Devolatilization equilibria in H₂O–CO₂ and H₂O–CO₂–NaCl fluids: an experimental and thermodynamic evaluation at elevated pressures and temperatures

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Abstract
Experimental equilibrium brackets have been obtained in H₂O–CO₂ and H₂O–CO₂–NaCl fluids for several decarbonation equilibria. Using available thermodynamic data and activities for H₂O and CO₂ calculated from the modified hard-sphere Redlich-Kwong (HSMRK) equation of Kerrick and Jacobs (1981), thermodynamic extrapolations in P–T–XCO₂ space of devolatilization equilibria yield close agreement with the experimental equilibrium brackets, implying that the experimental and thermodynamic data are internally consistent, and that the activities of H₂O and CO₂ predicted by the HSMRK equation of Kerrick and Jacobs (1981) are quite reasonable. The significance of assuming ideal vs. non-ideal mixing of H₂O and CO₂ for the calculation of T–XCO₂ topologies is demonstrated for a portion of the system CaO–Al₂O₃–SiO₂–H₂O–CO₂. Experiments in H₂O–CO₂–NaCl mixtures at P = 6 kbar show that, compared to binary H₂O–CO₂ fluids, the presence of small (5–10 wt.%) amounts of NaCl in the fluid phase significantly increase the activity of CO₂ for H₂O-rich compositions. At 2 kbar, however, little difference in the activity of CO₂ in H₂O–CO₂–NaCl vs. H₂O–CO₂ mixtures is implied by the experiments.

Introduction
Many authors (e.g., Chernosky, 1979; Kerrick and Gent, 1979; Kerrick and Slaughter, 1976; Perkins et al., 1977, 1980; Slaughter et al., 1975) have pointed out that direct experimentation as the only means of determining P–T–XCO₂ topologies for metamorphic systems is not practical. The time required to experimentally determine the P–T–XCO₂ coordinates of all important metamorphic equilibria over a wide range of pressure and temperature is prohibitive. Moreover, some equilibria (e.g., those stable at very low P–T conditions) may not be amenable to direct experimentation. Therefore, as the above authors conclude, the combination of careful experimentation and thermodynamic extrapolations is the best practical approach.

Helgeson et al. (1978), Kerrick and Gent (1979), Kerrick and Slaughter (1976), Perkins et al. (1977, 1980), Slaughter et al. (1975), and Wall and Essene (1972) have shown that thermodynamic P–T extrapolations for many solid–solid and dehydration (P₁₉₂O = Ptotal) equilibria are in close agreement with experimental determinations of the equilibria over a wide P–T range. This agreement implies that the available thermodynamic data for the solids and H₂O are consistent with the independently derived experimental equilibrium brackets. Helgeson et al. (1978), in deriving an internally consistent set of enthalpies and free energies of formation for minerals through the combination of experimental phase equilibrium data and thermodynamic calculations, used decarbonation and mixed-volatile equilibria only when no other choice was available. According to Helgeson et al. (1978), this was because of a lack of reliable fugacities for CO₂ (particularly at P ≥ 5 kbar) and the lack of a reliable method for predicting activities in H₂O–CO₂ mixtures at elevated pressures and temperatures. Shmulovich and Shmonov (1978) have since provided fugacities for CO₂ to 1000°C and 10 kbar which are in good agreement with the unpublished data of Burnham and Wall. In comparing mixed-volatile equilibria calculated from thermochemical data versus that obtained experimentally, Helgeson et al. (1978)
found that Holloway’s (1977) adaption of the MRK equation for H2O–CO2 mixtures yielded inconsistent agreement; however, Flower’s (1979) subsequent correction of Holloway’s (1977) formulation improved this correlation.

Because much of the experimental data on activities in H2O–CO2 mixtures has been obtained over very restricted P–T ranges (e.g., Chou and Williams, 1977, 1979a, 1979b; Eggler and Burnham, 1978; Eggler and Kadik, 1979; Eggler et al., 1979, Franck and Todheide, 1959; Gehrig et al., 1979; Greenwood, 1969, 1973; Jacobs and Kerrick, 1979; Shmulovich, 1977; Walter, 1963; Ziegenbein and Johannes, 1980), an equation of state which predicts accurate activities in H2O–CO2 mixtures over a wide range of pressure and temperature would be useful for accurately calculating P–T–XCO2 topologies. Kerrick and Jacobs (1981) derived a hard-sphere modified Redlich-Kwong (HSMRK) equation of state for H2O and CO2 which predicts mixing properties of H2O and CO2 that are in good agreement with much of the available experimental data on H2O–CO2 mixtures. The analysis of Kerrick and Jacobs (1981) also suggests that the HSMRK equation is superior to Holloway’s (1977) MRK equation (corrected version of Flowers, 1979) for prediction of the thermodynamic properties of H2O, CO2 and their mixtures to pressures and temperatures above the P–T range of the available P–V–T data.

Comparisons between calculated and experimentally determined devolatilization equilibria in P–T–XCO2 space provide a test for the available thermodynamic data of pure solids, pure gases (H2O and CO2), and the activities of H2O and CO2 in H2O–CO2 mixtures predicted by the HSMRK equation. Experimental determinations of the P–T–XCO2 conditions of equilibria involving both H2O and CO2 as components allow an evaluation of the product or ratio (as dictated by the equilibrium constant) of the activity coefficients of H2O and CO2. However, experimental determinations of dehydration and decarbonation equilibria allow a direct evaluation of the activity coefficients for H2O and CO2, respectively, not just a ratio or product. Unfortunately, most dehydration equilibria are not stable over a wide range of XCO2, making them unsuitable for such an analysis. Therefore, in addition to an analysis of previously published experimental work, the following decarbonation equilibria, stable over a wide range of fluid compositions, were studied experimentally in H2O–CO2 mixtures:

- calcite + quartz = wollastonite + CO2
- dolomite + 2 quartz = diopside + 2 CO2
- calcite + quartz + andalusite = anorthite + CO2
- calcite + quartz + kyanite = anorthite + CO2
- calcite + quartz + rutile = sphene + CO2

In order for calculated P–T–XCO2 topologies to better represent geologic systems, the presence of components in addition to H2O and CO2 in the fluid phase must be considered. Jacobs and Kerrick (1981a) have considered the effect of the presence of small amounts of CH4 on activities in H2O–CO2–CH4 mixtures, and the resulting effect on P–T–XCO2 topologies of metamorphic systems. In addition to CH4, chloride species have been shown to be present in significant amounts in geologic fluids (e.g., Crawford et al., 1979a,b; Hendel and Hollister, 1981; Hollister and Burruss, 1976; Hollister et al., 1979; Konnerup-Madsen et al., 1979; Luchsheiter and Morteani, 1980; Pecher, 1979; Rich, 1979; Roedder, 1972). Expansion of the H2O–CO2 solvus resulting from the addition of NaCl (Gehrig et al., 1979; Hendel and Hollister (1981); Hollister and Burruss, 1976; Takenouchi and Kennedy, 1965) may imply an increase in the activity of CO2 and/or H2O relative to the activities in binary H2O–CO2 mixtures. This increased activity may have a significant effect on the stability of mineral assemblages in equilibrium with H2O–CO2–NaCl fluids relative to assemblages in equilibrium with binary H2O–CO2 mixtures. Because the T–XCO2 position of a devolatilization equilibrium is dependent upon the activity of H2O and/or CO2 (in addition to the thermodynamic properties of the solid phases involved), a representative devolatilization equilibrium was chosen to experimentally compare equilibrium determinations in H2O–CO2 mixtures to results in H2O–CO2–NaCl mixtures.

**Experimental techniques**

The techniques discussed below are similar to those used by Eggert and Kerrick (1981), Hunt and Kerrick (1977), Kerrick and Ghent (1979), and Slaughter et al. (1975).

In the experiments, quartz was taken from a large single crystal of clear Brazilian quartz. Table 1 contains the sample provenance, a chemical analysis, and a structural formula for other minerals used.
in this study. Each sample was crushed to less than 325 mesh and elutriated in distilled water to remove the ultrafine particles.

Starting mixtures for equilibrium 1 consisted of calcite + quartz (equal weights) and wollastonite loaded into separate Ag_50Pd_50 capsules. For equilibria 2–4, however, starting mixtures consisted of equal weights of each solid reactant and product, with a quartz sphere replacing powdered quartz in one set of experiments for equilibrium 3k.

H_2O–CO_2 fluids were generated by adding known amounts of H_2O and silver oxalate (Ag_2C_2O_4) to capsules containing approximately 0.03 g of a starting mixture. The solid to fluid ratio was maintained at a constant value of approximately 5 to 1 (by weight). Compositions at the end of a run were
determined by the weight loss method of Johannes (1969). Analysis of "blank" capsules (initially containing only H2O and silver oxalate) indicated that the error in determining \(X_{CO_2}\) was probably less than \(\pm 0.01\). Aqueous solutions of 5 and 10 wt.% NaCl (0.90 and 1.90 molal, respectively), along with silver oxalate, were used to generate the fluid phase for runs with H2O–CO2–NaCl mixtures.

Runs at 2 and 6 kbar were respectively performed in cold-seal pressure vessels (H2O pressure medium) and internally-heated pressure vessels (Ar pressure medium). The cold-seal pressure vessels were mounted horizontally and contained filler rods to minimize temperature measurement error (Boettcher and Kerrick, 1971). Pressures were monitored with bourdon-tube gauges (estimated error = \(\pm 50\) bars) for the cold-seal vessels, while a manganin cell (estimated error \(= \pm 1\%\)) was used for the internally-heated vessels. Temperatures \((\pm 7^\circ C)\) in the cold-seal vessels were measured with external, inconel-sheathed, chromel-alumel thermocouples. Temperatures \((\pm 5^\circ C)\) in the internally-heated vessels were measured with three internal, inconel-sheathed, chromel-alumel thermocouples. Based on extensive testing of other thermocouples of this type against reference thermocouples constructed of wire calibrated by the National Bureau of Standards, the accuracy of the sheathed thermocouples is estimated to be \(\pm 2-3^\circ C\). The stated errors in the run temperatures include temperature fluctuation and an estimate of the error in accuracy. Quench duration was approximately three and five minutes for the cold-seal and internally-heated vessels, respectively. In all cases run duration was 7 days.

For equilibria (2–4), reaction direction was determined by monitoring the mass of CO2 lost or gained during a run. Since the decarbonation reactions studied involved CO2 as the only gas component, the difference between the final and initial number of moles of CO2 is a direct measure of reaction direction. Uncertainty associated with the value of \(\Delta\)moles CO2 (final moles minus initial moles) is believed to be less than \(\pm 1 \times 10^{-6}\) moles. Isothermal–isobaric runs were conducted for multiple capsules with a series of different initial \(X_{CO_2}\) values. As a check on experimental equilibrium data obtained by monitoring compositional changes of the fluid, reaction 3k was also monitored by the weight change of quartz spheres.

Equilibrium 1 was not amenable to monitoring changes in the mass of CO2, since, as Jacobs and Kerrick (1980) have shown, the quench reaction: wollastonite + CO2 → calcite + SiO2 (aq.) is very rapid. This reaction results in anomalous changes in the mass of CO2 gained or lost during a run, thus complicating interpretation of the results. Therefore, calcite + quartz and wollastonite were loaded into separate capsules and run isothermally–isobarically at a series of initial \(X_{CO_2}\) values. Reaction direction was measured by Guinier X-ray detection (minimum detectability = 1–2% by volume) of spontaneous nucleation and growth of new phases.

**Experimental results**

Table 2 contains the experimental equilibrium brackets for all equilibria studied. Results for individual equilibria in both H2O–CO2 and H2O–CO2–NaCl fluids are discussed below.

**H2O–CO2 fluids**

Table 3 summarizes the experimental results on equilibrium 1. Because the starting mixture in runs 1–6 was calcite + quartz, runs in the stability field of wollastonite should evolve CO2 (thereby increasing \(X_{CO_2}\)), whereas runs in the stability field of calcite + quartz should show no change in \(X_{CO_2}\). Because of back reaction during the quench, the

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**Table 2. Summary of experimental equilibrium brackets**

<table>
<thead>
<tr>
<th>Equilibrium No.</th>
<th>(P(\text{kbar}))</th>
<th>(T(\text{°C}))</th>
<th>(X_{CO_2})</th>
<th>wt.% NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>6</td>
<td>880</td>
<td>0.86 ± 0.03</td>
<td>0.0</td>
</tr>
<tr>
<td>(2)</td>
<td>5</td>
<td>575</td>
<td>0.60 ± 0.02</td>
<td>0.0</td>
</tr>
<tr>
<td>(3k)</td>
<td>6</td>
<td>460</td>
<td>0.05 ± 0.02</td>
<td>0.0</td>
</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>450</td>
<td>0.57 ± 0.05</td>
<td>0.0</td>
</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>500</td>
<td>0.70 ± 0.03</td>
<td>0.0</td>
</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>600</td>
<td>0.82 ± 0.03</td>
<td>0.0</td>
</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>450</td>
<td>0.20 ± 0.03</td>
<td>5.0</td>
</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>475</td>
<td>0.52 ± 0.04</td>
<td>5.0</td>
</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>520</td>
<td>0.67 ± 0.02</td>
<td>5.0</td>
</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>450</td>
<td>0.18 ± 0.02</td>
<td>10.0</td>
</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>475</td>
<td>0.53 ± 0.04</td>
<td>10.0</td>
</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>520</td>
<td>0.68 ± 0.02</td>
<td>10.0</td>
</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>550</td>
<td>0.18 ± 0.02</td>
<td>5.0</td>
</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>575</td>
<td>0.25 ± 0.03</td>
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</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>600</td>
<td>0.70 ± 0.02</td>
<td>5.0</td>
</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>550</td>
<td>0.17 ± 0.02</td>
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</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>575</td>
<td>0.19 ± 0.02</td>
<td>10.0</td>
</tr>
<tr>
<td>(4)</td>
<td>6</td>
<td>600</td>
<td>0.68 ± 0.02</td>
<td>10.0</td>
</tr>
</tbody>
</table>
Table 3. Run data for the reaction: calcite + quartz ⇌ wollastonite + CO₂ at P = 6 kbar, T = 880°C

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Starting material</th>
<th>Products</th>
<th>Initial* XCO₂</th>
<th>Final* XCO₂</th>
<th>Reaction direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>cc+qtz</td>
<td>cc+qtz+wo</td>
<td>0.500</td>
<td>0.617</td>
<td>→ wo</td>
</tr>
<tr>
<td>2</td>
<td>cc+qtz</td>
<td>cc+qtz+wo</td>
<td>0.655</td>
<td>0.768</td>
<td>→ wo</td>
</tr>
<tr>
<td>3</td>
<td>cc+qtz</td>
<td>cc+qtz+wo</td>
<td>0.715</td>
<td>0.786</td>
<td>→ wo</td>
</tr>
<tr>
<td>4</td>
<td>cc+qtz</td>
<td>cc+qtz+wo</td>
<td>0.806</td>
<td>0.842</td>
<td>→ wo</td>
</tr>
<tr>
<td>5</td>
<td>cc+qtz</td>
<td>cc+qtz</td>
<td>0.885</td>
<td>0.885</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>cc+qtz</td>
<td>cc+qtz</td>
<td>0.980</td>
<td>0.980</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>wo</td>
<td>wo</td>
<td>0.885</td>
<td>0.885</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>wo</td>
<td>wo+cc+qtz</td>
<td>0.980</td>
<td>0.895</td>
<td>cc+qtz =</td>
</tr>
</tbody>
</table>

*The precision error in measurements of XCO₂ is ± 0.01.

The CO₂ value of run 4 (see Table 3) represents the minimum XCO₂ value of the equilibrium bracket, since runs 5 and 6 showed no apparent reaction. Run 12 (see Table 3), with nucleation and growth of calcite + quartz (detected by X-ray diffraction), defines the maximum value of XCO₂ for equilibrium 1 because run 11, at a slightly lower XCO₂ value, had no apparent reaction. There should be no complications involving reaction during the quench for runs 11 and 12, because quench reactions involving wollastonite in H₂O–CO₂ fluids are minimized at high values of XCO₂ (Jacobs and Kerrick, 1980).

Results of the experiments on equilibria 2–4 in H₂O–CO₂ mixtures are summarized in Figures 1–5. For each set of runs, the change in the number of moles of CO₂ during a run is plotted against the final XCO₂ value. In Figure 3 (500°C run), the change in moles of quartz is plotted in addition to change in moles of CO₂. The weight of quartz spheres before and after the run (an average of 5 replicate weighings; see Hunt and Kerrick, 1977) defined the change in moles of quartz. As expected from the stoichiometry of equilibrium (3k), the change in moles of quartz is approximately symmetrical with the CO₂ data. Optical and X-ray analysis of run products indicated that no unwanted phases nucleated during the runs represented in Figures 1–5. In addition, because decarbonation equilibria were studied, the constant mass of H₂O before and after the runs suggests that no competing reactions involving H₂O occurred.

A second degree polynomial (Δmoles = f(XCO₂)) was fit to each set of data using the least-squares regression program ‘Minitab 2’ (Ryan et al., 1976).

The form of the equation, fit to all the data of this study, was arbitrarily chosen, since a theoretically valid equation which fits the data is not known at this time. The XCO₂ value where a curve passes through the line of Δmoles = 0 is taken to represent
Fig. 3. Experimental data pertaining to equilibrium 3k in H₂O-CO₂ mixtures at $P = 6$ kbar. This is a plot of $\Delta$ moles of CO₂ (circles) and $\Delta$ moles of quartz (squares) as a function of final fluid composition. Significance of the curves and brackets is identical to those in Figure 1.

Fig. 4. Experimental data pertaining to equilibrium 4 in H₂O-CO₂ mixtures at $P = 2$ kbar. Significance of the curves and brackets is identical to those in Figure 1.
$X_{\text{CO}_2} = 0.58$, whereas the upper limit would be the point at $X_{\text{CO}_2} = 0.65$. This method yields an equilibrium $X_{\text{CO}_2}$ bracket considerably larger than that determined by the least-squares fit. In essence, the “classical” bracketing method leads to an overestimate of the uncertainty in the $X_{\text{CO}_2}$ bracket. Indeed, as demonstrated by Demarest and Hazelton (1981), refined statistical treatment of experimental data may, in many cases, lead to narrower uncertainties in experimentally-determined equilibrium curves. Although data points in the vicinity of the equilibrium crossover can lead to relatively large uncertainties with the “classical” bracketing method, they are very important for constraining the equilibrium location of the fitted curve. Without points close to the crossover there would be considerable latitude in the curvature of the fitted curve and, thus, in the equilibrium $X_{\text{CO}_2}$ determination. Further support for the validity of determining equilibrium by the curve-fitting technique is given by the data for the 500°C isotherm in Figure 3. As required theoretically, curves for Δmoles CO$_2$ and Δmoles quartz, which represent independent monitors of reaction, intersect at Δmoles = 0. Hunt and Kerrick (1977), and Eggert and Kerrick (1981) noted similar relationships between independent monitors of reaction rate. Furthermore, except for some slight differences in curvature, the curves for quartz and CO$_2$ are antithetic (i.e., they are nearly mirror images of one another). This geometric relationship is predicted on the basis that quartz and CO$_2$ are on the opposite sides of the balanced reaction and that there are equal numbers of moles of these components in the balanced reaction.

The general shape of most of the curves in Figures 1–5 implies that the rate of the forward (CO$_2$-forming) reaction is faster than the rate of the reverse (CO$_2$-consuming) reaction. This is evidenced by the fact that the slopes of most curves are steeper for positive values of Δmoles than the curves in the region of negative Δmoles values. This behavior of the slope also implies that the rates of the forward reactions do not reach maximum values, whereas the rates of the reverse reactions do reach maximum values at $X_{\text{CO}_2}$ values away from the equilibrium $X_{\text{CO}_2}$ value. Hunt and Kerrick (1977) found that a similar relationship existed for the forward and reverse reaction rates of equilibrium 4 as a function of temperature for runs performed at a constant initial $X_{\text{CO}_2}$.

**H$_2$O–CO$_2$–NaCl fluids**

The experimental results on equilibrium 4 in H$_2$O–CO$_2$–NaCl fluids are summarized in Figures 6 and 7. The method of determining equilibrium brackets for a particular pressure and temperature is identical to that discussed above for binary H$_2$O–CO$_2$ mixtures. The shapes of the curves in Figures 6 and 7 are similar to that of the curves in H$_2$O–CO$_2$ mixtures (Figs. 1–5), implying a similar relationship between the forward and reverse reaction rates in NaCl-bearing solutions compared to those in binary H$_2$O–CO$_2$ mixtures. The presence of NaCl in the fluid phase may enhance the kinetics of the reactions (compare Figs. 6 and 7 to Figs. 4 and 5), but more data of this type is necessary before any definitive conclusions can be reached regarding the kinetics of the reactions.

Capsules containing only calcite and H$_2$O–CO$_2$–NaCl solutions yielded no increase in the mass of CO$_2$ after a run, implying that there was little or no dissolution of calcite. Optical and X-ray analysis of the run products indicated that no extraneous phases not common to equilibrium 4 formed during the runs. Since equilibrium 4 involves decarbonation, the mass of H$_2$O before and after a run should remain unchanged, thus providing an additional
check on any unexpected fluid–solid reactions resulting from the presence of NaCl in the fluid. For all runs, the mass of H₂O remained essentially constant, implying that there were no reactions other than the forward and reverse reactions of equilibrium 4 occurring during the runs.

Some dissolution of Ag from the capsule is expected in Cl-bearing aqueous solutions. For the salinites in our experiments, Seward’s (1976) data on the solubility of AgCl in aqueous sodium chloride solutions at 353°C suggests that the concentration of NaCl is ten times larger than that of AgCl. Such low concentrations of AgCl suggest that the activities of components may be quite similar to those in the pure H₂O–CO₂–NaCl system.

**Thermodynamic analysis**

In this section, experimental equilibrium data are compared to equilibria derived by thermodynamic calculations. From one experimental equilibrium bracket, a curve can be extrapolated in P–T–XCO₂ space using available thermodynamic data. The method, discussed in detail by Kerrick and Slaughter (1976), requires evaluating the following equation (equation 17 of Kerrick and Slaughter, 1976) from one experimentally determined starting point (P₁, T₁, K₁) to the P–T–XCO₂ conditions of interest (P₂, T₂, K₂):

\[
\left(\frac{\Delta G_f}{T}\right)_P^P_2 - \left(\frac{\Delta G_f}{T}\right)_P^P_1 = 0
\]

\[
= \int_{P_1}^{P_2} \Delta V_f^0 \, dP - \int_{T_1}^{T_2} \Delta S_f^0 \, dT + RT_2 \ln K_2 - RT_1 \ln K_1
\]

(1)

The computer programs of Slaughter et al. (1976), modified to incorporate hsmrk-derived activity coefficients for H₂O and and CO₂ (Jacobs and Kerrick, 1981), were used for all calculations. Thermodynamic data for pure H₂O and CO₂ were taken from Burnham et al. (1969) and Burnham and Wall (unpublished), respectively. High-temperature entropies were calculated from an integrated form of the Maier–Kelley heat capacity equation: \( A \ln T + B(10^3 \times T) + C(10^5/T^2) + D \). The constants of this equation (A, B, C, and D) for the minerals considered in this study, which are listed in Table 4, were
derived from a least-squares fit to the entropy data of Robie and Waldbaum (1968), with the following exceptions: anorthite: Robie et al. (1978); diopside: Krupka et al. (1980); grossular: Perkins et al. (1977); margarite and zoisite: Perkins et al. (1980). Extrapolations (both ideal and activity-corrected) were started at experimental equilibrium brackets \((P_1, T_1, K_1)\) which resulted in calculated curves most consistent with the other experimental data.

### T–X\(_{\text{CO}_2}\) relations

Comparison of multiple experimental equilibrium brackets for decarbonation and dehydration equilibria with curves calculated from thermodynamic data gives a direct measure of the activity coefficients for \(\text{CO}_2\) and \(\text{H}_2\text{O}\). Comparisons using "two-volatile" \((\text{H}_2\text{O}–\text{CO}_2)\) equilibria, on the other hand, only give a measure of the ratio or product of activity coefficients for \(\text{H}_2\text{O}\) and \(\text{CO}_2\). Nevertheless, both types of equilibria are useful for evaluating the reliability of thermodynamic data and HSMR-K derived activities for \(\text{H}_2\text{O}\) and \(\text{CO}_2\). An isobaric \(T–X_{\text{CO}_2}\) section calculated for equilibrium 2 demonstrates the effect of assuming ideal versus non-ideal mixing of \(\text{H}_2\text{O}\) and \(\text{CO}_2\) for the calculation of decarbonation equilibria (Fig. 8.). At a given pressure and temperature, the difference between the solid and dashed curves is a measure of the activity coefficient for \(\text{CO}_2\). As both temperature and pressure are increased, the magnitude of the activity coefficients for \(\text{CO}_2\) remains approximately constant, reflecting the offsetting tendencies of increasing pressure and increasing temperature predicted by the HSMR-K equation for the \(P–T\) increases in Figure 8.

The experimental equilibrium brackets for equilibria 3 and 4 are shown on log \(K–1/T\) diagrams in Figures 9 and 10. Listed in Table 5 are the equations for the straight lines\(^2\), which are plotted on these diagrams and which represent, at any temperature, minimum and maximum values of log \(X_{\text{CO}_2}\), which are consistent with all of the experimental brackets. This approach is preferred over that of fitting lines of maximum and minimum slope to equilibrium brackets (e.g., Hunt and Kerrick, 1977; Kerrick and Slaughter, 1976; Skippen, 1971), because such lines do not yield realistic uncertainty bands for all \(P–T–X_{\text{CO}_2}\) conditions of the experiments. For example, in the region where lines of maximum and minimum

### Table 4. \(S_{298}\) and coefficients for high-temperature entropy equations* of minerals

<table>
<thead>
<tr>
<th>Phase</th>
<th>(S_{298})</th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
<th>(D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andalusite</td>
<td>21.28</td>
<td>42.270</td>
<td>5.516</td>
<td>7.026</td>
<td>-230.260</td>
</tr>
<tr>
<td>Anorthite</td>
<td>48.43</td>
<td>68.630</td>
<td>3.937</td>
<td>10.810</td>
<td>-405.100</td>
</tr>
<tr>
<td>Calcite</td>
<td>21.92</td>
<td>19.020</td>
<td>3.672</td>
<td>1.442</td>
<td>-115.075</td>
</tr>
<tr>
<td>Omphacite</td>
<td>22.18</td>
<td>28.792</td>
<td>2.062</td>
<td>5.502</td>
<td>-170.610</td>
</tr>
<tr>
<td>Dolomite</td>
<td>37.09</td>
<td>46.630</td>
<td>16.979</td>
<td>8.683</td>
<td>-280.869</td>
</tr>
<tr>
<td>Diopside</td>
<td>34.02</td>
<td>55.028</td>
<td>5.865</td>
<td>8.440</td>
<td>-324.625</td>
</tr>
<tr>
<td>FORsterite</td>
<td>22.75</td>
<td>35.966</td>
<td>6.688</td>
<td>4.614</td>
<td>-212.128</td>
</tr>
<tr>
<td>Geolinite</td>
<td>47.40</td>
<td>65.262</td>
<td>7.361</td>
<td>9.533</td>
<td>-384.302</td>
</tr>
<tr>
<td>Grossular</td>
<td>60.87</td>
<td>105.245</td>
<td>16.022</td>
<td>16.756</td>
<td>-620.978</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>36.94</td>
<td>65.573</td>
<td>11.771</td>
<td>9.846</td>
<td>-388.125</td>
</tr>
<tr>
<td>Kyanite</td>
<td>20.02</td>
<td>42.874</td>
<td>5.386</td>
<td>7.671</td>
<td>-554.380</td>
</tr>
<tr>
<td>Magnesite</td>
<td>15.70</td>
<td>26.314</td>
<td>5.345</td>
<td>6.376</td>
<td>-158.055</td>
</tr>
<tr>
<td>Margarite</td>
<td>63.01</td>
<td>94.000</td>
<td>32.345</td>
<td>11.647</td>
<td>-558.379</td>
</tr>
<tr>
<td>Muscovite</td>
<td>69.00</td>
<td>98.298</td>
<td>25.440</td>
<td>12.723</td>
<td>-582.200</td>
</tr>
<tr>
<td>Periclasia</td>
<td>6.44</td>
<td>11.954</td>
<td>0.581</td>
<td>1.699</td>
<td>-70.091</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>75.90</td>
<td>105.049</td>
<td>13.993</td>
<td>13.553</td>
<td>-617.675</td>
</tr>
<tr>
<td>Quartz</td>
<td>9.88</td>
<td>11.100</td>
<td>8.389</td>
<td>1.331</td>
<td>-67.238</td>
</tr>
<tr>
<td>Rutile</td>
<td>12.04</td>
<td>17.653</td>
<td>0.477</td>
<td>2.221</td>
<td>-107.979</td>
</tr>
<tr>
<td>Sphene</td>
<td>30.88</td>
<td>45.271</td>
<td>3.395</td>
<td>7.632</td>
<td>-266.589</td>
</tr>
<tr>
<td>Talc</td>
<td>62.34</td>
<td>106.487</td>
<td>20.236</td>
<td>19.962</td>
<td>-631.963</td>
</tr>
<tr>
<td>Tremolite</td>
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<td>192.908</td>
<td>54.819</td>
<td>26.396</td>
<td>-1144.273</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>19.60</td>
<td>27.650</td>
<td>2.854</td>
<td>4.234</td>
<td>-162.650</td>
</tr>
<tr>
<td>Zoisite</td>
<td>70.71</td>
<td>98.922</td>
<td>36.357</td>
<td>12.039</td>
<td>-587.914</td>
</tr>
</tbody>
</table>

*Coefficients are for an equation of the form: \(A (\ln T) + B (10^3 x T) + C (10^2/T^2) + D\).
slope intersect on log $K-1/T$ diagrams, estimation of an uncertainty band is difficult. In Figures 9 and 10, the series of experimental brackets sufficiently constrain the slope of the lines and the error envelopes of the brackets define the uncertainty band consistent with all the data.

The experimental equilibrium brackets and the uncertainty bands derived from Figures 9 and 10 for equilibria 3 and 4 are plotted together in Figures 11 and 12, respectively. Since the data at each pressure cover a wide range of $T-X_{CO_2}$ values, a stringent test is provided for the thermodynamic data and HSMRK-derived activities for CO$_2$. The 2 kbar experimental data (see Figures 11 and 12) indicate that ideal mixing of H$_2$O and CO$_2$ is an adequate assumption at these $P-T$ conditions. The HSMRK equation predicts only small positive deviations ($\gamma_{CO_2} > 1.0$) from ideality at 2 kbar, which results in calculated curves in good agreement with the experiments except at $T \approx 400^\circ$ C (the lower temperature limit investigated by Kerrick and Jacobs, 1981). With the exception of low $X_{CO_2}$ values, curves calculated for equilibrium (3k) at 6 kbar (Fig. 11) assuming ideal mixing and those calculated with HSMRK-derived activities are both in good agreement with the experimental data. However, for equilibrium 4 at 6 kbar (Fig. 12) the curve calculated with HSMRK-derived activities is in much better agreement with the experimental data than that calculated assuming ideal mixing and those calculated with activities derived from equilibrium (4) at 6 kbar (Fig. 12).

Table 5. Limiting log $K-1/T$ equations for equilibria 3 and 4

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>$P$ (kb)</th>
<th>$a$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3a)</td>
<td>P = 2</td>
<td>6.89</td>
<td>-5.16</td>
</tr>
<tr>
<td>(3k)</td>
<td>P = 6</td>
<td>7.27</td>
<td>-6.32</td>
</tr>
<tr>
<td>(4)</td>
<td>P = 2</td>
<td>4.82</td>
<td>-3.97</td>
</tr>
<tr>
<td>(4)</td>
<td>P = 6</td>
<td>5.76</td>
<td>-5.23</td>
</tr>
</tbody>
</table>

* For each equilibrium, the pair of $a$ and $b$ values listed in a column relates to a limiting line plotted in Figures 9 or 10.
calculated with the assumption of ideal mixing of H$_2$O and CO$_2$.

A similar $T$-$X_{CO_2}$ analysis of the HSMRK equation is presented in Figure 13 for the 1 and 2 kbar data of Greenwood (1967) and Harker and Tuttle (1956) on equilibrium 1. At these relatively high temperatures and low pressures, Greenwood (1967) noted that assuming ideal mixing resulted in no significant errors in calculated curves (Fig. 13). At these $P$-$T$ conditions, the HSMRK equation predicts only slight positive deviations from ideality, resulting in calculated curves in close agreement with the experimentally determined equilibrium data. Equilibrium 1 is again addressed in Figure 14, where data from Ziegenbein and Johannes (1974) and that of the present study are presented. The data in Figure 14 indicate that curves calculated with HSMRK-derived activities result in better agreement with the experiments than those assuming ideal mixing. It should be noted that the 2 kbar data of Greenwood (1967) is inconsistent with that of Ziegenbein and Johannes (1974). However, Greenwood (1967) may have overestimated the experimental temperatures (Kerrick, 1974, p. 741). Overestimation of experimental temperatures may have occurred in the study of Harker and Tuttle (1956) also, since no filler rods were used in the hydrothermal vessels (see Boettcher and Kerrick, 1971). Providing that any errors in temperature measurement in the studies of

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**Fig. 11.** $T$-$X_{CO_2}$ sections for equilibria 3a and 3k at $P = 2$ and 6 kbar, respectively. The rectangles are experimental equilibrium brackets. The dotted curves were calculated with the equations in Table 5. The solid and dashed curves were calculated assuming HSMRK-derived activities and ideal mixing of H$_2$O and CO$_2$, respectively. The starting points for the ideal and activity-corrected extrapolations were the upper and lower temperature limits at $X_{CO_2} = 1.0$, respectively, calculated with the equations in Table 5.

**Fig. 12.** $T$-$X_{CO_2}$ sections for equilibrium 4 at $P = 2$ and 6 kbar. The rectangles are the experimental equilibrium brackets. The dotted curves were calculated with the equations in Table 5. The solid and dashed curves were calculated assuming HSMRK-derived activities and ideal mixing of H$_2$O and CO$_2$, respectively. The starting points for the ideal and activity-corrected extrapolations at $P = 6$ kbar were $T = 625^\circ C$, $X_{CO_2} = 0.79$ and $T = 615^\circ C$, $X_{CO_2} = 0.85$, respectively. At $P = 2$ kbar, the starting points for the ideal and activity-corrected curves were the upper and lower temperature limits at $X_{CO_2} = 1.0$, respectively, calculated from the equations in Table 5.

**Fig. 13.** $T$-$X_{CO_2}$ sections at $P = 1$ and 2 kbar for equilibrium 1 using the data of Greenwood (1967) and Harker and Tuttle (1956). The solid and dashed curves were calculated assuming HSMRK-derived activities and ideal mixing of H$_2$O and CO$_2$, respectively. The starting points for the extrapolations were $P = 1$ kbar, $T = 670^\circ C$, $X_{CO_2} = 1.0$ and $P = 2$ kbar, $T = 730^\circ C$, $X_{CO_2} = 1.0$.\n
---
This study follows the initial work by Ziegenbein and Johannes (1974) and Greenwood (1967) systematically and not large, little error should be introduced using this experimental data in the $T-X$ analysis of this paper.

Figures 15-18 provide a $T-X$ analysis for mixed-volatile equilibria. In Figure 15 a curve calculated with HSMRK-derived activities provides a much better fit to the experimental data of Gordon and Greenwood (1970) than that calculated assuming ideal mixing (Lewis and Randall rule) of H$_2$O and CO$_2$. As shown in Figure 16, similar improvement in calculated curves is obtained for the data of Metz and Puhan (1970, 1971). In addition, from their 6 kbar data on the equilibrium: 5 dolomite + 8 quartz + H$_2$O = tremolite + 3 calcite + 7 CO$_2$, Eggert and Kerrick (1981) show that the isobaric $T-X$ curve calculated with HSMRK-derived activities is in much closer agreement than a curve calculated assuming ideal mixing of H$_2$O and CO$_2$. Figure 17 shows that assuming either ideal mixing or HSMRK-derived activities yields calculated curves consistent with the 6 kbar data of Hewitt (1973) on the equilibrium: muscovite + calcite + quartz = K-feldspar + anorthite + H$_2$O + CO$_2$. The larger deviation from ideal mixing in the H$_2$O-rich portion of Figure 17 resulting from calculation...
with HSMRK-derived activities is compatible with the skewness of the H$_2$O–CO$_2$ solvus (Tödheide and Franck, 1963). Figure 18 shows that at both 1 and 5 kbar, HSMRK-derived activities yield calculated curves in better agreement with the data of Metz (1967) on another mixed-volatile equilibrium, though at 1 kbar the difference is not large.

Figures 11–18 illustrate that combining HSMRK-derived activities with thermodynamic data yields calculated curves in close agreement with experimental brackets of many devolatilization equilibria. Figures 19 and 20 illustrate the effect that ideal versus non-ideal mixing can have on the calculation of $P$–$T$–$X_{CO_2}$ topologies. The magnitude of the effect will depend on the experimental constraints used in the construction of the topology and on the extent of the extrapolations in $P$–$T$–$X_{CO_2}$ space. The high (Fig. 19) and low (Fig. 20) temperature portions of the system CaO–Al$_2$O$_3$–SiO$_2$–CO$_2$–H$_2$O have been calculated by combining experimental data with thermodynamic extrapolations assuming ideal and non-ideal mixing of H$_2$O and CO$_2$. The largest differences in the positions of invariant points occur when extrapolations are made over a wide range of temperature and/or $X_{CO_2}$. For example, in Figure 19 the stability field of grossular is shifted by approximately 10 mole% to more H$_2$O-rich compositions at temperatures of 600–800°C when calculated curves are corrected for non-ideal mixing of H$_2$O and CO$_2$ with the HSMRK equation. This difference is quite significant for quantifying the $P$–$T$–$X_{CO_2}$ conditions of metamorphic assemblages using equilibrium data. As seen in Figure 20, the stability field of zoisite defined by the equilibrium: 2 zoisite + CO$_2$ = anorthite + calcite + H$_2$O is significantly expanded at lower temperatures when the calculated curve is corrected for non-ideality in H$_2$O–CO$_2$ mixtures via the HSMRK equation. In addition, for the topologies calculated with HSMRK-derived activities, each invariant point in Figure 20 is shifted to higher temperatures (circles) compared to that derived with the assumption of ideal mixing of H$_2$O and CO$_2$ (squares).

$P$–$T$ relations

The $T$–$X_{CO_2}$ analysis in the preceding section suggests that the thermodynamic data result in calculated curves that are quite consistent with experimental equilibrium data. However, to confidently calculate topologies at a variety of pressures, the consistency of experimental and thermodynamic data as a function of pressure and temperature must be evaluated. As noted in the introduction,
several authors have carried out such an analysis for solid-solid and dehydration equilibria, but the internal consistency between experiments and thermodynamic calculations for decarbonation and mixed-volatile equilibria has not been thoroughly evaluated. Figures 21-24 provide such an evaluation for several devolatilization equilibria at constant values of $X_{\text{CO}_2}$. In these diagrams, the brackets from this study and that of Eggert and Kerrick (1981) were derived by the statistical curve-fitting method described in the section on Experimental Results, whereas the brackets from other studies are directly from the published paper. In $P-T$ section, little difference exists between curves calculated assuming ideal mixing of H$_2$O and CO$_2$ and those calculated using HSMRK-derived activities due to the offsetting effects of pressure and temperature on the activity coefficients for these $P-T$ ranges (see Fig. 8), so for clarity only curves calculated with HSMRK-derived activities are presented in Figures 21-24.

Thermodynamic extrapolations of equilibria 1, 3, and 4 in $P-T$ section are compared to experimental equilibrium brackets in Figure 21. An extrapolation from the 2 kbar data of equilibrium 3 is consistent with the 6 kbar experimental bracket if the total uncertainty in the calculation resulting from errors in the thermodynamic data is considered. The 6 kbar data (at $X_{\text{CO}_2} = 1.0$) for equilibrium 4 lies at temperatures below those derived from an extrapolation from the 2 kbar bracket. However, the equilibrium bracket of Hunt and Kerrick (1977) at 3.5 kbar is in excellent agreement with the extrapolation from 2 kbar. The reason for the discrepancy at 6 kbar for equilibrium 4 is as yet unexplained. As
Fig. 21. $P$--$T$ sections at $X_{CO_2} = 1.0$ for equilibria 1, 3, and 4. The experimental brackets at $X_{CO_2} = 1.0$ were taken from Figs. 11-14. The extrapolations for each equilibrium used the respective 2 kbar brackets as starting points. Note the two extrapolations for equilibrium 3. The Al$_2$SiO$_3$ triple point is taken from Holdaway (1971).

Fig. 22. $P$--$T$ sections for three decarbonation equilibria. The brackets at $P = 5$ and 6 kbar, $X_{CO_2} = 0.95$ for equilibrium 2, were from the experimental brackets obtained by extrapolation at lower $X_{CO_2}$ values of this study and that of Eggert and Kerrick (1981). The starting points for calculating each $P$--$T$ curve were the lowest pressure experimental brackets.

Figures 23 and 24 illustrate that $P$--$T$ extrapolations for several mixed-volatile equilibria are also consistent with experimental determinations. Extrapolations of two mixed-volatile equilibria are shown along with experimental determinations in Figure 24. In each case, the agreement between the calculated curve and the experiments is excellent. As seen in Figure 23, calculated $P$--$T$ slopes for equilibria with $H_2O$ and $CO_2$ having stoichiometric coefficients of opposite sign are in generally close agreement with experimental determinations. Agreement for an extrapolation from 1 to 6 kbar on the equilibrium in Figure 23B is excellent. The equilibrium extrapolated in Figure 23A is in close agreement with all the experimental equilibrium brackets except the 1 kbar determination of Metz and Puhan (1970, 1971). Considering uncertainties in the entropies for the solid phases alleviates this discrepancy, however. The agreement in Figure

seen in Figure 21, comparison of the 6 kbar bracket for equilibrium 1 to the low pressure data of Harker and Tuttle (1956) results in an experimental $P$--$T$ slope which is too steep relative to that calculated from thermodynamic data. On the other hand, an extrapolation from the 2 kbar bracket of Ziegenbein and Johannes (1974) is in good agreement with the higher pressure data. This analysis supports the earlier suggestion that the experimental temperatures in the study by Greenwood (1967) and Harker and Tuttle (1956) may have been overestimated. As noted before, these inconsistencies associated with equilibria 1 and 4 should in no way alter the conclusions reached from the $T$--$X_{CO_2}$ analysis of the preceding section, which was accomplished at constant pressure.

Extrapolations for three other decarbonation equilibria, each at a different, constant $X_{CO_2}$ value, are shown in Figure 22. In each case, an extrapolation from the lowest pressure bracket is in excellent agreement with the higher-pressure experimental determinations, implying internal consistency between the thermodynamic data for the various phases involved and the experimental equilibrium brackets.
23A is very satisfying, since the experimental data originates from three different hydrothermal laboratories using different methods of determining equilibrium $P-T-X_{CO_2}$ conditions.

$H_2O-CO_2-NaCl$ analysis

The importance of precisely quantifying the calculation of $P-T-X_{CO_2}$ topologies was illustrated by the analyses in Figures 11-24. However, to best represent geologic systems, the effect which the presence of species in addition to $H_2O$ and $CO_2$ in the fluid phase has on $P-T-X_{CO_2}$ topologies must be considered. Jacobs and Kerrick (1981) have shown that the presence of small amounts of $CH_4$ can significantly affect the activity relations of $H_2O$ and $CO_2$, thereby affecting $P-T-X_{CO_2}$ topologies. As noted in the introduction, NaCl also has been shown to be an important species in metamorphic fluids.

Figure 25 compares the results of experiments on equilibrium 4 in $H_2O-CO_2-NaCl$ fluids with those in $H_2O-CO_2$ fluids. At 2 kbar, the experimental equilibrium brackets for both 5 and 10 wt.% NaCl are consistent with the results of experiments in binary $H_2O-CO_2$ fluids. This agreement implies that, for NaCl salinities of 5-10 wt.% at these $P-T$ conditions, the activity of $CO_2$ is not significantly different from that in binary $H_2O-CO_2$ fluids. This agreement also suggests that unmixing of the fluid phase does not occur at these $P-T-X_{CO_2}$ conditions, although the addition of small amounts of NaCl to $H_2O-CO_2$ fluids has been shown to expand the solvus (Hendel and Hollister, 1981, Hollister and Burruss, 1976; Takenouchi and Kennedy, 1965). At 6 kbar, little difference is observed between equilibrium brackets in NaCl-bearing vs. NaCl-absent fluids at high $X_{CO_2}$ values (Fig. 25). However, for $H_2O$-rich compositions, significant departures from the equilibrium curve in binary $H_2O-CO_2$ mixtures are
Fig. 25. T-X CO2 sections at P = 2 and 6 kbar for equilibrium 4 in H2O-CO2-NaCl mixtures. The wt.% NaCl represents the composition of the aqueous solutions which, along with silver oxalate, were used as starting materials to generate the experimental fluid compositions. The dashed curves were calculated with the equations in Table 5, and represent equilibrium constraints in H2O-CO2 mixtures. The rectangles represent experimental determinations of equilibrium 4 in H2O-CO2-NaCl mixtures.

observed for both 5 and 10 wt.% NaCl. These departures in H2O-rich fluids suggest an increased activity of CO2 resulting from the presence of NaCl in the fluid phase. It has been shown that the addition of NaCl to H2O-CO2 fluids expands the solvus (Hendel and Hollister, 1981; Gehrig et al., 1979; Takenouchi and Kennedy, 1965). The experimental data of Gehrig et al. (1979) demonstrate that unmixing of the fluid could not have occurred in the runs with 5 wt.% NaCl. Although no experimental data exist for the complete delineation of the solvus for salinities corresponding to our 10 wt.% NaCl runs, extrapolation of the lower salinity data to this composition suggests that the solvus in the H2O-CO2-NaCl system lies at lower temperatures than those of our experiments. Although more work on this subject is necessary, the implications are clear: the addition of NaCl to H2O-CO2 fluids affects the activity of CO2, thereby affecting the stability of mineral assemblages which are dependent upon the activity of this component.

Discussion

Calculated Clapeyron slopes for decarbonation and mixed-volatile equilibria have been shown to be in good agreement with experimental equilibrium data. As noted in the introduction, several authors have shown similar agreement between calculated and experimental curves for dehydration and solid-solid equilibria. The HSMRK equation of Kerrick and Jacobs (1981) provides reasonable estimates for activities in H2O-CO2 mixtures at elevated pressures and temperatures. Consequently, with a few, narrow experimental equilibrium brackets, precise P-T-XCO2 topologies can be calculated for use in the analysis of natural assemblages.

Experimental results on equilibrium 4 in NaCl-bearing fluids reinforce the need to accurately determine the thermodynamic properties of H2O-CO2-NaCl solutions over a wide range of pressure and temperature.

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