished to thicknesses of 30–60 μm measured with a digital micrometer with a precision of ±1–2 μm. Glass density was calculated to be 2950 g/L using the Gladstone-Dale rule and the Church-Johnson equation (Silver et al., 1990). The spectrum of a decarbonated basanitic glass was subtracted from each sample spectrum as a background correction; absorbance and integrated absorbance measurements were made on reference-subtracted spectra.

CHARACTERIZATION OF GLASSES

Glasses were prepared by quenching CO_2-saturated basanitic melts generated under *P-T* conditions ranging from 1 to 20 kbar and 1200–1550 °C. Details of the experimental procedure are given in Pan and Holloway (in preparation). The starting material is a basanite from Peridot Mesa, San Carlos Arizona (Table 1). The source of CO_2 in the >1 kbar experiments was siderite, calcite, magnesite, and Na_2CO_3 mixed with proportions of reagent-grade Al_2O_3 and SiO_2 to yield the correct stoichiometry of the original basanite. The CO_2 source in the 1 kbar experiment was silver oxalate. Samples were placed in Fe-saturated platinum capsules. The >1 kbar experiments were performed in a non-endloaded piston-cylinder apparatus. The 1 kbar experiment was performed in a rapid-quench, internally heated gas vessel (Holloway et al., 1992).

Bulk C values were obtained using a LECO JR-12 carbon analyzer. C analysis was performed on 18–28 mg of glass hand-picked to be free of bubbles. Analytical precision was determined to be ±0.006 wt% C. The accuracy of these concentrations was confirmed by ion probe and found to be within 10% of the LECO measured values (Pan and Holloway, in preparation).

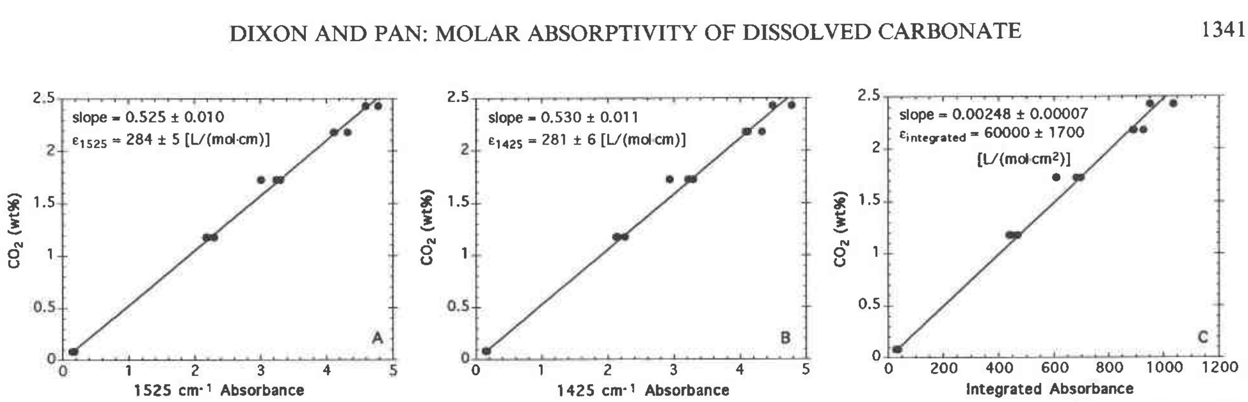

Fig. 1. Measured C concentrations plotted against intensities of absorptions normalized to a sample thickness of 100 μm. (**A**) Concentration vs. 1525 cm^{-1} absorbance. (**B**) Concentration vs. 1425 cm^{-1} absorbance. (**C**) Concentration vs. integrated molar absorbance. The molar absorptivities and integrated molar absorptivity were calculated using the Beer-Lambert law, $\epsilon = [MW \cdot Abs/(D\rho c)]$, where MW is the molecular weight in grams/mole (44.01 g/mol for concentration reported as weight fraction CO_2), Abs is the measured absorbance, ρ is the glass density (2950 g/L), D is the sample thickness in centimeters, and c is the concentration in weight fraction. The slope of the best-fit line on a plot of concentration (in parts per million) vs. measured absorbance normalized to 100 μm is related to the molar absorptivity by slope = $[(MW \times 10^4)/(\rho\epsilon)]$.

RESULTS

Spectroscopic data are listed in Table 2. C is dissolved as carbonate groups with absorptions at 1525 and 1425 cm^{-1}. The observed splitting between the two carbonate bands in basanitic glass is 100 cm^{-1}, larger than the 80 cm^{-1} observed for tholeiitic glasses (Fine and Stolper, 1986) but within the range observed for Ca-rich silicate glasses (Sharma, 1979; Sharma et al., 1979; Taylor, 1990). Absorbances at 2350 cm^{-1} were not observed, indicating that C does not dissolve in these glasses as molecular CO_2, which is consistent with observations for other Ca-rich silicate glasses (Brey, 1976; Sharma, 1979; Sharma et al., 1979; Fine and Stolper, 1986; Taylor, 1990). Small amounts of H_2O (<0.23 wt%) are also present in the glasses.

CO_2 concentrations are plotted in Figures 1A–1C against absorbances normalized to 100 μm sample thickness. Linear regressions through the data and forced through the origin yield molar absorptivities and 2σ errors of 284 ± 5 and 281 ± 6 L/(mol·cm) for the 1525 and 1425 cm^{-1} bands, respectively, with an average of 283 ± 8 L/(mol·cm) for both bands, and an integrated molar absorptivity of 60000 ± 1700 L/(mol·cm^2) (see caption to Fig. 1).

DISCUSSION

The ϵ_{1525} for carbonate groups in basanitic glasses are compared with those for other silicate melt compositions in Figure 2. Only ϵ_{1525} is shown because $\epsilon_{1525} \cong \epsilon_{1425}$ for Ca-rich glasses, and insufficient data exist for comparison of the integrated molar absorptivities. Our values for the molar absorptivity of the carbonate bands of basanitic glass are intermediate between values for NaAl-rich silicate glasses and CaMg-rich silicate glasses. The molar absorptivity of carbonate in basanitic glass is 20–25% lower than the values determined for tholeiitic and leucititic glasses, which is consistent with the higher Na/(Na + Ca) for basanite. In fact, there is a systematic compositional dependence of the ϵ_{1525} of basaltic glasses on the molar ratio Na/(Na + Ca). Note that we have plotted a revised value for the molar absorptivity of leucititic glass of 340 ± 20 L/(mol·cm), which incorporates a more realistic model for glass density (see caption to Table 1).

The relationships shown in Figure 2 may help to predict the molar absorptivities of carbonate that have not been measured directly in other mafic silicate glasses. For the basaltic compositions, molar absorptivity can be calculated using $\epsilon_{1525} = 451 - 342[Na/(Na + Ca)]$. The systematic variations in molar absorptivity likely reflect relationships between carbonate groups and metal cations or aluminosilicate units in glasses and may ultimately

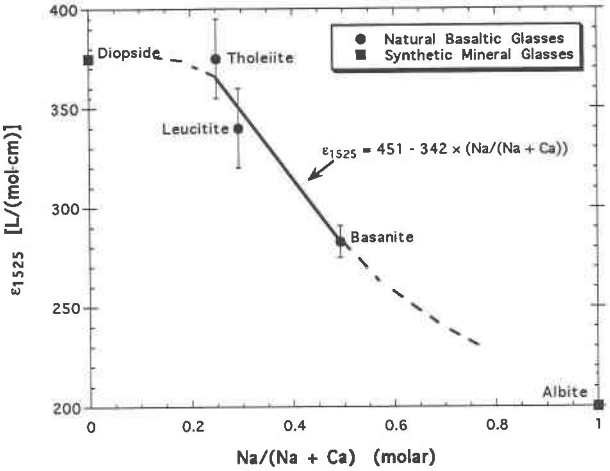

Fig. 2. Plot of ϵ_{1525} vs. molar Na/(Na + Ca) for a range of silicate melt compositions. Data sources are Fine and Stolper (1985) for jadeitic and albitic glasses, Fine and Stolper (1986) for tholeiitic and diopsidic glasses, and revised Thibault and Holloway (1994) for leucititic glass (see Table 1 note).

provide useful tests of models of chemical and structural interactions between these species and the major components of the glass structure. Although the parameter Na/(Na + Ca) appears to be important for determining ϵ_{1525} in fully depolymerized basaltic melts, it is naive to assert that this compositional dependence is valid over the full range (e.g., more polymerized) of natural and synthetic silicate glass compositions. More work is required to understand fully the compositional dependence of mechanisms of CO_2 dissolution into silicate melts (see Blank and Brooker, 1994). However, the key point in this study is that the systematic compositional dependence of the molar absorptivities determined in several laboratories on a range of glass compositions gives us confidence in our calibration of the infrared spectroscopic technique for determining concentrations of carbonate groups in silicate glasses.

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