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Carbon dioxide speciation in silicate melts: a restart

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Abstract

Using infrared spectroscopy, we investigated the speciation of carbon dioxide in albitic and synthetic iron-free dacitic glasses after annealing the glasses below the glass transition temperature in the temperature range 673–973 K at 0.5 GPa. Samples were rapidly quenched under constant pressure. The experiments show that the ratio of the integrated intensities of the 2350 cm^{-1} band (due to molecular CO_2) to that of the band doublet at 1700–1375 cm^{-1} (due to CO_3^{2-}) increases with higher annealing temperatures for both glass compositions. Our study demonstrates that in contrast to recent suggestions, the equilibrium of the CO_2 species reaction $CO_2+O^{2-}=CO_3^{2-}$ in silicate glasses/melts shifts towards molecular CO_2 with increasing temperature. The CO_2 species concentrations and an ideal solution model were used to determine equilibrium constants for the homogeneous species reaction. We derived preliminary values for the enthalpy ΔH^0 and entropy ΔS^0 of this reaction, assuming that the species concentrations reflect those at experimental temperatures ($\Delta H^0=-12\pm2$ kJ mol^{-1} and $\Delta S^0=-23\pm3$ J mol^{-1} K^{-1} for albitic composition; $\Delta H^0=-29\pm2$ kJ mol^{-1} and $\Delta S^0=-32\pm3$ J mol^{-1} K^{-1} for dacitic composition).
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1. Introduction

Next to H_2O, carbon dioxide is the second most abundant volatile in terrestrial magmas. CO_2 plays an important role in the petrogenesis of silica-undersaturated peralkaline magmas at mantle depth [1], in the evolution of oceanic basalts [2], and in the degassing processes of magmas and volcanic systems [3,4]. In a wide range of melt compositions from rhyolitic to basaltic, CO_2 is one order of magnitude less soluble than H_2O [5,6]. However, even small amounts of dissolved CO_2 in H_2O-bearing melts shift the fluid saturation limit to higher pressures and thus to greater depths [3]. Degassing of volatile-bearing ascending magmas is controlled by the volatile solubilities as a function of P, T, viscosity, surface tension, and by the mobility of the volatiles in the melt. Data on CO_2 speciation in silicate liquids is crucial for understanding the CO_2 dissolution mechanisms, the diffusion mechanisms, and the degassing processes.

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Raman, NMR, and IR measurements at ambient P and T on CO_2-bearing glasses have shown that CO_2 is dissolved as molecular CO_2, distorted CO_3^{2-} linked to the silicate network, and CO_3^{2-} linked to network modifying cations [7–10]. The concentration of CO_2 species in the glasses depends strongly on the bulk composition. In highly polymerized rhyolitic glasses CO_2 is incorporated exclusively as molecular CO_2 [6,11], and in depolymerized basaltic glasses CO_2 is incorporated exclusively as CO_3^{2-} [8,9].

Stolper et al. [12] and Brooker et al. [13] suggested that in albitic, jadeitic, and in phonolitic melts the CO_2 speciation shifts towards CO_3^{2-} with increasing synthesis temperature. Stolper et al. [12] used the CO_2 speciation data measured at ambient P and T in combination with the P and T conditions of the syntheses to derive thermodynamic parameters for the homogeneous species reaction:

$$CO_2(\text{melt}) + O^{2-}(\text{melt}) = CO_3^{2-}(\text{melt}) \quad (1)$$

in the melt assuming that the CO_2 species are preserved during quenching from run temperature. This contrasts with H_2O speciation ($H_2O + O^{2-} = 2OH^-$), that changes dramatically during quenching hydrous silicate melts [14–18]. Recently, it was demonstrated that with annealing and rapid quenching experiments of CO_2-bearing albitic and dacitic glasses [19] and jadeitic glasses [20] the species reaction (1) shifts towards molecular CO_2 with increasing annealing temperature. In order to provide more insight into the thermodynamics of CO_2 in silicate melts, we have performed additional long-term isothermal heating experiments with CO_2-bearing albitic glasses and iron-free synthetic dacitic glasses below the glass transition temperature. The CO_2 spectra of the quenched samples were measured using infrared spectroscopy.

2. Experimental and analytical methods

Melts with albitic ($NaAlSi_3O_8$) and iron-free dacitic composition were synthesized by fusion of mixed powders of SiO_2, TiO_2, Al_2O_3, MgO, $CaCO_3$, Na_2CO_3, and K_2CO_3 in a high-temperature furnace at 1873 K. The Pt crucibles were quenched rapidly in water to form glasses. The densities of the glasses given in the footnotes in Table 1 were determined using the buoyancy method. The compositions of the glasses were analyzed by an electron microprobe (Cameca Camebax MB, 15 kV acceleration voltage, 18 nA beam current and 2–5 s counting time for each element). The beam was defocused to 20 μm to optimize the analysis of Na. The analyses gave a total of 99.77 with $SiO_2 = 69.03$, $Al_2O_3 = 19.33$, and $Na_2O = 11.41$ wt% for the albitic glass and a total of 100.33 with $SiO_2 = 71.78$, $TiO_2 = 0.40$, $Al_2O_3 = 15.31$, $MgO = 2.26$, $CaO = 3.09$, $Na_2O = 4.52$, and $K_2O = 2.97$ wt% for the dacitic glass.

Silver oxalate ($Ag_2C_2O_4$) was used as the CO_2 source in the synthesis experiments. The purity of $Ag_2C_2O_4$ was tested with an ELTRA IR carbon analyzer and by gravimetric determination of the weight loss upon heating. The observed amount of CO_2 was 95.9% of the expected value.

Approximately 150 mg of dried glass powder (grain size < 500 μm) for the synthesis of CO_2-free glass cylinders and additional dried $Ag_2C_2O_4$ powder equivalent to 0.2 wt% CO_2 for the synthesis of CO_2-bearing glasses were sealed inside 3-mm-diameter $Au_{80}Pd_{20}$ capsules. The $Ag_2C_2O_4$ powder was wrapped in $Au_{80}Pd_{20}$ foil to prevent contamination of the glass with Ag. Using $Au_{80}Pd_{20}$ as capsule material prevents loss of CO_2 during the experiments [21]. The sealed capsules were heated in an oven at 473 K for 1 h to decompose the $Ag_2C_2O_4$ before the high-P and high-T experiments. Synthesis experiments were conducted at 1573 K (albitic composition), 1623 K (dacitic composition), and 0.5 GPa for 15–17 h in an internally heated pressure vessel (IHPV) pressurized with argon and equipped with a rapid quench device. The temperature in the rapid quench device was measured over 3 cm with calibrated S-type thermocouples with an accuracy of ± 10 K. The pressure was measured with a strain-gauge manometer with an accuracy of ± 0.002 GPa at 0.5 GPa.

At the chosen P and T conditions the melts were CO_2 undersaturated. After the runs the samples were isobarically cooled rapidly to room temperature by dropping the capsules into the lower

Table 1
Experimental data and results

Run No.	Starting material	T (K)	P (GPa)	t (min)	d (μm)	A_{CO_2} (cm^{-1})	$A_{CO_3^{2-}}$ (cm^{-1})	$[CO_2]\times10^{-4}$[a]	$[CO_3^{2-}]\times10^{-4}$[a]	$[O^{2-}]$[a]	K
AbCO2[b]	Albitic glass+$Ag_2C_2O_4$	1573	0.5	1020	98	13.18	8.24	10.28(72)	2.73(22)	0.9987	0.26(3)
AbSpez02Q01	AbCO2	673	0.5	2550	92	11.14	13.87	9.25(69)	4.90(31)	0.9986	0.53(5)
AbSpez02Q02	AbCO2	773	0.5	2400	96	12.74	11.53	10.14(72)	3.90(26)	0.9986	0.39(4)
AbSpez07	AbCO2	873	0.5	3720	99	13.78	10.60	10.64(74)	3.48(24)	0.9986	0.33(3)
AbSpez06	AbCO2	973	0.5	1290	105	15.31	9.75	11.14(75)	3.01(22)	0.9986	0.27(3)
DaCO201[c]	Dacitic glass+$Ag_2C_2O_4$	1623	0.5	1020	100	9.59	16.57	8.47(71)	5.85(36)	0.9986	0.69(7)
DaSpez02	DaCO201	773	0.5	2760	91	4.95	25.15	4.80(58)	9.75(57)	0.9985	2.03(27)
DaSpez08	DaCO201	789	0.5	3030	106	6.46	27.52	5.38(54)	9.16(52)	0.9985	1.71(20)
DaSpez04	DaCO201	873	0.5	3000	98	7.64	21.69	6.88(64)	7.81(46)	0.9985	1.14(12)
DaSpez06[d]	DaCO201	878	0.5	30	105	7.17	17.05	6.03(58)	5.73(35)	0.9988	0.95(11)
DaSpez10	DaSpez07	879	0.5	2880	106	8.04	24.43	6.70(60)	8.13(47)	0.9985	1.22(13)
DaSpez11	DaSpez08	879	0.5	2880	109	8.95	25.70	7.25(62)	8.32(47)	0.9984	1.15(12)
DaSpez09	DacO201	888	0.5	2898	114	9.31	25.75	7.21(61)	7.97(45)	0.9985	1.11(11)
DaSpez05	DaCO201	973	0.5	2820	97	9.23	17.80	8.40(72)	6.48(39)	0.9985	0.77(8)
DaSpez07	DaCO201	973	0.5	3030	98	9.68	17.93	8.72(73)	6.46(39)	0.9985	0.74(8)
DaCO202[e]	Dacitic glass+$Ag_2C_2O_4$	1603	0.5	900	98	7.00	11.84	6.35(39)	4.28(29)	0.9989	0.68(6)
DaCO25001	DaCO202	773	1 atm	1	106	8.03	14.53	6.70(40)	4.84(30)	0.9988	n.d.
DaCO2500100	DaCO202	773	1 atm	100	98	4.70	19.38	4.25(27)	6.99(40)	0.9989	n.d.
DaCO25001000	DaCO202	773	1 atm	1000	98	4.51	21.40	4.08(26)	7.73(44)	0.9988	1.90(16)

All annealing experiments were rapidly quenched with about 200 K s^{-1}. Errors in brackets are calculated from uncertainties of total CO_2 contents, thickness measurements, densities and determination of the peak areas.

[a] Molar fractions of molecular CO_2, CO_3^{2-}, and oxygens of the glasses based on a single oxygen basis.

[b] Total CO_2 content = 0.19(1) wt%; ρ = 2382(5) g l^{-1}; total H_2O content = 0.10 wt% (determined from the linear absorption of the fundamental OH stretching mode at 3500 cm^{-1} using the linear molar absorptivity of 70 l mol^{-1} cm^{-1} [12].

[c] Total CO_2 content = 0.20(1) wt%; ρ = 2312(5) g l^{-1}; total H_2O content = 0.13 wt%.

[d] This short time experiment was not considered in the determination of the molar absorption coefficients because of many cracks in the sample that disturbed the IR measurement and in the determination of the reaction enthalpy and entropy because equilibrium was not reached.

[e] Total CO_2 content = 0.15 wt% determined from IR spectra using the integrated molar absorption coefficients ε_{CO_2} = 16000 ± 1000 and $\varepsilon_{CO_3^{2-}}$ = 40100 ± 2000 l mol^{-1} cm^{-2}; ρ = 2382(5) g l^{-1}; total H_2O content = 0.13 wt%.

cold part of the rapid quench device. The quench rate of the samples was determined to be approximately 200 K s^{-1} by using H_2O speciation data of quenched hydrous rhyolitic glasses that were run parallel in some synthesis runs [22].

Transparent and bubble-free glass slabs of 3 mm thickness were cut out of the capsules for the heating experiments. Each glass slab was welded inside a 3-mm-diameter $Au_{80}Pd_{20}$ capsule. Pairs of CO_2-bearing and CO_2-free samples were heated simultaneously in an IHPV below the glass transition temperatures of the synthesized glasses at 0.5 GPa and 673–973 K for 21.5–62 h and quenched isobarically at a rate of 200 K s^{-1} to room temperature (Table 1).

Additional annealing experiments with dacitic glass were conducted to check whether the experiment duration was sufficient to allow equilibration of the CO_2 speciation and whether the quenching rate was fast enough to preserve the CO_2 speciation. CO_2-free and CO_2-bearing glass slabs were heated at 0.5 GPa for 2 days at 789 K and at 973 K. Both pairs of glasses were then heated at 0.5 GPa for 2 days at 879 K for reequilibration. Furthermore, rapidly quenched dacitic glass slabs were heated at 0.5 GPa and 878 K for only 0.5 h to test if this short time is sufficient to reequilibrate the CO_2 speciation. Furthermore we conducted an additional set of time-dependent annealing experiments of CO_2-free and CO_2-bearing dacitic glasses at 773 K in a furnace at ambient pressure conditions similar to the method described by Morized et al. [20]. Annealing times were 1–1000 min. After annealing, the samples were quenched rapidly in air.

Pairs of corresponding CO_2-bearing and CO_2-free glass slabs were embedded into epoxy and ground and polished to an identical sample thickness within 3 μm for IR spectroscopy. The sample thickness was determined using a digital micrometer with a precision of ±2 μm. Transmission IR spectra at ambient P and T conditions were monitored with a resolution of 2 cm^{-1} using a Bruker IFS 88 spectrometer equipped with an IR-scope II microscope, a global light source, a KBr beam splitter and an InSb-MCT sandwich detector. 30–50 scans were collected for each spectrum. An adjustable slit aperture was used to maintain a local resolution of 100 μm. The microscope and the spectrometer were flushed with purified air to minimize disturbances due to changes in the H_2O and CO_2 content of the air. The spectra of CO_2-free samples were measured for reference.

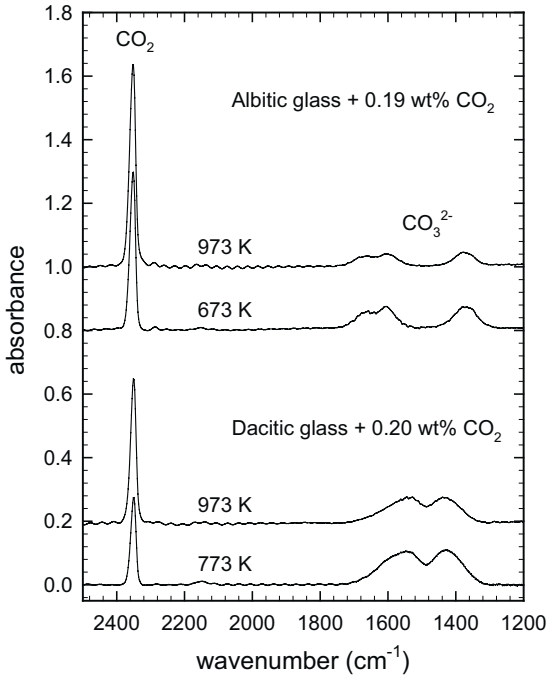

Fig. 1. Background subtracted IR spectra of quenched CO_2-bearing albitic and dacitic glasses measured at ambient P and T conditions normalized to 100 μm thickness. Spectra are offset for clarity. Note the systematic increase of the 2350 cm^{-1} band due to dissolved molecular CO_2 and the corresponding decrease of the band doublet at 1700–1300 cm^{-1} due to CO_3^{2-} with increasing annealing temperature for both glass compositions.

3. Experimental results

Background subtracted IR spectra of CO_2-bearing albitic and dacitic glasses are shown in Fig. 1. The sharp absorption band at 2350 cm^{-1} is due to the ν_3 antisymmetric stretching vibration of CO_2 molecules dissolved in the glass. The band system at 1600–1375 cm^{-1} is due to CO_2 dissolved as distorted CO_3^{2-} [1,23,24]. The spectra of the quenched dacitic and albitic glasses clearly show

that the ratios of the integrated intensities of the 2350 cm^{-1} band to that of the band doublet at 1700–1375 cm^{-1} increase with annealing temperatures. Peak areas of the molecular CO_2 band and the band system due to CO_3^{2-} were determined for both glass compositions directly from the spectra (Table 1).

Quantitative measurement of CO_2 species concentrations using IR spectroscopy requires calibration of the molar absorption coefficients of the bands for the glass composition of interest. We used the Beer–Lambert law, rewritten below to determine the integrated molar absorption coefficients:

$$\frac{4401A_{CO_2}}{d\rho c_{CO_2,\,total}} = \varepsilon_{CO_2} - \frac{\varepsilon_{CO_2}}{\varepsilon_{CO_3^{2-}}} \frac{4401A_{CO_3^{2-}}}{d\rho c_{CO_2,\,total}} \quad (2)$$

The peak areas of the absorption band at 2350 cm^{-1} (A_{CO_2}) and the band system at 1700–1300 cm^{-1} ($A_{CO_3^{2-}}$) are normalized by the molecular weight of CO_2, the sample thickness (d, in cm), the density of the glass (ρ, in g l^{-1}) and the total CO_2 content ($c_{CO_2,\,total}$, in wt%). The normalized absorbances $A_{CO_3^{2-}}$ (norm.) vs. A_{CO_2} (norm.) for the albitic and the dacitic glasses are shown in Fig. 2. Linear regressions through the individual data sets provide ε_{CO_2} and $\varepsilon_{CO_3^{2-}}$ as the intercepts on the y- and x-axis. The integrated molar absorption coefficients ε_{CO_2} and $\varepsilon_{CO_3^{2-}}$ are 18 000 ± 1000 and 42 250 ± 2000 l mol^{-1} cm^{-2} for the albitic glass and 16 000 ± 1000 and 40 100 ± 2000 l mol^{-1} cm^{-2} for the dacitic glass, respectively. Errors are estimated from the uncertainties of total CO_2 content (± 0.01 wt%), thickness measurements (± 2 μm), density measurements (± 5 g l^{-1}), determination of the peak areas (± 0.5 cm^{-1}), and the limited number of experimental data.

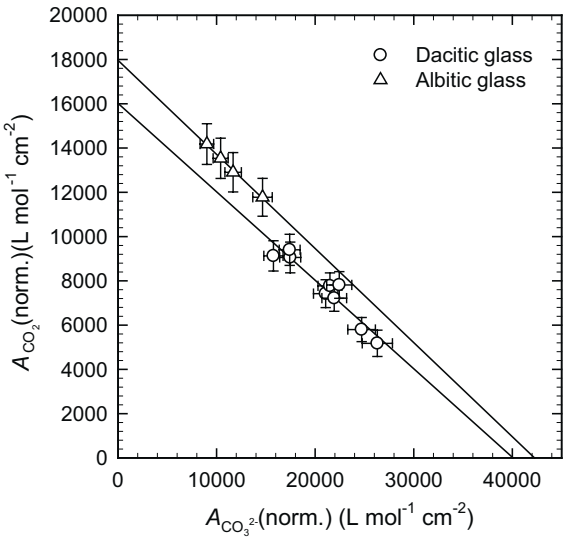

Fig. 2. Normalized integrated absorbances of the CO_3^{2-} and molecular CO_2 bands for albitic and dacitic glasses. The solid straight lines were obtained by linear least-square regressions of the corresponding data.

4. Discussion

The CO_2 species concentrations for the albitic and dacitic glasses (Table 1) were calculated using the integrated molar absorption coefficients. The speciation data allow the calculation of equilibrium constants assuming ideal mixing and equilibrium species concentrations that represent the CO_2 speciation at run conditions:

$$K = \frac{[CO_3^{2-}]}{[CO_2][O^{2-}]} \quad (3)$$

where $[CO_3^{2-}]$, $[CO_2]$, and $[O^{2-}]$ are the molar fractions of CO_3^{2-}, CO_2 molecules, and oxygen of the glass/melt, respectively, based on a single oxygen basis of the volatile-free melt composition:

$$[CO_2] = \frac{c_{CO_2}(wt\%)/44.01}{c_{CO_2}(wt\%)/44.01 + \frac{100 - c_{CO_2}(wt\%)}{Mo}} \quad (4)$$

and

$$[CO_3^{2-}] = \frac{c_{CO_3^{2-}}(wt\%)/44.01}{c_{CO_3^{2-}}(wt\%)/44.01 + \frac{100 - c_{CO_3^{2-}}(wt\%)}{Mo}} \quad (5)$$

where Mo is the molecular weight of the anhydrous glass on a single oxygen basis (Mo: albitic glass = 32.69 g mol^{-1} oxygen; dacitic glass = 32.73 g mol^{-1} oxygen).

In the investigated temperature range of 673–973 K the equilibrium constants for both glasses

decrease significantly with increasing annealing temperature. The observation that the equilibrium constants of the dacitic glasses rapidly quenched from the melt are slightly lower than the equilibrium constants of the glasses heated at 973 K (Table 1, Fig. 3) indicates that the fictive temperature at which the CO_2 speciation is frozen in during the quench from the melt is slightly higher than 973 K. From these data we suggest that the CO_2 speciation adjusted at 973 K is not affected during the quench and thus represents the equilibrium temperature. Within error the calculated equilibrium constants for the albitic glasses quenched from the melt and quenched from 973 K are identical. From these data we cannot decide whether the CO_2 speciation adjusted at 973 K is affected slightly during the quench.

The equilibrium constants of the two dacitic glasses preheated for 2 days at 973 K (DaSpez07) and at 789 K (DaSpez08) and then heated at 879 K for 2 days (DaSpez10 and DaSpez11) are within error identical to the glasses quenched from 1623 K and then heated for 50 h at 873 K (DaSpez04) and for 48.3 h at 888 K (DaSpez09) (Table 1, Fig. 3). A heating time of 2 days at 879 K is sufficient to allow reequilibration of the CO_2 speciation. Heating the glass for 0.5 h at 878 K (DaSpez06) is sufficient to change the CO_2 speciation in the glass quenched rapidly from the melt but the equilibrium value is not reached (Table 1, Fig. 3). The time-dependent annealing experiments of the dacitic glasses at 773 K and ambient pressure conditions show that an annealing time of 2 days is also sufficient to equilibrate the CO_2 speciation (Fig. 4). We have to emphasize that we do not as yet know the heating times required for complete reequilibration of albitic glasses.

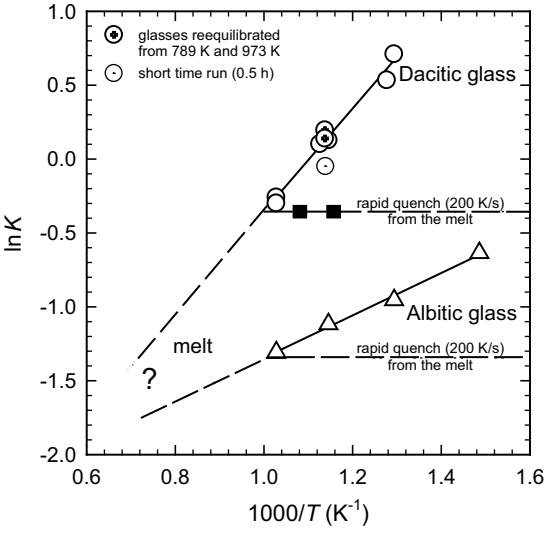

Fig. 3. Temperature dependence of the equilibrium constants K of the homogeneous reaction $CO_2+O^{2-}=CO_3^{2-}$ in albitic and in dacitic glasses. For details see text.

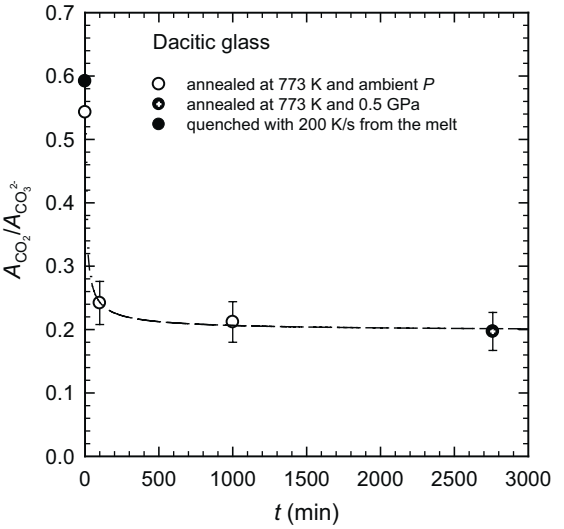

Fig. 4. Ratios of the CO_2 and CO_3^{2-} peak areas of dacitic glasses tempered at 773 K versus annealing time.

Nevertheless, for both glasses the reaction enthalpy ΔH^0 and the reaction entropy ΔS^0 of Eq. 1 were preliminary determined by linear least-square regressions of:

$$\ln K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (6)$$

in the temperature ranges 673–973 K for the albitic composition and 773–973 K for the dacitic composition. This procedure provides a ΔH^0 of -12 kJ mol^{-1} and a ΔS^0 of -23 J mol^{-1} K^{-1} for albitic composition and a ΔH^0 of -29 kJ mol^{-1} and a ΔS^0 of -32 J mol^{-1} K^{-1} for dacitic composition. We estimate the errors to be ± 2 kJ mol^{-1} for ΔH^0 and ± 3 J mol^{-1} K^{-1} for ΔS^0 based on the uncertainties in the peak area, thickness, density and total CO_2 content. The enthalpy

and entropy of the CO_2 species reaction in dacitic and albitic glass are similar to the thermodynamics of CO_2 speciation in jadeite glass ($\Delta H^0 = -17$ (+4/−8) kJ mol^{-1}; $\Delta S^0 = -24$ (+6/−9) J mol^{-1} K^{-1}) [20]. We emphasize that ΔH^0 and ΔS^0 for the CO_2 species reaction in albitic glass are preliminary results because of the uncertainties of the required quenching rates at 973 K and the required equilibration times for albitic glass. Based on these considerations, ΔH^0 and ΔS^0 are minimum values. Nevertheless, our experiments demonstrate that the CO_2 species reaction shifts towards CO_2 molecules with increasing temperature below and near the glass transition. This observation indicates CO_2 speciation is opposite to the trend of H_2O speciation that shifts towards hydroxyl with increasing temperature [14–18]. Furthermore, our observed temperature dependence of the CO_2 species reaction opposes trends determined for albitic, and jadeitic composition in previous studies [12,13]. These authors suggested that with increasing run temperature of the syntheses experiments the CO_2 species observed at ambient P and T shift towards CO_3^{2-}.

Ab initio calculations showed that the back reaction of (1) had an activation energy one order of magnitude larger than the forward reaction from which Kubicki and Stolper [25] inferred that the carbonate species present at high temperatures might either be retained metastably during quenching or also represent an intermediate situation between complete preservation of the speciation in the melt at high temperature and complete reequilibration during quenching far above the glass transition temperature. An estimate of the relaxation time of the albitic network structure based on viscosity data [26] gives 126 yr at 773 K and 7.7 m.y. at 673 K. This is far above the heating duration of 2 days. Nevertheless, we observe a significant change in CO_2 speciation even at 673 K in the albitic glass. We conclude that in contrast to the H_2O species reaction the relaxation of the CO_2 speciation is decoupled from the network structure relaxation of the melt/glass following the idea of Zhang [27] that melt–glass transitions probably involve the quenching of homogeneous reactions that may have different apparent equilibrium temperatures for a given quench rate. The CO_2 molecule attached to a bridging oxygen to form carbonate without breaking oxygen bridges proposed by Kohn et al. [28] for albitic glasses and attachment of CO_2 molecules to bridging oxygens without breaking Si–O–Si bonds and/or reaction of CO_2 molecules with non-bridging oxygens in the case of dacitic glass can explain the observed change of CO_2 speciation below the glass transition temperature. The CO_2 species reaction involving attachment and detachment of CO_2 molecules from bridging and non-bridging oxygens does not affect the highly polymerized rigid glass network structure.

The dependence of the CO_2 speciation on run temperature observed by Stolper et al. [12] and Brooker et al. [13] might be related to different H_2O contents of the samples. Even a small increase of H_2O content modifies the network structure and as a consequence the glass transition temperature decreases [14]. We suggest that dissolved H_2O affects the fictive temperature of the CO_2 speciation during quench. A rough reinterpretation of the experimental data of Stolper et al. [12] supports this suggestion. The equilibrium constant of the CO_2 species reaction of the albitic glass with the lowest water content (0.14 wt%) is about 0.23 whereas the equilibrium constant of the glass with the highest water content (0.76 wt%) is about 0.58. Our results are not affected by different H_2O contents because the corresponding CO_2-bearing glass slabs used in the heating experiments originate from the same charges with H_2O contents of 0.10 wt% in the albitic glass and 0.13 wt% in the dacitic glass.

In contrast to the H_2O species reaction in silicate melts [29], the CO_2 species reaction may strongly depend on bulk composition of the glass/melt. The reaction enthalpy of the CO_2 species reaction in the depolymerized dacitic glass is more than twice as compared to the reaction enthalpy in the fully polymerized albitic glass. We have to emphasize that the enthalpy of the CO_2 species reaction of albitic glass is a minimum value. Nevertheless, we suggest that the reaction enthalpy may depend on the concentration of excess network modifiers and thus on the degree of polymerization of the glasses/melts.

For the accurate determination of the thermo-

dynamic quantities and kinetic properties of the CO_2 species reaction in silicate glasses/melts additional isothermal heating/quenching experiments, especially with different run times, are needed to get more detailed knowledge of the thermodynamics and kinetics of the CO_2 species reaction. We emphasize that the importance of constant H_2O contents in each experimental series is crucial to fully resolve the CO_2 speciation using quenched melts.

Recently published in situ data on H_2O speciation in rhyolitic melts demonstrate that extrapolating speciation data based on quenched glasses to magmatic temperatures may lead to significant errors [17] because of possible non-Arrhenian behavior of homogeneous species reactions in silicate melts. Therefore, in situ measurements of CO_2 speciation in silicate melts would be highly desirable in order to fully understand the mechanisms of CO_2 dissolution, diffusion, and degassing processes of magmas.

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