Reports

Calcite-Dolomite-Magnesite Stability Relations in Solutions at Elevated Temperatures

Abstract. *The stability relations of calcite, dolomite, and magnesite in aqueous $CaCl_2$-$MgCl_2$-CO_2 solutions have been determined between 275° and 420°C. Small quantities of the carbonates were allowed to equilibrate with large volumes of aqueous solutions, permitting the approach of phase boundaries from two directions. Experimental data indicate that the stability field of calcite narrows toward higher temperatures, dolomite is incongruently soluble, and magnesite stability extends into the calcium-rich portion of the system.*

The relationship between the composition of hydrothermal solutions and the mineralogy of carbonates with which they are in equilibrium has proved to be a very durable problem. Although the solubility of calcite, $CaCO_3$, in aqueous solutions up to about 300°C is now fairly well understood (*1*), attempts to measure the solubility of dolomite, $CaMg(CO_3)_2$, have not been particularly successful. As a contribution to this problem, the stability relations of calcite, dolomite, and magnesite, $MgCO_3$, in 2*M* chloride solutions have been studied in the temperature range from 275° to 420°C by a technique which permitted phase boundaries to be approached from two directions.

Standard hydrothermal techniques were employed throughout this study. Gold-lined pressure vessels of 50-ml capacity with simple gasket closures were used at temperatures up to 320°C. For experiments at higher temperatures gold-lined pressure vessels described by Morey (*2*) were found to be more suitable, as the solutions were completely enclosed in precious metal, and iron contamination due to corrosion was, therefore, minimized. The mole (*m*) fraction of iron—$m_{Fe^{++}}/m_{Fe^{++}} + m_{Ca^{++}} + m_{Mg^{++}}$—in the final solutions was always less than 0.01, and the solid products contained less than 0.1 percent of iron. The effect of this amount of iron contamination on the position of the phase boundaries is probably negligible.

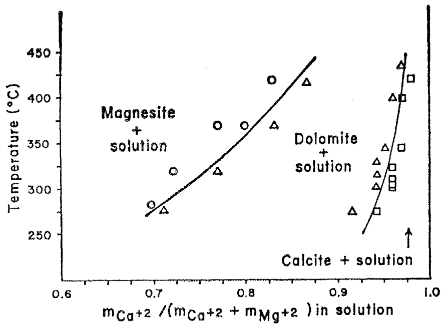

Fig. 1. The mole fractions, $m_{Ca^{++}}/(m_{Ca^{++}} + m_{Mg^{++}})$, in solutions in equilibrium with calcite + dolomite and dolomite + magnesite at temperatures between 275° and 420°C. Squares indicate runs in which dolomite was replaced by calcite; circles, dolomite replaced by magnesite; and triangles, calcite or magnesite replaced by dolomite. The presence of the vapor phase and the possible intervention of critical phenomena have been ignored.

Fifteen to 30 mg of natural dolomite (analyzed), synthetic magnesite, or reagent-grade calcite were placed in a pressure vessel together with enough 2*M* $CaCl_2$-$MgCl_2$ solution so that the reaction vessel was approximately half full. As nucleation of dolomite and magnesite is known to be difficult, many runs were seeded with about 1 mg of the phase which was expected to be stable. After CO_2 (at a pressure of approximately 60 bars) had been admitted to the reaction vessel, the vessel was sealed and placed in an electric resistance furnace. The partial pressure of CO_2 was not measured during the experiments, as the phase boundaries, magnesite-dolomite and dolomite-calcite, are almost certainly affected only very slightly by variation in the CO_2 pressure under the conditions of this study. The main function of the added CO_2 was to prevent the appearance of brucite, $Mg(OH)_2$. Reaction of the solid phases with solutions, although not complete, was sufficient after 8 days at 275°C and 24 hours at 420°C for the stable phase to be identified. In a number of experiments the reaction was allowed to go to completion. After rapid quenching the solid phase or phases were examined by means of x-ray powder diffractometry. The quantity of calcium and magnesium in solution was always very much larger than the quantity of these elements in the solid phases, so that the mole fraction of calcium and magnesium in solution was not disturbed to any significant extent by reaction with the solid phases during the experiments.

Figure 1 is a summary of the critical data used in the determination of the calcite-dolomite and dolomite-magnesite boundaries. The calcite-dolomite boundary is believed to be fixed to within a mole fraction, $m_{Ca^{++}}/(m_{Ca^{++}} + m_{Mg^{++}})$, of 0.01, the dolomite-magnesite boundary to within a mole fraction, $m_{Ca^{++}}/(m_{Ca^{++}} + m_{Mg^{++}})$, of 0.02.

X-ray ordering reflections were observed in all phases referred to as dolomite in this report. Compositions of dolomite were estimated by measurement of the position of the (211) x-ray reflections relative to an internal standard by means of the relationship between angular displacement of the (211) reflection ($\Delta 2\theta$) and composition described by Harker and Tuttle (*3*). Within the limits of measurement ($\pm .01°2\theta$) most dolomites were found to lie very close to ideal composition. Dolomites which were found to contain more than 2 percent (mole) excess $CaCO_3$ were not considered in the determination of the boundaries shown in Fig. 1.

The stability field of dolomite (Fig. 1) lies entirely in the calcium-rich portion of the system between 275° and 420°C

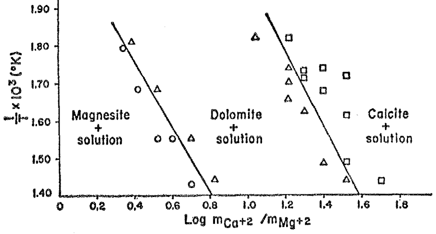

Fig. 2. Variation of log $m_{Ca^{++}}/m_{Mg^{++}}$ with $1/T$ (°K) in solutions in equilibrium with calcite + dolomite and dolomite + magnesite. Symbols as in Fig. 1.

and, therefore, dolomite is incongruently soluble in this temperature range. The stability field of dolomite broadens with decreasing temperature while toward higher temperatures solutions in equilibrium with calcite + dolomite, or with dolomite + magnesite become progressively richer in calcium. In the absence of phase data for the system $CaCl_2$-$MgCl_2$-CO_2-H_2O, the presence and composition of the vapor phase and the possible intervention of critical phenomena have been neglected in this study.

In view of the data in Fig. 1, the predominance of calcite and dolomite over magnesite in hydrothermal veins suggests that calcium is normally more abundant than magnesium in hydrothermal solutions. This conclusion is confirmed by many analyses of the composition of fluids in fluid inclusions from hydrothermal minerals (*4*), although some low-temperature fluid inclusions have been found in which the magnesium concentration apparently somewhat exceeds the calcium concentration (*5*). The process of the dolomitization of calcite above 275°C must involve solutions in which calcium predominates over magnesium despite the frequent references to magnesium-rich solutions as the dolomitizing agents. Small variations in the ratio of calcium to magnesium in a hydrothermal solution could, of course, transform it from a dolomitizing to a dedolomitizing fluid if the solution composition is near the calcite-dolomite boundary.

The equilibrium between calcite, dolomite, and solution can be written in the form

$$2\ CaCO_3 + Mg^{++} \rightleftharpoons CaMg(CO_3)_2 + Ca^{++}.$$

In the temperature range investigated, the solid solution of Mg^{++} in calcite and of Ca^{++} in dolomite is small, so that, to a close approximation, the equilibrium constant for the reaction is

$$K_{\text{calcite-dolomite}} = \frac{a_{Ca^{++}}}{a_{Mg^{++}}} = \frac{\gamma_{Ca^{++}}\, m_{Ca^{++}}}{\gamma_{Mg^{++}}\, m_{Mg^{++}}}$$

where a is activity, and γ is activity coefficient. If the activity coefficient of Ca^{++} is about the same as that of Mg^{++}, then

$$K_{\text{calcite-dolomite}} = \frac{m_{Ca^{++}}}{m_{Mg^{++}}}$$

and a diagram plotting the logarithm of this ratio against $1/T$ (°K) should yield a nearly linear relationship.

Similarly, the equilibrium between dolomite, magnesite, and solution can be written

$$CaMg(CO_3)_2 + Mg^{++} \rightleftharpoons 2\ MgCo_3 + Ca^{++}.$$

The equilibrium constant for this reaction will also be approximately

$$K_{\text{dolomite-magnesite}} = \frac{m_{Ca^{++}}}{m_{Mg^{++}}}$$

and plotting the logarithm of this ratio against $1/T$ (°K) should also yield nearly a straight line. The predicted linear relationships are confirmed in Fig. 2.

At the calcite-dolomite boundary

$$\log \frac{m_{Ca^{++}}}{m_{Mg^{++}}} = \frac{-1.00 \times 10^3}{T} + 2.98 \qquad (275°\text{–}420°C)$$

and at the dolomite-magnesite boundary

$$\log \frac{m_{Ca^{++}}}{m_{Mg^{++}}} = \frac{-1.10 \times 10^3}{T} + 2.34 \qquad (275°\text{–}420°C)$$

Both lines might be extrapolated to lower temperatures, particularly to room temperature where so much controversy has surrounded the phase relationships among these carbonates. However, such an extrapolation is very long, and the results cannot be taken seriously. On the other hand, an extrapolation of the dolomite-magnesite boundary to 200°C does not seem too extravagant. Near that temperature dolomite becomes congruently soluble. If the dolomite-calcite boundary continues to sweep toward smaller values of the mole fraction of calcium in solution with decreasing temperature, dolomite will again become incongruently soluble at some temperature below 200°C. An extrapolation of the dolomite-calcite boundary in Fig. 2 puts this lower limit near 60°C. But analytical data for ground-water samples from limestone-dolomite terrain (*6*) suggest that the lower temperature limit is below 10°C. In the absence of definitive experimental or field data, the problem of the lowest temperature at which dolomite is congruently soluble is still unsolved.

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Xenon Hexafluoride: Preparation of Pure Form and Melting Point

Abstract. *Xenon hexafluoride forms an addition compound with sodium fluoride which can be used to separate it from the other xenon fluorides and oxyfluoride. The melting point of pure xenon hexafluoride prepared in this way was 47.7 ± 0.2°C.*

One of the problems in studying the fluorides of xenon has been the difficulty of obtaining pure materials. This is especially true for xenon hexafluoride. Pure xenon difluoride can be obtained photochemically by irradiation of a mixture of xenon and fluorine with a high-pressure mercury arc (*1*). A bath maintained at −78°C in the system condenses pure XeF_2 as soon as it is formed and prevents further reaction to XeF_4. Pure xenon tetrafluoride can be obtained by heating a mixture of xenon and fluorine in a closed system at 400°C (*2*). If the preparation is carried out to insure that no XeF_2 remains unreacted, the small amounts of XeF_6 formed can easily be removed, because of its greater volatility, with very little loss of XeF_4. Xenon hexafluoride is prepared by heating xenon with a large excess of fluorine at pressures up to several hundred atmospheres (*3, 4*). The best preparations to date have a fluorine to xenon ratio of about 5.9, indicating a mixture of about 95 percent XeF_6 and 5 percent XeF_4. The infrared spectrum of this material showed absorption bands attributable to $XeOF_4$, XeF_4, and XeF_2.