Natural versus experimental control of oxidation state: Effects on the composition and speciation of C-O-H fluids

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ABSTRACT

In high-pressure, solid-media apparatus, the oxidation state of a sample is usually controlled by imposing a known hydrogen fugacity (f_{H_2}) on the system. The oxidation state of natural systems, in contrast, is often defined by an internally or externally fixed oxygen fugacity (f_{O_2}). This contrast has fundamental implications for the application of experimental results to natural systems containing C-O-H fluids (Eugster and Skippen, 1967).

The composition and speciation of a C-O-H fluid were calculated for a given pressure, temperature, and either an imposed f_{H_2} or an imposed f_{O_2}. The requisite fugacity coefficients were calculated with the modified Redlich-Kwong equation of state (MRK EOS) of Holloway (1977, 1981). Comparison of the composition and speciation of the fluid calculated with the two sets of constraints illustrates the differences between the imposed-f_{O_2} and the imposed-f_{H_2} cases.

The solidus of $NaAlSi_3O_8$(Ab)-C-O-H, with f_{H_2} buffered by Ni-NiO-H_2O (NNO, OH) was experimentally determined at 10 and 15 kbar to constrain the calculations of the composition and speciation of the fluid. The temperature of the solidus of this system is lower than that of Ab-CO_2 by ~90 °C and ~170 °C at 10 and 15 kbar, respectively. With the f_{H_2} fixed by the NNO buffer, the fluid coexists with graphite, and contains 77% CO_2, 16% H_2O, 6.6% CO, and <1% CH_4 and H_2 at 10 kbar and 69% CO_2, 28% H_2O, 2.4% CO, and <1% CH_4 and H_2 at 15 kbar at the temperature of the solidus. The predominance of H_2O and CO_2 in the NNO-buffered fluid allows comparison of these results with previous experimental data for the solidi of Ab-CO_2-H_2O having known values of $CO_2/(CO_2 + H_2O)$ in the fluid (Bohlen et al., 1982). This comparison suggests that the calculated fluid compositions are too H_2O rich.

To achieve fluid compositions with values of f_{O_2} near those of the quartz-fayalite-magnetite (QFM) buffer, as proposed for many regions of the lower crust and upper mantle, the oxidation state of an experiment that contains a mixed-volatile fluid must be controlled by a buffer that has a higher value of f_{O_2} than does QFM, because of the imposition of f_{H_2} rather than f_{O_2} on the sample. Furthermore, the f_{O_2} of the buffer required to maintain the f_{O_2} of the sample at QFM increases with decreasing X_{H_2O} in the vapor; such *continuous* variation in the f_{O_2} of the buffer required to maintain a constant f_{O_2} of the sample is not attainable with present experimental applications of the f_{O_2} buffers.

INTRODUCTION

The oxidation state of a source region of a magma exerts a fundamental control on the conditions under which a magma can be generated, on the composition of the magma once it is generated, and on the composition of a coexisting fluid phase, if one is present. For this reason, it has long been recognized that the oxidation state of an experimental system must be controlled to simulate the natural situation. The oxidation state of either a natural or an experimental system may be quantified by measuring or calculating the oxygen fugacity (f_{O_2}) of the assemblage. This f_{O_2} may be compared with that of other phase assemblages to ascertain the relative degree of oxidation or reduction. The f_{O_2} of a source region may be controlled by reduction-oxidation reactions involving Fe, C, S, or a C-O-H-S fluid, if present, at different times during the evolution of the region.

The oxidation state influences the phase equilibria of the system both directly, by affecting the stability relations of phases such as spinel (e.g., Hill and Roeder, 1974), and indirectly, by affecting the composition and speciation of a fluid, if present (e.g., Woermann and Rosenhauer, 1985). For example, whereas the dominant species in a C-O-H fluid are CO_2 and H_2O at high f_{O_2}, CH_4 and H_2 may become significant species at lower f_{O_2}, depending upon the bulk composition of the fluid. The temperature of the solidus, as well as the composition of the melt

produced, will depend on the composition of the fluid (e.g., Mysen and Boettcher, 1975a, 1975b; Wyllie, 1979; Eggler and Baker, 1982; among many others).

A common assumption for natural systems is that the mineral assemblage present defines the f_{O_2} and, therefore, that f_{O_2} may be taken as an independent variable in calculations of the composition and speciation of the fluid (e.g., French, 1966; Holloway, 1977, 1981; Frost, 1979; Eggler and Baker, 1982). In contrast, f_{O_2} is not an independent variable in experimental systems wherein f_{H_2}, not f_{O_2}, is imposed on the sample. This difference must be kept in mind when attempting to apply the results of experiments to natural systems.

The oxidation state of a sample in a high-pressure apparatus can be controlled by a variety of techniques, as reviewed by Huebner (1971). The simplest technique is to place the sample in a loosely crimped capsule, which is equilibrated with an external fluid phase that controls the oxidation state. This fluid could be the pressure medium, with or without some modification by an oxygen buffer surrounding the capsule (Huebner, 1969; French, 1971).

Because solid-media high-pressure apparatus lacks a gas-pressure medium, this technique must be modified by sealing a fluid phase and an oxygen buffer into an outer capsule along with the crimped inner capsule. The sample would then equilibrate with the fluid. This technique requires that the sample not be affected by communication (via the fluid) with the buffer phases. This requirement is unlikely to be fulfilled in experiments that contain a silicate melt or that are at sufficiently high temperature and pressure that significant amounts of solute dissolve into the fluid phase. For these reasons, control of oxidation state of experiments in solid-media high-pressure apparatus has typically been achieved using membrane equilibrium, a technique pioneered by Eugster (1957). The sample is sealed into a noble-metal capsule that is permeable only to H_2, and this capsule in turn is placed into an outer capsule containing a buffer assemblage such as Ni + NiO + H_2O or Fe_2SiO_4 + Fe_3O_4 + SiO_2 + H_2O. Membrane equilibrium establishes the equality of the H_2 fugacities in the outer and inner capsules. Eugster and Skippen (1967) and Huebner (1971) presented applications and extensions of this technique. The notation of Eugster and Skippen (1967) is adopted here. For example, the notation "NNO, OH(GX, COH)" means that the inner capsule contains graphite (G), sample (X), and a C-O-H fluid phase (COH). The parentheses denote the sealed, H_2-permeable inner-capsule wall. The outer capsule in this case contains Ni + NiO (NNO) and an O-H fluid phase (OH).

Eugster and Skippen (1967) pointed out that f_{O_2} in the inner and outer capsules are the same only when the fluids in the inner and outer capsules have the same composition. The implications of this observation for subsolidus equilibria involving solids and vapors have been thoroughly explored; however, the implications for melting equilibria are worth examining as well. In this report,

some of the implications of the experimental control of oxidation state by the use of H_2-permeable membranes for equilibria involving melting in the presence of C-O-H fluids in solid-media high-pressure apparatus are explored. Compositions and speciations of fluids in the system C-O-H are calculated for two sets of boundary conditions. One set of boundary conditions is the imposition of known pressure, temperature, and f_{O_2} on the system. This hypothetical set of conditions will be denoted O_B, X, COH or O_B, X, G, COH (O_B = oxygen buffer). No parentheses separate the oxygen buffer (O_B) from the sample (X) to emphasize that these conditions are not attained in these experiments. The other set of boundary conditions imposes a known pressure, temperature, and f_{H_2} on the system, denoted by O_B, OH(X, G, COH) or O_B, OH(X, COH) depending on the presence or absence of graphite (G). To provide some insight into the quality of the calculations, and to illustrate the difficulties in calibrating an equation of state at near-solidus conditions, the results of some experiments in the system NaAl-Si_3O_8(Ab)-C-O-H are presented. Finally, the implications of this method of controlling the oxidation state for the experimental simulation of natural systems are explored.

CALCULATION OF FLUID COMPOSITION

The composition and speciation of the O-H fluid in the outer capsule and of the C-O-H fluid in the inner capsule were calculated with a modification of the technique described by Eugster and Skippen (1967). These authors considered the case where the C-O-H fluid was constrained to be in equilibrium with graphite [e.g., O_B, OH(GX, COH)]. The present work extends this analysis into the quadrivariant, graphite-absent field by fixing a bulk-compositional variable, as well as P, T, and f_{H_2}. Fixing these four variables defines the composition and speciation of the fluid in the absence of graphite. The bulk-compositional variable selected was the ratio of total C to total O (X_C/X_O); the value of X_C/X_O of 0.50 selected for most of these calculations represents the case where the fluid is pure CO_2 prior to the diffusion of H_2 into the system. If graphite is stable, the variance is reduced to three, and the specification of P, T, and f_{H_2} uniquely determines the fluid composition.

In an analogous fashion, the composition and speciation of the C-O-H vapor was calculated for the case of imposed P, T, f_{O_2}, and, if graphite is not stable, X_C/X_O.

The fugacity coefficients (ϕ_i) of the species in the fluid are calculated with the modified Redlich-Kwong equation of state (MRK EOS) of Holloway (1977), with the correction of Flower (1979), and the values for the a and b parameters of the MRK EOS of Holloway (1981). This equation of state was used because of the availability of the parameters necessary to calculate fugacities for CO_2, H_2O, CO, CH_4, and H_2. The free-energy data required for calculating the equilibrium constants for the reactions between the fluid-phase species H_2, H_2O, CO_2, CO, CH_4, and O_2 [Eqs. 1–6 of Frost (1979)] are taken from Robie
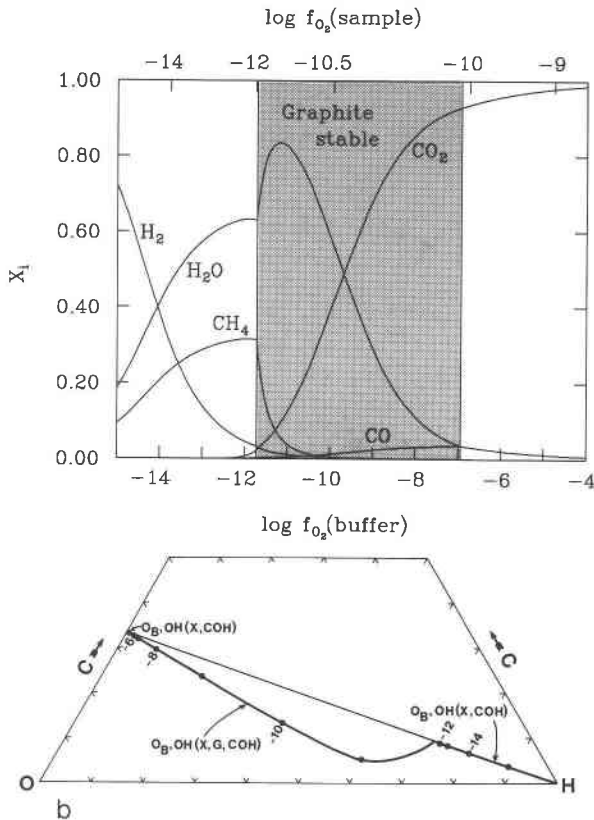
Fig. 1.　Composition of a C-O-H fluid at 15 kbar and 1050 °C for the case where f_{H_2} (sample) = f_{H_2} (buffer). O_B, OH(X, COH), and O_B, OH(X, G, COH). (a) Speciation of the fluid. The abscissa is the log f_{O_2} of the buffer (O_B). The f_{O_2} of the sample fluid is noted on the top of the diagram. Prior to equilibration with the imposed f_{H_2} of the buffer, the vapor was pure CO_2. After equilibration, the system may be described by O_B, OH(X, COH), C/O = 0.5 where graphite is not stable, and by O_B, OH(X, G, COH), where graphite is stable (shaded region). (b) Composition of fluid in the system C-O-H (heavy line). Numbers beside curve are the log f_{O_2} of the buffer for that fluid composition. The departure of the composition of the fluid from the CO_2-H_2 join (light line) reflects the stability of graphite and corresponds to the shaded region in (a).

et al. (1979), and the equilibrium constants for the buffer reactions were taken from Huebner (1971).

The addition of $NaAlSi_3O_8$ as a component also affects the variance. In the subsolidus region, where albite + vapor ± graphite coexist, the variance is four if graphite is unstable and three if graphite is stable. Once the assemblage starts to melt, so that albite + vapor + liquid ± graphite coexist, the variance is three if graphite is unstable and two if graphite is stable. This last result is interesting in that it implies that once the graphite-containing system starts to melt, and as long as albite, liquid, vapor, and graphite coexist, the specification of pressure and temperature suffices to define the system. The temperature of the solidus at a given pressure, however, is not independent of the imposed f_{H_2} or imposed f_{O_2}, because

the composition of the vapor, and therefore the temperature of the solidus, will differ depending on the f_{H_2} or f_{O_2} imposed on the subsolidus experiments.

EXPERIMENTAL TECHNIQUE

The starting material for the experiments in the Ab-C-O-H system was a natural albite containing 0.01 wt% Fe_2O_3, 0.03 wt% CaO, and 0.04 wt% K_2O. Heating at 20 kbar, 1150 °C for 24 h converted the albite to the high structural state, as verified by the $\delta 1\bar{3}1$ technique (Kroll and Ribbe, 1980). Approximately 5 mg of the high albite was loaded into a 3-mm-diameter Pt capsule and dried for ~16 h at 400 °C. An appropriate amount of silver oxalate to yield ~10 wt% CO_2 (relative to mass of sample + CO_2) upon decomposition was then loaded into the capsule, and the capsule was welded shut. No water was added to any of the sample capsules. The sample capsule, along with the buffer assemblage of Ni, NiO, and H_2O, was sealed into a 5-mm-diameter Pt capsule.

The double-capsule assembly was loaded in a 19-mm-diameter furnace assembly composed of talc, Pyrex glass, a tapered graphite heater, AlSiMag, and crushable alumina (Kushiro, 1976). The assembly was run in a solid-media apparatus (Boyd and England, 1960); the hot-piston-out technique was used to attain the final run conditions, with a friction correction of −7%. The temperature was monitored with a Pt-$Pt_{90}Rh_{10}$ thermocouple in contact with the top of the capsule. No pressure correction was applied to the emf of the thermocouple.

After the experiment, the outer capsule was cleaned, weighed, punctured, heated at 120 °C, and reweighed to insure that H_2O was present in the buffer after the run. Examination of the buffer with X-ray diffraction verified the presence of both Ni and NiO. After the inner capsule was cleaned and opened, the run products were examined in immersion oils with the petrographic microscope.

RESULTS

Composition of the fluid

The calculated speciation and composition of the fluid are shown in Figures 1 and 2 for the temperature of the solidus at 15 kbar for the imposed-f_{H_2} and imposed-f_{O_2} cases, respectively. To facilitate comparisons of the two cases, the abscissa in both figures is the log f_{O_2} of the buffer. In the experimentally attained, imposed-f_{H_2} case (Fig. 1), the f_{O_2} of the buffer is not equal to the f_{O_2} of the sample fluid (Whitney, 1972), which is shown across the top of Figure 1. In the imposed-f_{O_2} case (Fig. 2), the f_{O_2} imposed on the sample is equal to that of the buffer, which is plotted on the abscissa. The marked, abrupt changes in slope of the X_{CH_4} and the X_{H_2O} curves (Figs. 1a, 2a) result from the precipitation of graphite and the consequent deviation of the fluid from the CO_2-H_2 join, as illustrated by the changes in the bulk composition of the fluid in Figures 1b and 2b. The MRK EOS predicts that when the f_{H_2} of a fluid is controlled by an external NNO buffer, the fluid will coexist with graphite and be composed predominantly of CO_2 and H_2O, with <5% CO and <1% CH_4 and H_2. In contrast, if the f_{O_2}, rather than the f_{H_2}, of the fluid is imposed by NNO, graphite is not stable at these conditions, and the fluid will contain ~98% CO_2, ~1% H_2O and CO, and ≪1% H_2 and CH_4.
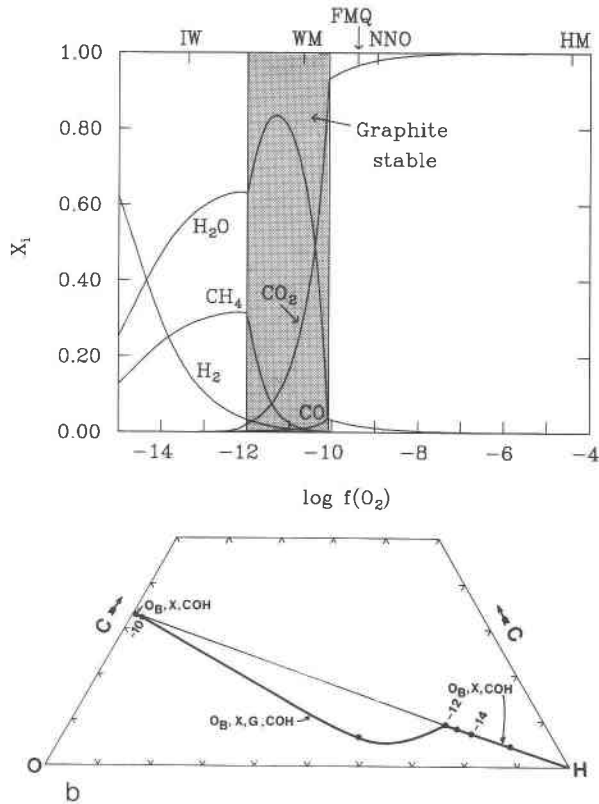
Fig. 2. (a) Speciation of a C-O-H fluid at 15 kbar and 1050 °C for the hypothetical case where f_{O_2} (sample) $= f_{O_2}$ (buffer) [i.e., O_B, X, COH]. The abscissa is the log f_{O_2} of the buffer, which equals that of the sample fluid. Prior to equilibration with the imposed f_{O_2}, the vapor was pure CO_2. In the shaded region, graphite is stable, and the system may be described by O_B, X, G, COH. (b) Composition of fluid in the system C-O-H (heavy line). Numbers beside curve are the log f_{O_2} of the buffer for that fluid composition. The departure of the bulk composition from the CO_2-H_2 join (light line) reflects the stability of graphite, and corresponds to the shaded region in (a).
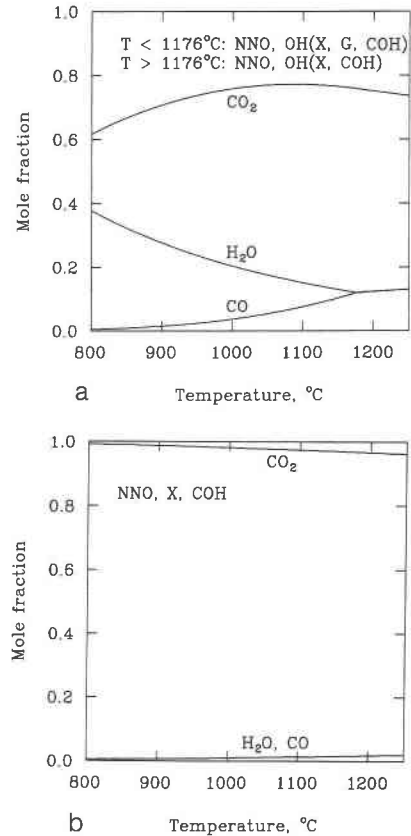

Fig. 3. Concentration of the species CO_2, CO, and H_2O in the fluid at 10 kbar buffered by NNO as a function of temperature. The concentrations of CH_4 and H_2 are too low to be visible above the abscissa in these diagrams. $X_C/X_O = 0.50$ for $T > 1176$ °C, where graphite is not stable. (a) f_{H_2} (sample) $= f_{H_2}$ (buffer). Inflections in X_{CO} and X_{H_2O} curves correspond to the highest temperature at which graphite is stable. (b) f_{O_2} (sample) $= f_{O_2}$ (buffer). Graphite is not stable in this temperature range.

The variation with temperature of the speciation of a C-O-H fluid buffered by NNO at 10 kbar is shown in Figure 3 for both sets of boundary conditions. When f_{H_2} is imposed, $X^v_{CO_2}$ increases with increasing temperature until CO becomes quantitatively significant, whereupon $X^v_{CO_2}$ decreases slightly. The $X^v_{H_2O}$ decreases continually with increasing temperature, whereas both CO and H_2 increase in concentration with increasing temperature, with abrupt changes in slope in the X_{CO} and X_{H_2O} curves at the temperature where graphite ceases to be stable. In contrast, when f_{O_2} is imposed, $X^v_{CO_2}$ decreases slightly from ~0.98 as temperature increases from 800 °C to 1250 °C. The concentrations of H_2 and CH_4 are too low to be visible above the abscissa in Figure 3.

Uncertainties in the composition of the fluid

The possible sources of error in the calculation of the composition of the fluid include errors in the fugacity coefficients, errors in the free energy (ΔG) of the reaction that defines the f_{O_2} of the buffer, and errors in the data for the free energy for the reactions that control the speciation of the fluid. Kerrick and Jacobs (1981) reported that the MRK of Holloway (1977) overestimates both the f_{CO_2} and the f_{H_2O} for a given composition, which requires that ϕ_{CO_2} and ϕ_{H_2O} are too large. Reducing both ϕ_{CO_2} and ϕ_{H_2O} by the same percentage decreases $X^v_{CO_2}$ because ϕ_{CO_2} is larger than ϕ_{H_2O}; for example, at 10 kbar and 1000 °C, reducing ϕ_{CO_2} and ϕ_{H_2O} by 50% decreases $X^v_{CO_2}$ by 7%, from 0.757 to 0.703.

The equilibrium for the NNO buffer has been previously determined at 1-atm pressure; Huebner and Sato (1970) gave an uncertainty of log f_{O_2} (NNO) of 0.24 log f_{O_2} units. This uncertainty in f_{O_2} would lead to an uncertainty in $X^v_{CO_2}$ of ±4% and ±6% at the temperature of the solidus at 10 and 15 kbar, respectively. The magnitude of the additional uncertainty at elevated pressure as a result of the uncertainty in the volume term depends on the precision of the data for the molar volume and compressibilities of the solid phases. A change of the volume
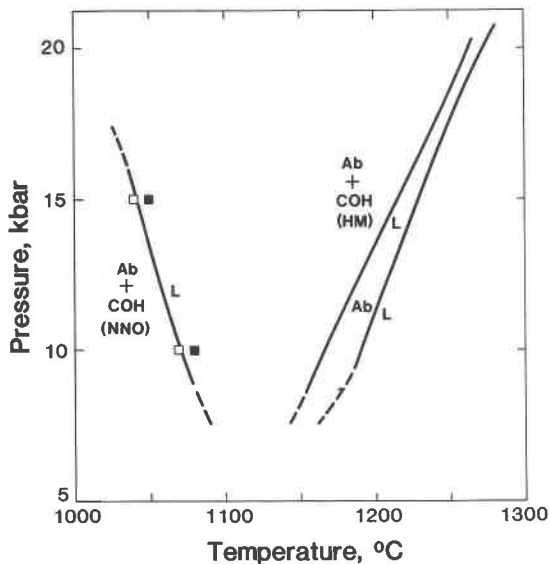
Fig. 4. Pressure-temperature projection of experimental results for the temperature of the solidus of $NaAlSi_3O_8$-C-O-H in the system NNO, OH(Ab, G, COH). Filled symbols represent subsolidus experiments; open symbols are supersolidus. For comparison, the solidus for the vapor-absent melting of NaAlSi$_3$O$_8$ buffered by HM from Boettcher et al. (1982) and the solidus of $NaAlSi_3O_8$-C-O-H in the system HM, OH(Ab, COH) from Boettcher et al. (1987) are shown. In the latter case, the vapor is essentially pure CO_2.

TABLE 1. Summary of experimental conditions and results

Run	P (kbar)	T (°C)	CO_2 (wt%)	Duration (h)	Results*
212	10	1040	13.0	8	Ab + C
224	10	1070	12.3	7	Ab + C
213	10	1080	11.4	7	Ab + C
219	10	1090	10.2	7	Ab + L + C
218	10	1100	10.4	7	Ab + L + C
217	10	1120	10.5	7	Ab + L + C
204	15	920	16.7	8	Ab + C
205	15	980	12.9	8	Ab + C
206	15	1020	12.0	7	Ab + C
209	15	1040	10.6	7	Ab + C
210	15	1050	11.4	7	Ab + L + C
208	15	1060	11.5	7	Ab + L + C
207	15	1100	10.3	7	L + C

* Ab = albite, C = carbon, L = liquid.

term by 100% changes log f_{O_2} (NNO) at 1000 °C and 10 kbar by ±0.50 log f_{O_2}, which in turn changes $X_{CO_2}^v$ by ±12%.

Uncertainties in the free energies of the equations governing the speciation of the fluid will also affect the calculated fluid composition. The fluid composition is most sensitive to variations in ΔG of the reactions

$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O \qquad (1)$$

and

$$C + O_2 \rightleftharpoons CO_2 \qquad (2)$$

that control the major species, H_2O and CO_2, in the fluid. A 5% change in either ΔG_1 or ΔG_2 results in a change in $X_{CO_2}^v$ of a NNO-buffered fluid by as much as 50%, depending upon the pressure and temperature. For example, at 10 kbar and 1000 °C, a 5% decrease in ΔG_1 or a 5% increase in ΔG_2 increases $X_{CO_2}^v$ from 0.76 to >0.86. Because of the considerably lower concentration of CO and CH_4 relative to CO_2 and H_2O, variations in the free energies of reactions involving these species result in much smaller changes in the calculated fluid composition. Unfortunately, available data are insufficient to evaluate quantitatively the uncertainties in the values for the ΔG of these reactions.

Experiments

The experimental results for albite + C-O-H vapor buffered by NNO are summarized in Table 1 and Figure

4. The temperature of the solidus was delineated by the lowest-temperature experiment in which glass (quenched liquid) is present; at both pressures, the lowest-temperature supersolidus experiment contained >5% glass. The solidus of Ab-C-O-H buffered by NNO is lower than the solidus of Ab-C-O-H (C/O = 0.5) buffered by HM by ~90 °C and ~170 °C at 10 and 15 kbar, respectively. In contrast to the results of the HM-buffered experiments, graphite was present in all experiments buffered by NNO. The presence of graphite requires that the composition of the vapor was no longer along the CO_2-H_2 join in the C-O-H ternary system, in agreement with the calculations outlined above. The calculated composition of the fluid, at the temperature of the solidus, is 77 mol% CO_2, 16 mol% H_2O, 6.6 mol% CO, and <1 mol% CH_4 and H_2 at 10 kbar and 69 mol% CO_2, 28 mol% H_2O, 2.4 mol% CO, and <1 mol% CH_4 and H_2 at 15 kbar. It was not possible to reverse these experimental curves because the NNO buffer became exhausted before the reversal experiments were completed.

DISCUSSION

Comparison with previous work

The calculated composition of the fluid present in the experiments in equilibrium with the f_{H_2} of the NNO buffer consists primarily of CO_2 and H_2O, with a minor amount of CO, as discussed above and illustrated in Figures 1 to 3. Therefore, the present data on the system NNO, OH(Ab, G, COH) may be compared with previous experiments on Ab-H_2O-CO_2 (Bohlen et al., 1982), which were buffered by HM, thereby minimizing formation of H_2O and CO by diffusion of H_2 into the capsule. As shown in Figure 5, the present results have solidus temperatures higher than those for Ab-H_2O-CO_2 with $X_{CO_2}^v$ = 0.90 (Bohlen et al., 1982). Based on the calculated fluid compositions of $X_{CO_2}^v$ = 0.77 and 0.69 at 10 and 15 kbar, respectively, the solidus determined in the present study is higher by >200 °C than expected from the results of Bohlen et al. (1982). This discrepancy cannot be a result of the insolubility of the CO present in the NNO-buffered

experiments, because Eggler et al. (1979) demonstrated that the solubility of CO is of the same order of magnitude as the solubility of CO_2. Therefore, the calculated fluid compositions must be incorrect.

The difference in the composition of the fluid inferred from the comparison with the experimental work of Bohlen et al. (1982) and that calculated in this paper, coupled with the sensitivity of the calculated composition of the fluid to uncertainties in the ΔG data for the species-controlling equations, illustrates the need to obtain more data on the composition and speciation of C-O-H fluids at elevated pressures and temperatures. Such data may be obtained by determining dehydration and decarbonation reactions in mixed-volatile fluids under controlled f_{H_2} or f_{O_2} conditions (e.g., Huebner, 1969, and French, 1971, among others). These experiments would provide data on the relationship between the fugacities of the species and the composition of the fluid and would avoid the requirement of complementary data on the temperature of the solidus in the silicate-H_2O-CO_2 system at low f_{H_2}, which was required for this study. Such experiments are not a panacea, however, because they are limited in their coverage of pressure-temperature space; in particular, few appropriate reactions exist for combined high pressure and high temperature (>1000 °C).

An alternative approach is to equilibrate a fluid at known pressure, temperature, and f_{H_2}. Analysis of the fluid after the experiment is quenched would provide information on the composition and speciation of the fluid. Re-equilibration of the species in the fluid and diffusion of H_2 out of the capsule during the quenching of the experiment will hinder such experiments. Although previous workers who have applied this approach experimentally have not discussed this problem in detail (e.g., Eggler et al., 1974; Holloway and Jakobsson, 1986), clearly some reaction takes place during the quenching of the experiment, insofar as H_2O condenses and separates from a CO_2-rich vapor. It is of interest, however, to note that the analysis of a fluid quenched from 20 kbar, 1400 °C, with imposed f_{H_2} near HM, contained 98% CO_2, 1% CO, and 1% H_2O (Eggler et al., 1974). The predicted fluid composition in equilibrium with HM at those conditions, calculated as discussed above, is 97% CO_2, 1.5% CO, and 1.5% H_2O. At this low imposed f_{H_2}, however, the speciation of the fluid is less sensitive to the imposed f_{H_2} than would be the case at higher f_{H_2} (lower f_{O_2}), such as that in equilibrium with NNO.

A third possibility is to use the f_{H_2} sensor technique of Chou (1978). The applicability of this technique at $P > 10$ kbar and $T > 800$ °C remains to be demonstrated, but the potential utility of this technique is tremendous. The problem of diffusion of H_2 out of the capsule during the quench must again be evaluated.

Experimental simulation of nature

Many of the previous melting studies in CO_2-bearing systems in solid-media apparatus have used the intrinsic f_{H_2} of the furnace assembly to constrain the composition
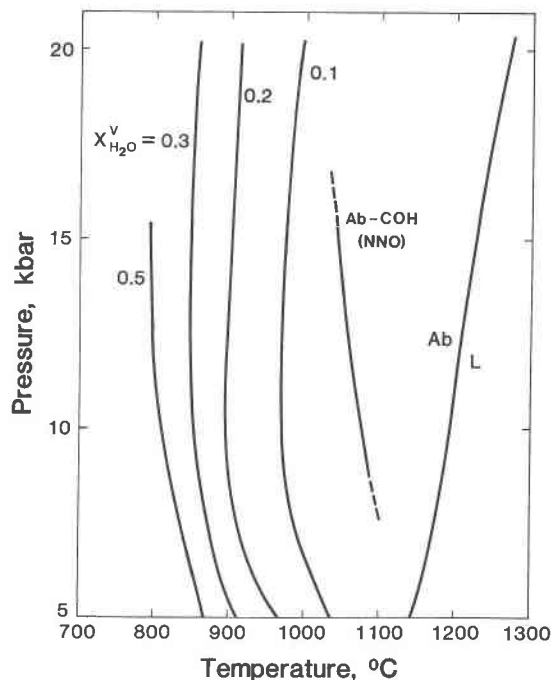

Fig. 5. Pressure-temperature projection of the results of Ab-C-O-H in the system NNO, OH(Ab, G, COH) and the results of Bohlen et al. (1982) for the system $NaAlSi_3O_8$-CO_2-H_2O, with $X^V_{H_2O} = 0.1$, 0.2, 0.3, and 0.5. See text for discussion.

of the fluid phase. This technique relies on minimizing sources of H_2 in the assembly as well as attempting to impede the ingress of H_2 into the capsule. This technique can be effective, at least to a first approximation, in maintaining a nearly pure CO_2 fluid phase, but the f_{H_2} of the sample assembly depends on the materials used, which differ between laboratories. For example, Eggler et al. (1974) reported that the intrinsic f_{H_2} of their sample assembly was near that of the assemblage HM + OH fluid, whereas the assembly of Allen et al. (1972) reportedly had an intrinsic f_{H_2} near that of NNO + OH fluid, as discussed by Boettcher et al. (1973), and that of Merrill and Wyllie (1974) had an intrinsic f_{H_2} higher than that of NNO + OH fluid. Furthermore, the intrinsic f_{H_2} of a sample assembly may change radically with varying temperature. For example, sample assemblies with talc parts should have a much higher imposed f_{H_2} at temperatures above the temperature of the dehydration reaction relative to the imposed f_{H_2} below this temperature. The imposed f_{H_2} in these assemblies will also be a function of time because of the finite amount of H_2O available and the continuous loss of H_2 by diffusion away from the area around the sample. It is necessary to document the intrinsic f_{H_2} of the experimental apparatus in use, as a function of pressure, temperature, and time, if the duration of the experiments required for the attainment of equilibrium precludes the use of the f_{H_2}-buffer technique.

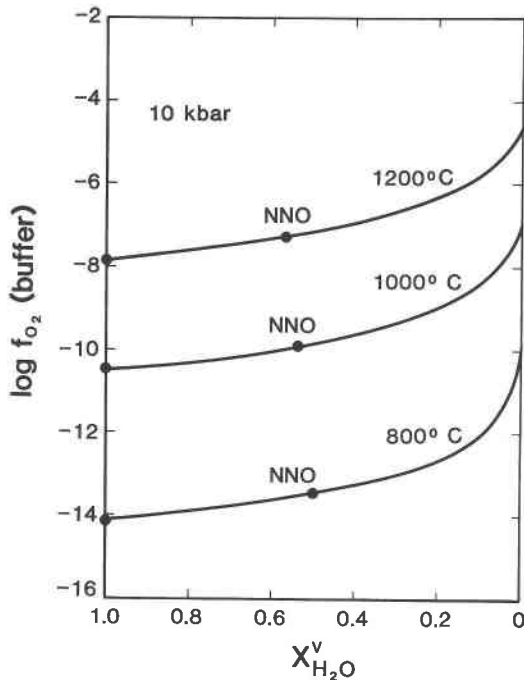The control of the fluid composition, including the oxidation state, during an experiment is necessary for two

Fig. 6. Log f_{O_2} (buffer) vs. $X^V_{H_2O}$ diagram showing the log f_{O_2} (buffer) required, as a function of $X^V_{H_2O}$, to maintain the fluid in a H_2-permeable inner capsule at the f_{O_2} of QFM. The results for three different temperatures at 10 kbar are shown. For reference, the value of log f_{O_2} for the NNO buffer is shown for each temperature.

presence of a C-O-H fluid increased the concentrations of H_2O, CH_4, and H_2 at the expense of CO_2, as has been seen previously at lower pressure and temperature (e.g., Eugster and Skippen, 1967). This change in the fluid composition will decrease the temperature of the solidus.

CONCLUSIONS

The calculations and experiments summarized in this paper indicate that experiments containing a CO_2-bearing fluid phase should be buffered at low f_{H_2} in order for the f_{O_2} of the system to be near that of the QFM buffer. The exact f_{O_2} required to maintain the f_{O_2} (sample) at QFM depends upon the $X^V_{H_2O}$ of the fluid in equilibrium with the sample. Ignoring or neglecting such constraints on the oxidation state of experimental studies seriously handicaps the potential applicability of the results of such studies to conditions of magma genesis in the Earth. Finally, present thermodynamic models are not sufficiently refined to allow reliable calculation of the composition and speciation of C-O-H fluids at high pressure and high temperature.

reasons. First, as discussed above, the oxidation state is related to the composition and speciation of the fluid phase, if present, which influences the phase equilibria. Second, the oxidation state controls the Fe^{2+}/Fe^{3+} of the system, which also affects the phase equilibria. A variety of evidence from heterogeneous equilibria (Buddington and Lindsley, 1964; Eggler, 1983; Haggerty and Tomkins, 1985; Haggerty, 1986; Mattioli and Wood, 1986) and intrinsic f_{O_2} measurements (Arculus and Delano, 1981; Arculus et al., 1984) indicates that portions of the upper mantle and the lower crust are characterized by values of f_{O_2} near those of the QFM buffer. Figure 6 illustrates the f_{O_2} (buffer), as a function of $X^V_{CO_2}$, that is required to maintain the f_{O_2} (sample) at the f_{O_2} of the QFM buffer. As $X^V_{CO_2}$ increases, the f_{O_2} (buffer) must increase from the value for the QFM buffer. Such continuous variation of the f_{H_2} of the buffer cannot be achieved at present in double-capsule experiments using conventional f_{H_2} buffers. Therefore, the extent to which the oxidation state affects the phase equilibria of the system under study must be determined at the f_{H_2} of the available f_{H_2} buffers in order to interpolate to the appropriate f_{O_2} conditions.

The experiments performed in this study, although buffered externally by the NNO buffer, had vapor composition and speciations appropriate for vapors in equilibrium with the f_{O_2} of the WM buffer. Conclusions that may be drawn from this are that the decreased f_{O_2} in the

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