Introduction

Carbon dioxide has attracted the attention of igneous petrologists because of its influence on phase equilibria relevant to partial melting in the upper mantle (e.g., Yoder, 1973; Eggler, 1973, 1975, 1978; Eggler and Rosenhauer, 1978; Huang and Wyllie, 1976; Wendlandt and Mysen, 1978; Mysen and Boettcher, 1975a,b). Some of these authors have shown that the presence of CO₂ in the upper mantle results in partial melts that contain less silica than those formed in the absence of CO₂. It has also been noted (e.g., Eggler, 1973) that the presence of CO₂ during fractional crystallization tends to enhance the stability of minerals that are more polymerized than the liquidus minerals in CO₂-free systems. Subsequent studies of CO₂-solubility mechanisms in relevant melt compositions have shown that in melts that contain a significant number of nonbridging oxygens per tetrahedral cation (NBO/T), CO₂ is dissolved in the form of a carbonate complex (Mysen et al., 1975, 1976; Brey and Green, 1976; Eggler and Mysen, 1976; Mysen and Virgo, 1980).

As a result of the formation of such carbonate complexes, the number of nonbridging oxygens per tetrahedral cation in the melt has decreased. In other words, CO₂ solution in such melts results in polymerization of the melt.

Melts on the joins NaAlSi₃O₈−SiO₂ and CaAl₂Si₂O₈−SiO₂ contain the petrologically important plagioclase components. It is necessary, therefore, to understand the solubility mechanisms of CO₂ in such melts before the role of CO₂ in magmas can be completely understood. Determinations of carbon dioxide solubility in melts on the join NaAlO₂−SiO₂−CO₂ have shown that several weight percent CO₂ may dissolve in these melts at high temperatures and pressures and that at least some of this CO₂ exists as CO₃⁻ (Mysen, 1976). Inasmuch as CO₂-free melts on this join have NBO/T = 0 (Mysen et al., 1980a), the influence of dissolved CO₂ on the melt structure must differ from that for melts with NBO/T > 0. The melt compositions on the joins NaAlO₂−SiO₂ and CaAl₂O₄−SiO₂ are also important because possible contrasting roles of Na⁺ and Ca²⁺ on CO₂-solubility mechanisms may be observed. We decided, therefore, to integrate studies of CO₂ solubility with Raman spectroscopy to determine the structural role of CO₂ in melts with no nonbridging oxygens.

The solubility behavior of CO₂ in melts on the join NaAlSi₃O₈−CaAl₂Si₂O₈−CO₂ at high pressures and temperatures: a Raman spectroscopic study

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Abstract

The solubility behavior of CO₂ in melts on the join CaAl₂Si₂O₈−NaAlSi₃O₈−CO₂ has been determined at high pressures and temperatures by Raman spectroscopy and beta-track autoradiography. The carbon dioxide dissolves predominantly as a metal carbonate complex in such melts and is 25 percent more soluble in CaAl₂Si₂O₈ than in NaAlSi₃O₈ melt at the same pressure and temperature. The Raman spectra of quenched NaAlSi₃O₈ + CO₂ melt indicate that some carbon dioxide is also dissolved as molecular CO₂.

The CO₂-free melts consist of two 3-dimensional aluminosilicate network units. In both CaAl₂Si₂O₈ and NaAlSi₃O₈ melt these two units become enriched in Si relative to Al as carbon dioxide is dissolved. In addition, there is a third structural unit with both Si and Al in tetrahedral coordination and with nonbridging oxygens. A consequence of the formation of a metal carbonate complex is that some of the aluminum in the melt is not in tetrahedral coordination in melts of CaAl₂Si₂O₈ + CO₂ and NaAlSi₃O₈ + CO₂ composition.
Experimental techniques

The starting materials were spectroscopically pure SiO₂, Al₂O₃, and CaCO₃ to make melts of CaAl₂Si₂O₆ (An) composition with CO₂ in solution. The carbonate was the source of CO₂. The composition An + CO₂ contains 13.66 wt. percent CO₂. Experiments with this composition were therefore conducted in the presence of excess CO₂ when the CO₂ solubility in the melt did not exceed 13.66 wt. percent CO₂. The NaAlSi₃O₈ + CO₂ composition (Ab + CO₂) was made from spectroscopically pure SiO₂ and Al₂O₃, and reagent-grade Na₂CO₃. The Na₂CO₃ was the source of CO₂ (8.60 wt. percent CO₂ in the starting material). Both An + CO₂ and Ab + CO₂ melting experiments were conducted in the presence of a nearly pure CO₂ vapor phase.

All experiments were carried out in a solid-media, high-pressure apparatus (Boyd and England, 1960) with a 0.5” diameter furnace contained within a Pyrex-glass sleeve. The furnace parts were thoroughly dried prior to the experiments to minimize the availability of H₂O, which dissociates to H₂ and O₂ during the experiments. The H₂ may enter the sample through the walls of the sealed Pt sample containers. Eggler et al. (1974) found that with the technique used here, the vapor contains at least 99 mole percent CO₂ (less than 1 mole percent CO and H₂O) after an experiment.

A -4 percent friction correction was applied to the experiments (calibrated against the quartz-coesite transition). The piston-out technique was used. The uncertainty of the pressure is ±1 kbar (Eggler, 1977).

The temperatures were measured with a Pt-Pt90Rh10 thermocouple with no correction for pressure on the electromotive force. The latter simplification results in an uncertainty in the temperature reading of 6°–10°C depending on the temperature at P > 10 kbar (Mao et al., 1971).

The carbon contents (reported as CO₂) of the melts were measured with beta-track counting (Mysen and Seitz, 1975). Carbon-14 was used as beta-active isotope, and K-5 nuclear emulsions were used as detectors (supplied by Ilford Inc., England). The analytical uncertainty is 2–3 percent relative to the amount present (Mysen and Seitz, 1975; Mysen, 1976; Kadik and Eggler, 1975; Eggler et al., 1979).

All aspects of the experiments pertaining to equilibrium CO₂ contents were performed according to the methods described by Mysen and Seitz (1975), Mysen et al. (1976), and Mysen and Virgo (1980). We consider, therefore, that the CO₂ contents were measured at equilibrium. The possible presence of trapped stable CO₂ vapor in quenched melts of Ab composition was discussed by Mysen (1976) and Mysen et al. (1976). They concluded that trapped stable CO₂ vapor most likely would not affect the analytical results. Possible problems with exsolution of vapor during quenching are discussed later.

All details of the Raman spectroscopic procedures have been described by Mysen et al. (1980a). The Raman spectra have been deconvoluted into individual bands according to the procedures discussed by Mysen et al. (1980a).

Melt vs. quenched melt

Both carbon analysis and spectroscopic measurements were carried out on quenched samples. It is necessary, therefore, to assess whether the quenching process has affected the carbon concentrations in the melts and the structural features that can be discerned with Raman spectroscopy.

Carbon analysis of quenched melts of a variety of bulk compositions has been compared with carbon contents determined with chemographic techniques (Mysen et al., 1976; Kadik and Eggler, 1975; Eggler et al., 1979). The compositional range, temperatures, and pressures of our experiments were covered by those studies. The results indicate that the carbon dioxide contents of the quenched melts equal those of the melts themselves.

In order to relate the structural information from quenched melts to structural features of silicate melts, it must be demonstrated that the features under consideration are not significantly affected by the quenching. Riebling (1968) and Taylor et al. (1980) found that anionic structural units (silicate polymers) in melts with a 3-dimensional network structure such as melt of NaAlSi₃O₈ composition remain the same as the melt is quenched. Direct experimental proof of structural similarity between melts and their quenched analogues on the join Na₂O-SiO₂ was provided by Sweet and White (1969) and Sharma et al. (1978). In those studies, infrared and Raman spectra of melts of Na₂Si₃O₈, Na₂Si₃O₇, and Na₂SiO₃ composition were compared with those of their quenched equivalents. It was concluded that the structures of these melts were not affected by the quenching process.

On the basis of the information given above, we conclude that both structural features discernible with Raman spectroscopy and carbon concentrations determined by beta-track mapping are quenchable. The results on quenched melts given in this report...
are believed to be applicable, therefore, to liquid silicates.

**Results**

Carbon dioxide solubility in melts of Ab composition is shown as a function of temperature and pressure in Table 1. The results agree with those of Mysen (1976) within the temperature and pressure ranges covered in both studies. The carbon dioxide solubility increases from about 1 wt. percent at 10 kbar to about 3 wt. percent at 30 kbar and 1650°C. The solubility increases isobarically with increasing temperature, as also found by others for other compositions (e.g., Mysen et al., 1975, 1976; Eggler, 1973; Holloway et al., 1976). The CO₂ solubility at a given temperature and pressure is less than in any melt containing nonbridging oxygen studied to date.

Carbon dioxide contents of An melt are shown as a function of pressure in Table 1. We note by comparing data in Table 1 that the CO₂ solubility in An melt is about 25 percent greater than in Ab melt at the same pressure and temperature. Furthermore, the data in Table 1 indicate that the CO₂ solubility in An melt may decrease with increasing temperature at temperatures above 1750°C. The temperature dependence of CO₂ solubility could not be determined at lower temperatures because of the high liquidus temperatures in the system CaAl₂Si₂O₈-Co₂O. Mysen and Virgo (1980) suggested that the fugacity of CO₂ may decrease with increasing temperature above about 1700°C at P(CO₂) greater than 10 kbar, a conclusion that agrees with MRK data for CO₂ by Holloway (1977). In that case, the CO₂ solubility in the melt will also decrease with increasing temperature, as observed by Mysen and Virgo (1980) and Holloway et al. (1976) for meta- and orthosilicate melts, and now for An melt. We conclude, therefore, that the negative temperature dependence of CO₂ solubility in An melt at P(CO₂) = 25 kbar and T > 1750°C is a result of the lowering of f(CO₂) and is not due to solubility mechanisms of CO₂ in the melt at these high temperatures.

The high-frequency envelopes of the Raman spectra of quenched An + CO₂ melt as a function of CO₂ content are shown in Figure 1. Detailed data from the complete spectral region are shown in Table 2. The high-frequency envelope of CO₂-free quenched An melt at 20 kbar consists of two (Si,Al)-coupled, asymmetric stretch bands (993 and 930 cm⁻¹, respectively) indicative of two 3-dimensional structural units in the melt (Mysen et al., 1980b). The band at the highest frequency (993 cm⁻¹) reflects stretch vibrations in the most aluminous structural unit. Addition of CO₂ to this melt results in the development of a shoulder near 1070 cm⁻¹ (Fig. 1). This shoulder becomes more pronounced with increasing CO₂ content. In the deconvoluted spectra [see Mysen et al. (1980a) for discussion of deconvolution procedures] it can be seen (Fig. 1) that this shoulder is due to a broad band near 1075 cm⁻¹. A sharp band near 1075 cm⁻¹ was also found in CO₂-saturated melts of CaMgSi₂O₆ (Di) and NaCaAlSi₂O₆ (Sm) composition by Mysen and Virgo (1980). They concluded, as did White (1974) and Verweij et al. (1977) for other compositions, that this is a C-O stretch band characteristic of the CO₃⁻ anion. There is no band near 1300 cm⁻¹ to indicate the presence of molecular CO₂ (Rosasco and Simmons, 1974) in An + CO₂. The broadness of the C-O stretch band in these melts compared with the form of the band in less polymerized silicate melts may indicate considerably more disorder (variable bond lengths and bond angles) of the CO₃⁻ complex in quenched An + CO₂ melt than in melts of Di + CO₂ and Sm + CO₂.

The frequency of the two (Si,Al)-O²⁻ bands remains essentially constant with increasing CO₂ content of the quenched An melt (Fig. 1). This result indicates that the Al/(Al + Si) of the individual 3-dimensional units does not change appreciably. The intensity ratio, I(1100)/I(1000), decreases (Fig. 2). This decrease indicates that the proportion of the most aluminous 3-dimensional structural unit decreases relative to that of the more silica-rich unit as carbonate complexes are formed in the melt.

From a spectroscopic point of view, the high-frequency envelope of quenched An + CO₂ can be satisfied with the three bands discussed above. In this case, the bulk Al/(Al + Si) of the melt must have decreased [the intensity ratio, I(1100)/I(1000), de-

**Table 1. CO₂ contents and other run data**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>P, kbar</th>
<th>T, °C</th>
<th>Run Duration, min.</th>
<th>Wt % CO₂</th>
<th>Mole % CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ab</td>
<td>10</td>
<td>1650</td>
<td>5</td>
<td>0.68 ± 0.02</td>
<td>3.92</td>
</tr>
<tr>
<td>Ab</td>
<td>20</td>
<td>1650</td>
<td>5</td>
<td>1.87 ± 0.04</td>
<td>10.19</td>
</tr>
<tr>
<td>Ab</td>
<td>20</td>
<td>1700</td>
<td>5</td>
<td>2.05 ± 0.05</td>
<td>11.09</td>
</tr>
<tr>
<td>Ab</td>
<td>20</td>
<td>1750</td>
<td>5</td>
<td>2.22 ± 0.05</td>
<td>11.91</td>
</tr>
<tr>
<td>Ab</td>
<td>30</td>
<td>1450</td>
<td>15</td>
<td>2.06 ± 0.04</td>
<td>11.13</td>
</tr>
<tr>
<td>Ab</td>
<td>30</td>
<td>1550</td>
<td>15</td>
<td>2.31 ± 0.04</td>
<td>12.34</td>
</tr>
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<td>1650</td>
<td>5</td>
<td>2.87 ± 0.09</td>
<td>14.96</td>
</tr>
<tr>
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<td>5</td>
<td>3.20 ± 0.05</td>
<td>16.44</td>
</tr>
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<td>5</td>
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<td>17.89</td>
</tr>
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<td>5</td>
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<tr>
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<td>15</td>
<td>1750</td>
<td>5</td>
<td>1.98 ± 0.05</td>
<td>11.32</td>
</tr>
<tr>
<td>An</td>
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<td>1750</td>
<td>5</td>
<td>2.68 ± 0.08</td>
<td>14.82</td>
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<td>25</td>
<td>1750</td>
<td>5</td>
<td>3.61 ± 0.09</td>
<td>19.13</td>
</tr>
<tr>
<td>An</td>
<td>25</td>
<td>1790</td>
<td>5</td>
<td>2.94 ± 0.09</td>
<td>16.06</td>
</tr>
</tbody>
</table>
creases with increasing CO₂ content). This decrease of Al/(Al + Si) can be accomplished in two ways. The carbonate complex may be stabilized as an aluminum carbonate complex. If this is the case, an amount of Ca²⁺ equivalent to the aluminum in the carbonate complex is no longer needed to charge-balance Al³⁺ in the 3-dimensional network. This Ca²⁺ is now a network modifier, thus producing non-

![CaAl₂Si₂O₈ + CO₂](image)

Fig. 1. Raman spectra of quenched melts in the system CaAl₂Si₂O₈–CO₂ as a function of CO₂ content (calculated on the basis of 8 oxygens).

![Fig. 2. Shifts of intensity ratio I(1100)/I(1000) as a function of mole percent CO₂ (O = 8) in solution for melts of Ab + CO₂ and An + CO₂ composition.](image)

bridging oxygens in the melt. Such a mechanism has been proposed for the solution of P₂O₅ in An melt, for example (Mysen et al., 1980b).

An alternative explanation for the decreased bulk Al/(Al + Si) is that the carbonate is a calcium carbonate complex much like that found in quenched Di and Sm melts with CO₂ (Mysen and Virgo, 1980). If this solution mechanism is correct, an amount of Al³⁺ equivalent to that needed to form the (CaCO₃) complex in the melt is no longer charge-balanced in tetrahedral coordination and will leave the network (Mysen et al., 1980a). As this Al³⁺ leaves the network, the Al/(Al + Si) of the remaining 3-dimensional units will have decreased and new nonbridging oxygens will be formed in the melt.

In summary, the existence of CO₃⁻ and the decrease of Al/(Al + Si) in the three-dimensional network units in quenched An + CO₂ melt require that nonbridging oxygens have been formed. Structural units with NBO result in stretch vibrations that have Raman bands at lower frequencies than Raman bands from structural units with no nonbridging oxygen (Furukawa and White, 1980). As a result of these considerations, a fourth band was fitted in the high-frequency envelope of the Raman spectrum of
quenched An + CO₂ melt. This band occurs between 870 and 880 cm⁻¹ (Fig. 1).

The 870 cm⁻¹ band may result from a sheet or a chain unit in the melt. If the band reflects the presence of a sheet unit, the band has shifted from 1050-1100 cm⁻¹, which is the frequency of Al-free, -O-Si-O⁰ stretching¹ (Furukawa and White, 1980; Verweij, 1979) to 870 cm⁻¹ as a function of Al content of the unit. If the 870 cm⁻¹ band reflects the presence of a chain unit in the melt, the shift would have been from about 950 cm⁻¹ (-O-Si-O⁻ asymmetric stretch; Verweij, 1979; Furukawa and White, 1980) as a consequence of the Al content of the structural unit. A choice between these alternatives cannot be made from the spectroscopic data.

In summary, the Raman spectroscopic data in Figure 1 are interpreted to indicate that solution of carbon dioxide in melt of An composition at high pressure and temperature results in the formation of carbonate complexes. In addition, the melt consists of two discrete 3-dimensional network units that have become depleted in Al relative to the CO₂-free melt. Furthermore, a third aluminum silicate unit with nonbridging oxygens has been formed.

The high-frequency envelope of Raman spectra of quenched melts in the system NaAlSi₃O₈-CO₂ is shown in Figure 3, and detailed data are given in Table 2. The Raman spectrum of CO₂-free, quenched Ab melt at 20 kbar is discussed by Mysen et al. (1980a). The high-frequency envelope of that spectrum is shown here for comparison (Fig. 3). There are two (Si,Al)-O⁰ stretch bands at 1083 and 984 cm⁻¹, where the 1083 cm⁻¹ band is due to the 3-dimensional structural unit with the largest Al/(Al + Si) (Virgo et al., 1979). The structures of An and Ab melt without CO₂ differ only in the Al/(Al + Si) of the two 3-dimensional structural units (Virgo et al., 1979).

At 10 kbar and 1650°C, 3.9 mole percent CO₂ dissolves in Ab melt (Table 1). The Raman spectra of such melts have two distinct bands at 1272 and 1377 cm⁻¹ with an intensity ratio, I(1272)/I(1377), near 0.6. The frequencies and the intensity ratio are characteristic of molecular CO₂ (Herzberg, 1945). There is no clear spectroscopic evidence for more than two bands in the high-frequency envelope. The two

1 The notations -O-Si-O⁰, -O-Si-O⁻, and Si-O⁰ refer to vibrations across an oxygen bond involving two, one, and no nonbridging oxygens, respectively, in the tetrahedron. Such vibrations are characteristic of chain, sheet, and 3-dimensional structural units. The notation (Si,Al) etc. implies the presence of Al in tetrahedral coordination.

![Fig. 3. Raman spectra of quenched melts of Ab + CO₂ composition as a function of CO₂ content (calculated as mole percent on the basis of 8 oxygens).](image-url)
Table 2. Raman spectroscopic data

<table>
<thead>
<tr>
<th>Composition</th>
<th>$P_{\text{F}}$ kbar</th>
<th>$T_{\text{o}}$ °C</th>
<th>Wavenumber, cm$^{-1}$</th>
<th>$I(1100)/I(1000)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>An</td>
<td>20</td>
<td>1760</td>
<td>513s 580(sh) 765(sh)</td>
<td>930m 993s</td>
</tr>
<tr>
<td>An + CO$_2$</td>
<td>10</td>
<td>1750</td>
<td>500s 580(sh) 786(sh)</td>
<td>875w 930m 986s 1073s</td>
</tr>
<tr>
<td>An + CO$_2$</td>
<td>15</td>
<td>1750</td>
<td>500s 570(sh) 786(sh)</td>
<td>882w 940m 978s 1073s</td>
</tr>
<tr>
<td>An + CO$_2$</td>
<td>20</td>
<td>1750</td>
<td>500s 570(sh) 780(sh)</td>
<td>871w 937m 988s 1077s</td>
</tr>
<tr>
<td>Ab</td>
<td>20</td>
<td>1450</td>
<td>468s 573(sh) 774(sh)</td>
<td>983m 1093s</td>
</tr>
<tr>
<td>Ab + CO$_2$</td>
<td>10</td>
<td>1650</td>
<td>470s 567w 786(sh) 950w 980s 1093s</td>
<td>1273m 1377a</td>
</tr>
<tr>
<td>Ab + CO$_2$</td>
<td>20</td>
<td>1600</td>
<td>468s 567w 780(sh) 1008s 1120s 1075s</td>
<td>1379a</td>
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<td>30</td>
<td>1700</td>
<td>473s 568(sh) 783(sh) 950m 1014s 1130s 1077s</td>
<td>1376a</td>
</tr>
</tbody>
</table>

*Abbreviations: (sh), shoulder; w, weak; m, medium; s, strong.

The $I(1100)/I(1000)$ reflects the $I(990)/I(930)$ in melts of An composition and $I(1100)/I(1000)$ in melts of Ab composition.

The addition of 11.1 mole percent CO$_2$ (calculated on the basis of 8 oxygens) to Ab melt results in several spectroscopic changes. Only one band (at 1379 cm$^{-1}$) characteristic of molecular CO$_2$ is observed (Fig. 3). The elimination of the 1272 cm$^{-1}$ band indicates that the symmetry of the CO$_2$ molecule has changed as the pressure is increased from 10 kbar and the CO$_2$ content has been increased from 3.9 to 11.1 mole percent.

The high-frequency envelope of quenched Ab + 11.1 mole percent CO$_2$ indicates the presence of at least three bands. These bands are near 1000, 1070, and 1120 cm$^{-1}$, respectively (Fig. 3). Bands were fitted near these frequencies. The 1008 and 1120 cm$^{-1}$ bands are the (Si,Al)-O$^-$ stretch bands indicative of two 3-dimensional structural units (Virgo et al., 1979; Mysen et al., 1980a). Their higher frequencies compared with the spectrum of CO$_2$-free, quenched Ab melt indicate that the AI/(Al + Si) of both structural units has been lowered. According to the calibration curve of Virgo et al. (1979), there is about a 20 percent reduction. The intensity ratio $I(1100)/I(1000)$ of quenched Ab + 11.1 mole percent CO$_2$ has also decreased relative to its value for quenched Ab + 3.9 mole percent CO$_2$ and CO$_2$-free, quenched Ab melt (Fig. 2; see also Table 2). This decrease further indicates a bulk decrease of AI/(Al + Si) of the 3-dimensional portion of the melt.

The 1075 cm$^{-1}$ band is the C-O stretch band characteristic of CO$_3^-$ complexes in quenched Ab + 11.1 mole percent CO$_2$. In the light of the above considerations, the discussion by Mysen et al. (1980a), and the discussion of the spectra of quenched An + CO$_2$ melt, quenched Ab + 11.1 mole percent CO$_2$ must contain nonbridging oxygen. The (Si,Al) stretch band reflecting the structural unit with nonbridging oxygen occurs at 950 cm$^{-1}$ (Fig. 3). If this structural unit is of the chain type, its frequency (950 cm$^{-1}$) coincides with that of -O-Si-O- asymmetric vibrations in Al-free systems (Brawer and White, 1975; Furukawa and White, 1980). Inasmuch as Ab melt contains a large proportion of aluminum, it is likely that this structural unit also contains Al$^{3+}$. In that case, the NBO/T of this unit must be less than 2. Mysen et al. (1980a) concluded that silicate melts relevant to rock-forming processes contain only monomers, dimers, chains, sheets, and 3-dimensional units. In view of the frequency of the 950 cm$^{-1}$ band, it is likely, therefore, that the structural unit with nonbridging oxygen in CO$_2$-bearing, quenched Ab melt is an aluminous sheet unit.

The Raman spectrum of quenched Ab melt with 16.7 mole percent CO$_2$ closely resembles that of quenched Ab + 11.1 mole percent CO$_2$ melt (Fig. 3; see also Table 2). The intensity of the 1075 and 950 cm$^{-1}$ bands has increased somewhat, but their frequencies have remained constant. Thus the proportion of carbonate anion and the structural unit with NBO have both increased with increasing CO$_2$ content of the melt. Finally, the $I(1100)/I(1000)$ is reduced further as the CO$_2$ content of the quenched Ab melt has increased from 11.1 to 16.7 mole percent.

In summary, the Raman spectra of quenched Ab + CO$_2$ melts indicate that the CO$_2$ is present as molecular CO$_2$ and as CO$_3^-$ where the proportion of CO$_3^-$ in the melt increases with increasing bulk CO$_2$ content. There are two 3-dimensional network units whose AI/(Al + Si) decreases as a function of CO$_2$ content of the melt and a structural unit with NBO/T greater than 0. The proportion of the latter unit also increases with increasing CO$_2$ content of the melt. With the exception of the possible presence of
dissolved molecular CO₂ in quenched Ab melt, the structures of quenched, CO₂-saturated melts of both CaAl₂Si₂O₈ and NaAlSi₃O₈ composition are similar.

**Solution mechanisms**

Before the interaction of CO₂ with the aluminosilicate melt structures is discussed, it is necessary to assess whether the spectroscopic evidence for molecular CO₂ in quenched Ab + CO₂ melt reflects molecular CO₂ in solution or CO₂-rich gas bubbles that are trapped in the quenched melts. Note that Mysen (1976) observed the presence of molecular CO₂ in quenched Ab + CO₂ melt on the basis of infrared measurements. He concluded, from SEM studies of the quenched melts with up to ×20,000 magnification (resolution: 0.005 μm), that the CO₂ is not present as bubbles. That evidence, however, does not rule out the presence of even smaller CO₂ bubbles.

The change of symmetry of the CO₂ molecule with increasing CO₂ concentration indicates that the CO₂ observed in the Raman spectra is related to the melt either as a quench feature (exsolved CO₂ from the melt during quenching) or as dissolved molecular CO₂. If the CO₂ were simply trapped stable vapor from the gas phase present during the experiments, it is unlikely that the gas molecules would be affected by the amount of CO₂ present.

The beta-track maps for carbon-14 indicate that carbon is homogeneously distributed in the quenched melt on an optical scale. Consequently, if the molecular CO₂ results from trapped submicroscopic bubbles, these bubbles must be homogeneously distributed in the sample. In other examples of exsolution of vapor from a melt during quenching, the residual volatile in the quenched melt tends to be heterogeneously distributed. This heterogeneity results from intermittent temperature, pressure, and activity gradients in the melt during the quenching. The consequence of this reasoning is that the molecular CO₂ in quenched Ab + CO₂ melt is, in fact, dissolved in the melt.

It is perhaps more important to determine the role of the carbonate complexes in the quenched melts in the system CaAl₂Si₂O₈–NaAlSi₃O₈–CO₂. These could be either aluminum or metal carbonate complexes. Silicon carbonate complexes are ruled out on the basis of the increased Si/(Si + Al) of the aluminosilicate portion of the melt and the absence of any Raman bands that could be assigned to Si–O–C stretching. The Si/(Si + Al) of the aluminosilicate portion of the melts would increase whether the carbonate is an aluminum or a metal carbonate, as discussed above. Furthermore, both types of complexes would result in the formation of nonbridging oxygens in the melt. Solubility studies and Raman spectroscopic work on carbon dioxide in (Ca,Mg) ortho- and meta-silicate melts at high pressures and temperatures (Holloway et al., 1976; Mysen and Virgo, 1980) indicate that the carbonate complex in those melts is closely associated with the metal cation (Ca²⁺). We conclude, therefore, that metal carbonate complexes of the type (CaCO₃)⁰ or (MgCO₃)⁰ do occur in silicate melts. We also note that in all determinations of the crystal structure of carbonate-bearing silicates the carbonate complex is bonded to the metal cation and not to the silicate framework (Smith, 1953; Smith et al., 1960; Papke and Stephenson, 1966; Canillo et al., 1973; Lin and Burley, 1973; Pluth and Smith, 1973). Finally, we expect that Al–O–C bonds from aluminum carbonate complexes would result in Raman bands in the frequency region between 600 and 700 cm⁻¹ (Greenwood, 1975). No such band has been found. We conclude, therefore, that the carbonate complexes in quenched An + CO₂ and Ab + CO₂ melts occur as (CaCO₃)⁰ and (Na₂CO₃)⁰ complexes, respectively.

Inasmuch as there is less Al in the 3-dimensional network units of the CO₂-bearing aluminosilicate melts and some of the Na⁺ and Ca²⁺ needed for charge balance of Al³⁺ in tetrahedral coordination now are associated with CO₃⁻, we conclude that some Al³⁺ may no longer be in tetrahedral coordination in the melts. The amount of such Al³⁺ is equivalent to the amount of carbonate formed in the melt. In An melt, the proportion of such Al³⁺ can be calculated from the CO₂ solubility in the melt because all the CO₂ is dissolved as CO₃⁻. The results of such calculations for melts of CaAl₂Si₂O₈ composition are shown in Figure 4. A similar calculation may be made for NaAlSi₃O₈ (Fig. 4). In the latter case, only maximum values for Al³⁺/ΣAl (Al* represents Al²⁺ that is no longer in tetrahedral coordination) can be obtained because some of the dissolved carbon exists as molecular CO₂.

The solubility mechanisms for carbonate formation in melt of NaAlSi₃O₈ composition may be expressed with the following equation:

\[
\begin{align*}
10\text{NaAlSi}_3\text{O}_8 \text{(melt)} + 2\text{CO}_2 \text{(vapor)} & = 6\text{NaAlSi}^2\text{O}_7 \text{(sheet)} + (\text{Na}_2\text{CO}_3)^0 \text{(melt)} + 4\text{Al}^* \text{(melt)} + 24\text{SiO}_2 \text{(3D)}
\end{align*}
\]

The entity called SiO₂ (3D) represents the increase of
Fig. 4. Proportion (percent) of Al\(^{3+}\) not in tetrahedral coordination as a function of CO\(_2\) content (O = 8) of the melt.

\[\frac{\text{Si}/(\text{Si} + \text{Al})}{\text{Si}/(\text{Si} + \text{Al})} \text{ in the 3-dimensional structures as a result of dissolved CO}_2\]. The entity Al* represents the portion of Al\(^{3+}\) that is no longer in tetrahedral coordination as a result of dissolved CO\(_2\). This aluminum is now a network-modifier. The entity (Na\(_2\)CO\(_3\))^\text{9}\ represents the carbonate complex that has been formed in the melt. In this expression, we assume that Al/Si of the sheet unit in the melt equals 1. If Al/Si < 1, a larger proportion of Al\(^{3+}\) is no longer in tetrahedral coordination and some Na\(^+\) will become a network modifier. The Si/(Si + Al) will increase by a smaller amount as a function of increasing CO\(_2\) content. If Al/Si > 1 in the sheet unit in the melt, a smaller proportion of Al\(^{3+}\) is no longer in tetrahedral coordination and Si/(Si + Al) will increase at a greater rate with increasing CO\(_2\) content than when Al/Si = 1.

The analogous expression for CO\(_2\) solution in melt of CaAl\(_2\)Si\(_2\)O\(_6\) composition is

\[
10\text{CaAl}_2\text{Si}_2\text{O}_8 \text{(melt)} + 4\text{CO}_2 = 6\text{CaAl}_2\text{Si}_2\text{O}_{10}^{+} \text{(sheet)} + 4(\text{CaCO}_3)^9 \text{(melt)} + 8\text{Al}^* \text{(melt)} + 8\text{SiO}_2 \text{(3D)}
\]

The solubility mechanism summarized in equations 1 and 2 shows that solution of CO\(_2\) in aluminosilicate melts with 3-dimensional network results in the formation of nonbridging oxygens. Mysen and Virgo (1980) noted that solution of CO\(_2\) in melt of NaCaAl\(_2\)Si\(_2\)O\(_4\) composition (NBO/T = 0.67) also results in the formation of new nonbridging oxygens through a solution mechanism similar to that shown by equations 1 and 2. This solution mechanism differs from that of melts without amphoteric oxides (e.g., Al\(_2\)O\(_3\)) for which Mysen and Virgo (1980) found that the following equation can be used to express the solution mechanism:

\[
5\text{Si}_2\text{O}_6^- \text{(chain)} + 2\text{CO}_2 \text{(vapor)} = 2\text{SiO}_4^- \text{(monomer)} + 4\text{Si}_2\text{O}_3^- \text{(sheet)} + 2\text{CO}_2^- \text{(melt)}
\]

(3)

Because the ratio of proportions Si\(_2\)O\(_6^-\)/SiO\(_4^-\) in equation 3 is greater than 1, solution of CO\(_2\) in such melts results in a bulk decrease of NBO/T, as first suggested by Eggler (1973) on the basis of phase-equilibrium measurements and solubility studies.

It should be emphasized that in both cases mentioned above the carbonate complex is associated with metal cations. If the metal cation is removed from a charge-balanced complex of Al\(^{3+}\) in a silicate polymer, this polymer will be broken up and the melt becomes less polymerized. If the metal cation is a modifying cation in the CO\(_2\)-free melt, the melt becomes more polymerized as CO\(_2\) is dissolved.

### Applications

Trace-element partition coefficients for transition metals and rare earth elements are very sensitive to NBO/T of the melt. Mysen et al. (1980c) have shown, for example, that at 1500°C and 1 atm, \(K_{\text{Ni-Si oxy}}\) decreases in a linear fashion by about 50 percent as NBO/T of the melt increases by about 0.2 unit. Solution of 15–20 mole percent CO\(_2\) (about 2.5 wt. percent) in a melt rich in plagioclase component also results in a decrease of NBO/T of about 0.2 unit. Consequently, nickel partition coefficients between a diopside clinopyroxene and a melt that is rich in plagioclase component (e.g., andesite) will decrease by about 50 percent if 2–3 wt. percent CO\(_2\) is dissolved in the melt. Similar calculations can be made for other trace elements (e.g., REE) and other crystal–liquid pairs.

Relatively little is known about phase equilibria of highly polymerized systems in the presence of CO\(_2\). Inasmuch as NBO/T of the melts increases with increasing CO\(_2\) content, it is expected that the liquidus minerals would be less polymerized (less silica-rich) in the presence of CO\(_2\) than in its absence. Pyroxene–plagioclase liquidus boundaries shift toward the silica-deficient portions of systems, for example, as a consequence of this solution mechanism.
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