The system SiO₂–H₂O–CO₂: melting, solubility mechanisms of carbon, and liquid structure to high pressures

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Abstract

To serve as a model for the solubility mechanisms of carbon in silicate liquids and as a model for melting relationships in systems containing multi-component vapors, the system SiO₂–H₂O–CO₂ was investigated to pressures of 27.5 kbar and temperatures from 1000 to 1650°C. The solubility of carbon in the hydrous liquids increases markedly above 10–15 kbar, probably entering the liquid as molecular CO₂, possibly in part as tetrahedral carbon. Phase transformations in the high-pressure liquids, such as quartz ≈ coesite structure, may enhance the solubility. The amount of carbon in solution is unknown, particularly at the lower pressures, and this precludes calculation of the activity coefficients of H₂O in the H₂O–CO₂ vapors. The solubility mechanisms and data on the liquids in this system may also apply to the more complex, aluminosilicate magmas.

Introduction

Throughout the last decade, there have been numerous studies of mixed volatile components in silicate systems at high pressures to assess their effect on melting relationships in rock systems (e.g., Wyllie, 1979; Mysen and Boettcher, 1975) and to determine thermodynamic properties of multicomponent fluids (e.g., Eggler and Kadik, 1979; Holloway, 1977). Of particular interest to our research group has been (1) the determination of activity coefficients of H₂O(γH₂O) in H₂O–CO₂ vapors coexisting with aluminosilicates (Bohlen et al. 1982; Bohlen et al., 1983) and (2) the use of phase equilibria to shed light on the thermal and structural properties of aluminosilicate liquids (Boettcher et al., 1982a; 1982b).

Towards these goals, Bohlen et al. (1982) experimentally determined the vapor-saturated solidi in the system NaAlSi₃O₈(Alb)-H₂O–CO₂ up to 25 kbar for various mole fractions of H₂O component in the vapor (xH₂O) from nearly pure H₂O(xH₂O = 1.0) to nearly pure CO₂(xH₂O = 0). These results revealed that CO₂ produces no detectable freezing-point depression and is essentially insoluble below about 15 kbar in the high-temperature, CO₂-rich part of the system. However, the solubility of CO₂ in the lower-temperature Alb–H₂O–CO₂ liquids could not be determined from our results, and for purposes of calculating values of γH₂O, it was assumed to be zero. In this and all other recent studies in our laboratory, care was exercised to remove external sources of H₂O and H₂ that would affect phase relationships (Boettcher et al., 1981).

The values of γH₂O calculated by Bohlen et al. (1982) ranged from nearly ideal values (unity) at large values of xH₂O to > 5.0 at high pressures and low values of xH₂O. Although these values are significantly lower than those calculated by Eggler and Kadik (1979) from their studies of melting, also in the system NaAlSi₃O₈–H₂O–CO₂, both sets of values are higher than those calculated using the Modified Redlich-Kwong formulation (e.g., Kerrick and Jacobs, 1981).

More recently, Bohlen et al. (1983) experimentally investigated melting in the system KAlSi₅O₁₇(Sa)–SiO₂(Qz)–H₂O–CO₂. Here, the calculated values of γH₂O, using the formulation of Burnham (1979) and the assumption that CO₂ is insoluble in the eutectic liquids, are ideal (γH₂O = 1) up to at least 15 kbar and from xH₂O = 0.1 to 1.0, within the uncertainties of the calculated and the experimental results.

Several factors strongly suggest that the disparate results from these two systems result from greater solubility of CO₂ in the NaAlSi₃O₈–H₂O–CO₂ liquids than in those in the system KAlSi₅O₁₇–SiO₂–H₂O–CO₂, yielding large values for the apparent solubility of CO₂ and, therefore, large apparent values of γH₂O. First, the values of γH₂O in the former system increase with pressure at any given value of xH₂O, as would be expected if the solubility of CO₂ in the liquid (xH₂O) increases with pressure. Second, the eutectic liquids in the latter system are richer in Si₄O₁₁ component and are more polymerized than are...
the liquids in the former, and the solubility of CO₂ is expected to be less (e.g., Mysen et al., 1976).

As a result of these uncertainties, I investigated melting relationships in the system SiO₂(Quz)-H₂O-CO₂, which has advantages compared to feldspar-bearing systems because of the compositional simplicity. The solubility of carbon-bearing species in silicate liquids is commonly thought to be predominantly as CO₃²⁻ anion (e.g., Mysen and Virgo, 1980), requiring (1) divalent or monovalent cations such as K⁺ or Ca²⁺ for charge-balance, and (2) non-bridging oxygen (NBO) ions. The system SiO₂-CO₂ has neither of these characteristics, but in the system SiO₂-H₂O-CO₂, if water dissolves as OH by breaking bonds between tetrahedra, NBO ions and H⁺ are created, and CO₃²⁻ may form in the liquid. Alternatively, CO₂⁻ may not be stable in these liquids, and molecular CO₂ or C may be significant species.

**Experimental methods**

**Starting materials (reactants)**

Natural Brazilian quartz was ground under reagent-grade acetone to about 200 mesh, leached in hot HNO₃, and fired at 1100°C for at least 24 hours and then at 800°C for at least 12 hours. Boiled, doubly distilled, deionized water was used as a source of H₂O. For nearly all experiments, the source of CO₂ was silver oxalate (Ag₂C₂O₄), which was dried under soft vacuum at 40°C for at least 48 hours and stored in a vacuum desiccator over KOH. Each batch of the Ag₂C₂O₄ was checked for purity and stoichiometry by the method described by Bohlen et al. (1982). For some of the experiments to prepare Ag-free glasses for spectral analyses and to compare results using different sources of CO₂, oxalic acid (dihydrate) was used. However, uncertainties in the content of H₂O in oxalic acid preclude using it as a source of CO₂ for experiments to determine the vapor-saturated solidi.

For each experiment, ~4 to 30 mg of quartz and appropriate amounts (Table 1) of Ag₂C₂O₄ and/or H₂O were loaded into 2.0-mm diameter Pt capsules welded at each end. These sealed capsules were in turn placed into 3.5-mm diameter Pt capsules with 150-160 mg of sintered hematite (Boettcher et al., 1973), which maintains a low fH₂ and low fCO₂ during the experiments. Special care was required to ensure that the desired quantities of H₂O and Ag₂C₂O₄ remained in the capsules until after they were sealed. The H₂O was loaded and immediately covered with a thin circle of Pt foil to prevent evaporation. Numerous tests demonstrated that this method prevented measurable loss of H₂O that otherwise occurs within several minutes. The capsules were handled only with special pliers during loading; touching them with the hands warmed them and increased evaporation. All weights were measured on a Mettler M-5 microbalance, reproducible to ±0.000002 gr.

**Apparatus and run procedure**

All experiments were conducted in piston-cylinder apparatus with a 25.4-mm diameter furnace assembly and piston. The assembly was constructed of NaCl, BN, AlSiMag, and glass (Boettcher et al., 1981); no hydrous phases such as talc were used, and all lubricants were fluorocarbons to eliminate most sources of H₂. Temperatures were measured and controlled with WRe-WR₂ thermocouples. We used the piston-in technique by bringing the pressure to about 5% below the final value, and then increasing the temperature and pressure, respectively, to the desired values. The furnace assembly was calibrated as described by Bohlen et al. (1982), revealing that the furnace assembly requires no pressure correction.

The vapor-saturated solidi for the various H₂O/CO₂ compositions were determined by noting the temperature of the first appearance of quenched liquid in the run products. To check the attainment of equilibrium for the determination of the vapor-saturated solidi, reversal experiments were conducted in two-stage runs. Here, the initial conditions were those known from other experiments to produce partial melting. The conditions were next changed isobarically to about 10°C below the inferred vapor-saturated solidus and held for sufficient time to react away all liquid, as evidenced by no quenched liquid in the run products.

**Run products**

After the experiments, the hematite, which partially reacts to magnetite during the experiment, was examined optically to ensure that sufficient (~>20%) hematite remained unreacted. The inner capsule was cleaned and boiled in dilute HCl to remove all traces of the hematite-magnetite buffer. It was then weighed, held at -5°C for at least 15 minutes, punctured with a fine needle, reweighed, dried at 112°C for 15 minutes, and reweighed. This procedure permitted verification that the H₂O and CO₂ in the reactants remained throughout the experiment. Successful runs had H₂O/CO₂ ratios usually within 1 mole% of the initial value, except for experiments well above the beginning of melting in which significant amounts of fluid remain in the quenched liquid. Also, the sample capsule would be puffed and hiss audibly when punctured.

The reactants were examined optically in immersion oils. The quartz occurred mostly as anhedral fragments, but euhedra were common in some runs. Attempts to locate the α ≈ β quartz transformation by the morphology of the quenched quartz or by visual evidence of strain in crystals passing through the transformation during quenching were unsuccessful.

The appearance of the quenched liquid varied with the conditions of the experiment. At the lower pressures, liquids quenched to bubble-rich glass, resulting from exsolution of H₂O and CO₂ during quenching. At pressures above ~15 kbar, the liquids dissolve sufficient volatile components to render them black, even opaque and reflective, during quenching (see Boettcher and Wyllie, 1969, especially Plate 1).

Quenched vapor occurs in several forms, commonly in the same experiment. The most obvious forms at pressures below ~15 kbar are the easily recognized glass spheres, appearing individually or in aggregates resembling fish roe. Also common are large (up to 0.5 mm), thin, generally bubble-free plates of glass, which are more abundant than the spheres at higher pressures. In these experiments with H₂O-rich vapors, critical points were encountered where the liquid and vapor coexisting with quartz become identical in all respects. As the critical points are approached from lower pressures, the quenched vapors become more abundant and more like the quenched liquid in appearance. At pressures above those of the critical point, there is no first-order transformation (melting), and the ratio of quenched fluid to quartz increases with increasing temperature until quartz disappears at a temperature that is a function of the bulk composition, as discussed below.
In some experiments, particularly near the vapor-saturated liquid, several percent or less quartz crystallized from the liquid during the quench. Commonly, when the experiment was repeated under similar or the same conditions, no crystalline phase appeared in the run products. The quench quartz was easily recognized by the sheafs of radial intergrowths, commonly in spherical aggregates.

**Experimental results**

Experimental data are presented in Table 1 and in Figure 1. For simplicity, these data are discussed in terms of the bounding sub-systems.

**SiO₂**

At its melting temperature at atmospheric pressure, β-quartz is presumably metastable with respect to tridymite (Fig. 1). However, the quartz ⇄ tridymite reaction is extremely sluggish at this temperature (if it occurs at all), and MacKenzie (1960) was able to experimentally partially fuse quartz at 1450°C in 2 hours, but no evidence of reaction occurred at 1400°C for a similar duration. Although the lower limit is uncertain, these data are consistent with the values of Gibbs free energy of fusion recently compiled by Richet et al. (1982). Following Richet et al., I have adopted a temperature of 1700 K (1427°C).

The melting of β-quartz from 7 to 25 kbar was experimentally determined by Jackson (1976). If we adopt a triple point between cristobalite, β-quartz, and liquid and the fusion temperature of cristobalite at atmospheric pressure of Greig (1927), then the fusion curve of cristobalite has a negative dP/dT slope (Fig. 1). The uncertainties in the high-temperature part of this system are large.

**SiO₂-H₂O**

Previous investigations in this system that bear on this study are those of Kennedy et al. (1962) and Stewart (1967) to pressures of 10 kbar; Ostrovskii et al. (1959) determined the temperature of the beginning of melting to vapor pressures of about 5 kbar. The results of all three studies are consonant with a temperature of 1130±10°C for the vapor-saturated solidus at 2 kbar. At 5 kbar, the brackets of Kennedy et al., Stewart, and Ostrovskii et al. are 1089–1095°C, 1055–1070°C, and ~1080°C. Similarly, at about 10 kbar, the values of Stewart (1040–1050°C) are lower than those of Kennedy et al. (1073–1086°C). The results of this study from 7 to 10 kbar are intermediate between those of Stewart and Kennedy et al. (e.g., 1060–1070°C at 9 kbar). The vapor-saturated solidus in Figures 1 and 2 is based on my brackets at 7 and 9 kbar and an average of the Kennedy et al. and Stewart data at 5 kbar.

Kennedy et al. concluded that the vapor-saturated solidus terminates at a critical end-point (point K₂ in Fig. 1), where the liquid and vapor in equilibrium with quartz are equal in all respects. Stewart’s data suggest that K₂ should be somewhat above 10 kbar. Because the compositions of liquid and vapor change markedly with pressure

**Table 1. Experimental results for SiO₂-H₂O-CO₂**

<table>
<thead>
<tr>
<th>Run #</th>
<th>$N_{H₂O}$</th>
<th>$N_{SiO₂}$</th>
<th>P (kbar)</th>
<th>Temp (°C)</th>
<th>Duration (h)</th>
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<td>20.0</td>
<td>7.0</td>
<td>1060</td>
<td>3.0</td>
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</tr>
<tr>
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<td>1.0</td>
<td>19.4</td>
<td>7.0</td>
<td>1065</td>
<td>4.0</td>
<td>Qe+LV</td>
</tr>
<tr>
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<td>20.0</td>
<td>7.0</td>
<td>1055</td>
<td>3.0</td>
<td>Qe+LV(3)</td>
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<tr>
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<td>20.0</td>
<td>9.0</td>
<td>1060</td>
<td>4.0</td>
<td>Qe+LV</td>
</tr>
<tr>
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<td>20.0</td>
<td>9.0</td>
<td>1090</td>
<td>2.0</td>
<td>Qe+V</td>
</tr>
<tr>
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<td>13.0</td>
<td>1030</td>
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<tr>
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<td>Qe+V</td>
<td></td>
</tr>
</tbody>
</table>

The experimental data are presented in Table 1 and in Figures 1 and 2.
near the critical end-point (e.g., see Kennedy et al., Fig. 8), the exact pressure is difficult to establish. A pressure of 10 kbar is consistent with my results at 9 kbar, where the beginning of melting was bracketed between 1060 and 1070°C, and at 11 kbar, where no first-order melting
reaction was observed and all of the run products contained glass that resembles quench liquid. A pressure of 10 kbar for $K^1_1$ is also consistent with the critical phenomena in the ternary system, as discussed below.

$SiO_2-H_2O-CO_2$

There are no previous studies of melting relationships in this system. However, Shettel (1973) investigated the solubility of quartz in the vapor in this system at 500–900°C at 5 kbar, and Nakamura (1974) studied the effects of reduced activities of H$_2$O on melting in the system $SiO_2-H_2O-H_2$.

The results of the experiments for various values of mole fraction of H$_2$O in the vapor ($X_{H_2O}$) are shown in Table I and Figure 1. In this figure, it should be noted that the vapor-saturated solidi do not always pass between the illustrated experimental brackets. This occurs because some of the capsules contain a slight excess or deficiency of H$_2$O relative to CO$_2$ (see Table 1), and the beginning of melting is thus slightly shifted up or down in temperature relative to the values expected for the labeled curves.

Some comparison experiments (e.g. #2665 for $X_{H_2O} = 0.5$) in Table 1 were performed with oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) as a source of CO$_2$ to ensure that the Ag in the Ag$_2C_2O_4$ did not affect phase relationships. However, a rigorous comparison is not possible because of the uncertainties in the H$_2$O content of oxalic acid (Boettcher et al., 1973). Experiments with Ag$_2C_2O_4$ and $C_2H_2O_4 \cdot 2H_2O$ were performed at the various vapor-saturated liquidi to elucidate phase relationships, which are discussed below, and to prepare glasses for Raman and infrared spectroscopy.

The vapor-saturated solidi for the larger values of ($X_{H_2O}$) intersect the $\alpha Qz \leftrightarrow \beta Qz$ transition boundary as determined by Cohen and Klement (1967). This transition may not be first-order, i.e., it may not exhibit a discontinuity in entropy or volume (Klement and Cohen, 1968, p. 2257), but such discontinuities ($\Delta_mS$ and $\Delta_mV$) are consistent with the brackets in Figure 1 and with changes in the slopes of univariant curves in other systems at high pressures and temperatures (e.g., Bohlen et al., 1980a; 1980b).

As shown in Figure 1, the vapor-saturated solidi for the H$_2$O-rich compositions terminate at critical points similar
to that encountered for SiO$_2$-H$_2$O (K$_i$). These points (e.g., K$_A$ for X$_{H_2O}$ = 0.95) are unlike K$_i$ in that they are not critical end-points and they are ternary. Ternary critical end-points occur where the critical phase coexists with two other phases (Boettcher and Wyllie, 1969); at points such as K$_A$, the critical fluid (L = V) coexists with quartz only.

The curves in Figure 1 labelled 0.95, 0.8, 0.6, etc., including that terminated by point K$_A$, are isopleths (constant X$_{H_2O}$) on a ternary, divariant surface in pressure-temperature-X$_{H_2O}$ space, similar to Wyllie’s (1962) petrogenetic model, where solid, liquid, and vapor coexist. Although these curves are ternary and univariant, they are the loci of points where only three phases coexist. That is, the variance (variations of phase) of the three-phase assemblage is reduced by one because of the restriction that the ratio of H$_2$O/CO$_2$ is constant along each curve.

The H$_2$O-rich part of the ternary, three-phase surface terminates along a smooth curve connecting points K$_i$, K$_A$, etc.; the termination is shown in projection in Figure 1 as the dashed curve L = V, (Qz), using the notation of Greig (1954). For compositions with X$_{H_2O}$ equal to or less than about 0.9, vapors and liquids remain as discreet phases to the highest pressures investigated (27.5 kbar). Although the solubility of carbon in the hydrous SiO$_2$ liquids increases markedly above about 10–15 kbar, the solubility of SiO$_2$ component in the vapors remains too low to form a critical point; that is, the miscibility gap between the liquids and vapors does not close. This is consonant with the conclusions of Shettel (1973) at 5 kbar that CO$_2$ greatly diminishes the solubility of SiO$_2$ in the vapor. The trajectory of the L = V, (Qz) curve is drawn to be consistent with the conclusion of Kennedy et al. (1962) that the critical end-point for SiO$_2$-H$_2$O is near 10 kbar.

Properties of liquids and vapors

Two of the major reasons for investigating this system were (1) to establish the conditions, if any, at which activity coefficients for H$_2$O in the vapor ($\gamma_{H_2O}$) could be determined from the phase relationships and (2) to determine the solubility, if detectable, of carbon in the ternary liquids and to use these data to shed light on the structures of the liquids.

Activity of H$_2$O in the H$_2$O–CO$_2$ vapor

Our earlier results in the system NaAlSi$_3$O$_8$-H$_2$O-CO$_2$ did not allow calculation of $\gamma_{H_2O}$ because of the significant, but unknown, quantities of carbon dissolved in the liquids; that is, the freezing-point depression attributable to H$_2$O was unknown. Although our results in the system KAlSi$_3$O$_8$-SiO$_2$-H$_2$O-CO$_2$ are consistent with values of $\gamma_{H_2O}$ equal to unity, we had to assume that carbon was totally insoluble in the liquid below 15 kbar; although not unreasonable for such SiO$_2$-rich compositions, this assumption remains unsubstantiated.

Similarly, to compare the experimental results (Fig. 1) in the SiO$_2$-H$_2$O-CO$_2$ system with those calculated assuming $\gamma_{H_2O}$ = unity, I used the procedure of Burnham (1981; 1979, particularly p. 446–448 and 458–461) to calculate the relationships in Figure 2. I calculated a value of 0.233 cal/bar for SiO$_2$ for the volume of melting of quartz ($\Delta V_{Qz}$) using the fusion curve of Jackson (1976) and the Gibbs free energy of melting ($\Delta_m G^\circ_{Qz}$) of Richet et al. (1982); this value compares favorably with the value of 0.232 cal/bar proposed by Burnham (1981). The values of $\Delta_m G^\circ_{Qz}$ of Richet et al. at lower temperatures do not agree with those derived from the experimental SiO$_2$-H$_2$O liquidus. Therefore, I calculated $\Delta_m G^\circ_{Qz}$ values using the solubility data of Kennedy et al. ($X_{H_2O}$ = 0.398 for SiO$_2$ at 2.0 kbar, 1125°C) and equations 16-12 and 16-14 of Burnham (1979). This calculated value of $\Delta_m G^\circ_{Qz}$ at 1398 K is 2313 cal, compared to 1386 cal from Richet et al. and 2267 cal from Burnham (1981, p. 207, assuming a melting temperature of quartz of 1715 K).

Clearly, there are many uncertainties involved in the calculated curves in Figure 2, as evidenced by the discrepancies in the positions of the curves of $X_{H_2O}$ = 1.0 and 0.0 compared to those determined experimentally. Nevertheless, the calculated curves do serve as a basis for discussion of the experimental results. In the calculated version, the temperatures of the curves for the various values of $X_{H_2O}$ increase at a nearly constant rate at any given pressure; similar configurations occur for the experimental solidi in NaAlSi$_3$O$_8$-H$_2$O-CO$_2$ and KAlSi$_3$O$_8$-SiO$_2$-H$_2$O-CO$_2$. However, the solidi for SiO$_2$-H$_2$O-CO$_2$ (Fig. 1) increase in temperature in an irregular, unpredictable manner. This probably results from complications in the solution of H$_2$O and CO$_2$ in the liquid, because the vapor is essentially pure H$_2$O-CO$_2$ at, say, 7 kbar, similar to those for the other two systems (see Eggler and Kadik, 1979, Fig. 2). I have no detailed explanation as to why this irregularity occurs in SiO$_2$-H$_2$O-CO$_2$, but not in KAlSi$_3$O$_8$-SiO$_2$-H$_2$O-CO$_2$; substitution of H$^+$ for K$^+$ (see Burnham, 1979) in the liquids of the latter system is one obvious difference in the solubility mechanisms.

Because of the complications associated with the solution of carbon in these silicate liquids, there is no way to use the melting curves to calculate $\gamma_{H_2O}$. At present, the best technique may be to obtain tightly constrained reversals on sub-solidus decarbonation or dehydration reactions in the presence of H$_2$O-CO$_2$ vapors. Until then, the near-ideal values obtainable from the KAlSi$_3$O$_8$-SiO$_2$-H$_2$O-CO$_2$ system appear to be the most reliable, and they agree fairly well with the values of $\gamma_{H_2O}$ of <1.5 at 700–800°C up to 15 kbar calculated from the modified Redlich-Kwong formulation (Kerrick and Jacobs, 1981).

Liquid structure and solubility mechanism of carbon

In the pressure interval up to about 10 kbar, there is no unequivocal evidence that CO$_2$, or carbon in any form, is appreciably soluble in the hydrous, silicate liquids. There
Fig. 2. Pressure-temperature projection for SiO$_2$-H$_2$O-CO$_2$ calculated using the method of Burnham (1979). The heavy curves are vapor-saturated solidi for the indicated values of $X_{H_2O}$. The lighter curves that are subparallel to the temperature axis are calculated isopleths (in mole%) of the solubility of H$_2$O in the liquid [on the L(V) surface]. The lighter curves with the steeper P-T slopes are calculated H$_2$O isopleths (in mole%) on the albite-H$_2$O liquidus [the L(S) surface]. The vapor-saturated solidus for $X_{H_2O} = 1.0$ is at the intersection of these L(S) and L(V) surfaces. $K_f$ is a critical end-point plotted at pressures determined experimentally (see Fig. 1). The experimental curve for the solidus for $X_{H_2O} = 1.0$ is from this study, Stewart (1967), and Kennedy et al. (1962).

is no observational evidence in the run products that suggests that carbon or CO$_2$ occurred in the liquids during the experiments. Also, the general configurations of the solidi in Figure 1 in this range resemble those in Figure 2, calculated assuming no solubility of carbon; however, the assumptions required to calculate these curves, including those of the activity-composition relationships in the system SiO$_2$-H$_2$O, possibly do not warrant this comparison.

At higher pressures, there are several lines of evidence that carbon in some form is dissolving in the liquids. First, the quenched liquids commonly contain two-phase fluid inclusions, presumably liquid H$_2$O and gaseous CO$_2$, that exsolved during the quench. Second, curves for the beginning of melting for H$_2$O-rich compositions terminate at critical points, where the liquid and vapor are identical in composition. At these conditions, the ratios of the components H$_2$O/CO$_2$ in the liquid and vapor are the same as that in the bulk composition (assuming that no H$_2$O and CO$_2$ dissolve in the quartz), but the absolute H$_2$O and CO$_2$ contents are unknown because the SiO$_2$ contents are unknown. In the system SiO$_2$-H$_2$O, Kennedy et al. (1962) reported that the critical fluid at the end-point contains $\sim 75$ wt.% (47.3 mole%) SiO$_2$. A similar percentage for the ternary liquids would yield a solubility of 1.3 wt.% CO$_2$ at point $K_A$.

A third line of evidence that carbon is dissolving in the liquids at the higher pressures are the negative slopes of the melting curves in Figure 1 for $X_{H_2O} \geq 0.5$. Thus, the experimentally determined melting curves are consistent with the concept that H$_2$O dissolves in the SiO$_2$-rich liquid (either as OH$^-$ (Burnham, 1979) or as H$_2$O + OH$^-$ (Stolper, 1982)) and attains near-maximum solubility at about 15 kbar. At high pressures, carbon becomes quite soluble, resulting in the observed freezing-point depression, similar to that observed above $\sim 15$ kbar for NaAl-SiO$_2$-CO$_2$ (Bohlen et al., 1982). The melting curve for $X_{H_2O} = 0.3$ (Fig. 1) is remarkably similar to the calculated curve (Fig. 2); this may be the result of nearly ideal behavior and the insolubility of carbon in these higher temperature liquids.

Any proposed mechanism by which carbon dissolves in the liquids is necessarily conjectural, but some limitations are possible. Non-bridging oxygen ions and mono- or divalent cations are probably necessary for the formation of CO$_3^{2-}$ species (Mysen and Virgo, 1980). In this system, water must dissolve as OH$^-$ by breaking bonds between Si-O tetrahedra to produce NBO ions and H$^+$. Al$_2$(CO$_3$)$_3$ is unknown as a crystalline solid and may not occur in liquids; it is less likely that Si$_2$(CO$_3$)$_4$ is a significant species in the liquid. It is conceivable that a carbon ion could be singly bonded to two bridging oxygen ions, each in different SiO$_2$ tetrahedra, and doubly bonded to a third bridging oxygen, but this would result in depolymerization of the liquid, rather than the polymerization observed with CO$_2$ in other systems (e.g., Mysen and Virgo, 1980).

It is also conceivable that carbon substitutes for Si in the tetrahedral sites of the liquid structure. Using a tetrahedral C-O bond length of 0.1378 nm estimated from the valence and electron configuration determined from the empirical trends of Brown and Shannon (1973), the closest O-O distance is $\sim 0.225$ nm (Wayne Dollase, UCLA, pers. comm., 1983). Although this is short relative to the 0.265 nm distances in silicates and even the 0.24 nm O-O distances in sulphates, it is comparable to the O-O distance in the planar NO$_3$ groups of nitrates (0.215 nm). Thus, tetrahedral carbon may be a significant component at high pressures. At present, we have insufficient data to compare the $\Delta V$ of solution as molecular CO$_2$ vs. that as tetrahedral carbon.

Also conceivable is the entry of carbon into the liquid as molecular CO$_2$. Increased solubility of the large CO$_2$ molecule at high pressures in aluminosilicate liquids might result from depolymerization of the liquid as Al transforms to octahedral coordination. Similarly, the in-
crease in the solubility of CO₂ with the addition of H₂O might also result from the disruption of the liquid as H₂O breaks some of the Si-O bonds (Burnham, 1979). The first mechanism is not applicable to the system SiO₂−H₂O−CO₂; the latter mechanism will result in depression of the freezing point by CO₂ only if entry of the CO₂ changes the energy of the system by breaking or distorting bonds in the liquid. Simple entry of CO₂ molecules as a microemulsion will not produce the observed freezing-point depression. Additional evidence for the solubility of CO₂ at high pressures in this system is found in the recent work of Fine and Stolper (1983). Using infrared spectroscopy on one of the glasses synthesized in this study (run #790), they detected only CO₂ without CO₃²⁻.

Another possible explanation for the negative slopes of the melting curves at high pressures, and one that bears on the solubility of CO₂, is that the liquids in the 20-kbar range undergo transitions analogous to quartz ⇄ coesite, resulting in an increase in density of the liquids. Transformations in liquids at pressures lower than those at which similar changes occur in the crystalline solids have been proposed for other systems, e.g., albite ⇄ jadeite + quartz, where Al changes from 4-fold to 6-fold coordination (Burnham, 1981; Boettcher et al., 1982a), and the electronic promotion in Cs (Klement and Jayaraman, 1966). It is conceivable that diminution of volume associated with structural changes in the liquids in the system SiO₂−H₂O−CO₂ contribute to the negative slopes of the fusion curves.

In a manner similar to depolymerization accompanying the change from tetrahedral to octahedral Al, the change from quartz to coesite structure in the liquid might open the structure and increase the solubility of CO₂, although no change in the coordination of Si occurs. The configuration of the SiO₄ tetrahedra in coesite is nearly unique in that one corner of every other tetrahedron is oriented 180° to another. Thus, although the coesite structure is denser than that of quartz, the peculiar orientation of some of the tetrahedra may permit ingress of CO₂ molecules.

In summary, molecular CO₂ and/or tetrahedral carbon may be significant components in this system at high pressures, and they may also be of importance in geologically relevant aluminosilicate liquids.

**Petrologic phase relationships**

Phase relationships in the system SiO₂−H₂O−CO₂ are conceptually simple and provide a useful basis for discussion of petrologic principles in multicomponent systems with two or more volatile components. For this purpose, let us use isobaric, polythermal diagrams similar to those developed by Wyllie and Tuttle (1960) and used extensively in the literature to portray phase elements on *liquidus* and *vapor-saturated liquidus*. Figure 3 schematically shows three-phase triangles that illustrate the composition of coexisting solid, liquid, and vapor at isobaric, isothermal conditions. At low pressures, the solubilities of H₂O and CO₂ in the liquid [as portrayed by the curve L(Qz,V)] are low; similarly, the solubility of SiO₂ in the vapor [V(Qz,L)] is low. At any temperature at this pressure, the compositions of the coexisting phases can be represented by a 3-phase triangle. At a pressure of ~10 kbar, not shown in Figure 3, the V(Qz,L) and L(Qz,V) curves meet at the binary critical end-point K₁ on the SiO₂−H₂O sideline. At higher pressures, this point moves into the triangle as a ternary critical point L = V, (Qz), as discussed earlier. As shown in Figure 3, as the temperature in the high-pressure diagram is lowered to that of the critical point (Kₐ), which requires an increase in the H₂O/CO₂ ratio to remain in the 3-phase triangle, the compositions of the liquid and vapor coexisting with quartz approach each other, and at Kₐ the triangle degenerates into the tie-line SiO₂−Kₐ, connecting the composition of quartz and the coexisting critical fluid. All compositions on the line labelled 0.95 have the same H₂O/CO₂ ratio and have the same phases, although in different proportions, at any temperature at this or higher pressures (compositions very near the H₂O−CO₂ sideline are an exception, because all of the quartz dissolves in the vapor).

Consider now the beginning of melting of compositions X, X', X'', and X''' under the conditions shown in the inset of Figure 3. All of these compositions have the same H₂O/CO₂ ratio (i.e., the same Xₚ(H₂O)), and they differ only in the ratio of quartz/(H₂O + CO₂); under the conditions shown in the inset, all are in the quartz-vapor field. As the temperature is increased and the triangle moves up-temperature, the Qz-V leg will contact all four compositions at the same temperature, and they will all then consist of quartz + liquid + vapor. Thus, the temperature

![Fig. 3. Schematic isobaric, polythermal projections at low pressure (below K₁, the critical end-point in the system SiO₂−H₂O) and at high pressure (equivalent to that of the critical point Kₐ in Fig. 1). Arrows on the vapor-saturated liquidus [L(Qz,V)] and on the liquid-saturated vaporus [V(Qz,L)] point down temperature. The isobaric, isothermal, 3-phase triangles show the compositions of coexisting quartz, liquid, and vapor. The inset shows the magnified area near the 3-phase triangle (see text).](image)
of the beginning of melting [where \(Qz(L,V)\)] is independent of the proportion of total volatiles, being dependent only on \(X_{H_2O}\).

As temperature continues to rise, the divariant (isobarically univariant), 3-phase field passes over all four compositions; at sufficiently high temperatures, each of the compositions emerges from the 3-phase triangle. For the illustrated conditions, \(X\) and \(X'\) leave the triangle and enter the \(Qz + L\) field (vapor absent) at the same temperature; this is rigorously correct only if the quartz dissolves no \(CO_2\) or \(H_2O\) components. If it does, then the \(Qz-V\) leg of the triangle will not pivot about the point \(SiO_2\). The liquidus, where \(L(Qz)\), for each composition is at a different temperature, as discussed below. In contrast, compositions \(X''\) and \(X'''\) leave the 3-phase triangle and enter the \(L + V\) region, each at a different temperature [that of the vapor-saturated liquidus, \(L(Qz,V)\)].

Thus, the temperature of the vapor-saturated solidus (beginning of melting) is dependent only on \(X_{H_2O}\). For any value of \(X_{H_2O}\) at a given pressure and temperature, the chemical potential of \(H_2O\) \((\mu_{H_2O})\), and those of all of the other components, are buffered. Alternatively, the temperatures of the liquidus and of the vapor-saturated liquidus are functions of \(X_{H_2O}\) (i.e., \(\mu_{H_2O}\) and \(\mu_{CO_2}\)) and the proportion of total volatile components (i.e., the bulk composition). Therefore, when stating temperatures for the liquidus, vapor-saturated liquidus, or the upper temperature limit of a phase, it is necessary to specify the bulk composition. For example, for \(X_{H_2O} = 0.8\), quartz disappears at \(-1280°C\) for 49\% \(H_2O + CO_2\) and at \(-1350°C\) for 31\% \(H_2O + CO_2\) at 15 kbar (Table 1).

It is not difficult to demonstrate that these principles apply to systems with more components and to systems that exhibit crystalline solution involving the non-volatile components. If the mineral phases in this or in more complex systems contain \(CO_2\) and/or \(H_2O\) component, then every composition for a given \(X_{H_2O}\) will have a unique \(\mu_{H_2O}\) and temperature for the beginning of melting, although the differences could be negligible. This can be easily visualized in the system \(SiO_2-H_2O-CO_2\) using Figure 3. If the quartz apex of the 3-phase triangle dissolves \(H_2O\) and/or \(CO_2\), then the \(Qz-V\) leg of the triangle will not rotate parallel to the lines of equal \(H_2O/CO_2\) ratios. As an example, the curves presented by Mysen and Boettcher (1975) for the vapor-saturated solids of amphibole-bearing peridotite in the presence of \(H_2O-CO_2\) vapor are strictly valid only for a specific value of \(H_2O + CO_2\). Although, in this case, the effect of small changes in the proportion of total volatile components is small, it would be significant for systems with large proportions of hydrous or carbonate minerals.

Experimentally, there are two ways to lower \(\mu_{H_2O}\) below that for a nearly pure \(H_2O\) vapor. One, already discussed, is to add another component, such as \(CO_2\), to the vapor. Another is to add a smaller proportion of \(H_2O\) than is necessary to saturate the system and produce all of the potential hydrous solid and/or fluid phases. Figure 4 shows such a situation for the system \(SiO_2-H_2O\). For example, \(SiO_2 + 5\% \ H_2O\) reacts completely to liquid along the vapor-saturated solidus up to about 3 kbar. At higher pressures, there is insufficient \(H_2O\) to saturate the liquid, and \(Qz + L\) coexist isobarically through a temperature interval up to the 5% isopleth, the liquidus for that composition. At pressures above that of the critical end-point \(K_1\), there is no distinction between liquid and vapor, and quartz coexists with a fluid phase up to the liquidus (or fluidus) temperature for that particular isopleth and pressure. For example, runs #548 and 549 define the liquidus between 15 and 18 \(wt.%\) \(H_2O\) at 17.0 kbar and 1380°C. These liquidus [L(S)] in Figure 4 (wt.\%) are analogous to the calculated curves labelled 0.65, 0.6, 0.55, etc. (in mole\%) in Figure 2: Also shown in Figure 2 are the isopleths \((X_{H_2O})\) on the L(V) surface.

It is possible to construct a similar liquidus diagram for the system \(SiO_2-H_2O-CO_2\), but representation is unwieldy because the liquidus are functions of \(X_{H_2O}\) and total volatile content.

**Summary**

The system \(SiO_2-H_2O-CO_2\) is sufficiently compositionally simple to allow investigations of mechanisms that are more complex in other systems, such as those containing feldspar components. The present results reveal that carbon is quite soluble in hydrous-silicate liquids at
pressures above 10–15 kbar, probably dissolving as molecular CO₂, and possibly as tetrahedral carbon. Phase transformations in the liquids change the trajectories of the melting curves and may result in increased solubility of carbon in the liquid.

This system also serves as a model for understanding the effects of changes in μ_H₂O, X₃[H₂O], etc. on melting relationships during the generation of magmas.

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