

mechanism also could explain the large crystal dimensions and the many variations from a regular crystal structure that are observed. The electrodeposition would be diffusion-controlled, favoring large crystals. Concentrations, current density, and temperature could vary considerably during the long period of deposit formation. Crystal structure variations could reflect this as they do in the electrodeposition of metals.

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SUBSOLIDUS PHASE RELATIONS IN THE SYSTEM
 CALCIUM CARBONATE-CADMIUM CARBONATE

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ABSTRACT

In the temperature range 400°-750°C, a miscibility gap of aragonite- and calcite-type phases forms in the Ca rich portion at 15 kbar. It diminishes in range with decreasing pressure, and at 10 kbar a complete series of solid solutions of the calcite-type structure was found.

Variation of lattice parameters of the solid solution series was calculated as a function of binary composition, and *c* shows a positive deviation from the Vegard's law.

Subsolidus phase relations among calcite-type carbonates have been studied extensively in recent years, but for the system CaCO₃-CdCO₃, equilibrium relationship has not been satisfactorily established. Because the two divalent cations involved in the system are of almost identical ionic size and distinct electronic structure, this system is of interest especially in three aspects; the effect of cadmium on the calcite-aragonite

phase transition, the extent of the calcite-type solid solution, and the solubility of cadmium in aragonite.

Experimental work was performed in the high-pressure, opposed-anvil apparatus with starting materials prepared as precipitates from reagent grade carbonates (Chang, 1965). The apparatus and the procedures to operate it were described in detail by Griggs and Kennedy (1956), and by MacDonald (1956), while Goldsmith and Newton (1969) discussed the suitability of this apparatus for carbonate research. In general, a period of eight hours was used for runs made above 700°C, forty-eight hours for runs in the temperature range 500°–700°C, and ninety-six hours for runs below 500°C. A small amount of Li_2CO_3 was added to some low-temperature runs, a procedure known to be effective in promoting reactions in carbonates (Goldsmith and Graf, 1957 and Chang, 1965). The uncertainties in the individual runs are estimated to be $\pm 5^\circ\text{C}$ and less than 0.5 kbars.

X-ray diffraction was used for the identification of solid phases and for the measurement of lattice parameters of the solid solutions. Four oscillations were made over the 2θ range, 35° – 55° , for each sample of measurement with a General Electric diffractometer. The (110) line of metallic tungsten (from Lamp Metals and Components Department, General Electric Co., Cleveland, Ohio, highly purified) at $2\theta = 40.26^\circ$ ($a = 2.1648 \text{ \AA}$, Swanson and Tatge, 1953) was used as an internal standard. Ni-filtered, Cu-radiation was used throughout this study.

Equilibrium relations at 15 kbar and in the temperature range 400°–750°C are shown in Figure 1. Aragonite is the stable form of CaCO_3 for the most part of this temperature range, and is transformed to calcite at

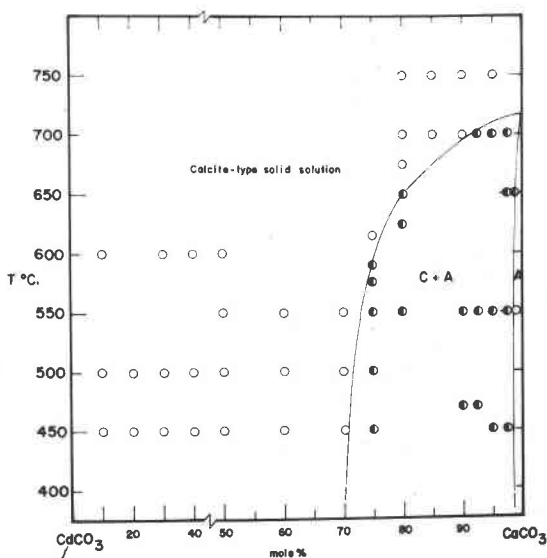


FIG. 1. Subsolidus phase relations in the system CaCO_3 – CdCO_3 at 15 kbar. Some regions in the diagram are labelled with symbols representing stable phases; A: aragonite-type solid solution and C: calcite-type solid solution.

718°C. This temperature of transformation agrees fairly well with reported data (MacDonald, 1956; Clark, 1957; Boettcher and Wyllie, 1967; and Goldsmith and Newton, 1969).

In the binary system, there is a two-phase region consisting of aragonite- and calcite-type solid solutions. The stability of this phase assemblage decreases with increasing amount of cadmium. On the basis of experimental data obtained, a continuous curve can be constructed to separate the two-phase region from the calcite-type solid solution. Also, this two-phase region diminishes in range with decreasing pressure. At 12 kbar, it is limited in the range of compositions between $\text{Ca}_{90}\text{Cd}_{10}$ and Ca_{100} and at temperatures below 530°C, whereas at 10 kbar, a complete series of solid solutions of the calcite-type structure forms in the system.

Lattice parameters as a function of composition in the system were calculated from measurements made on samples quenched from 650°C and 10 kbar by using calcite-type reflections (022) and (116). The plot is shown in Figure 2, illustrating a deviation in the c -axis from the Vegard's

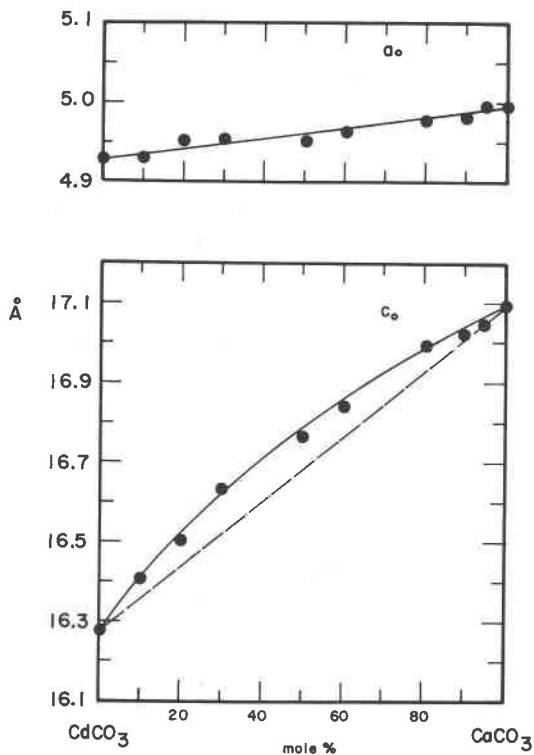


FIG. 2. Variation of lattice parameters of the calcite-type solid solutions in the system CaCO_3 - CdCO_3 .

law, which is most likely due to the difference in electronic structure between calcium and cadmium atoms. Goldsmith (private communication, 1968) made a preliminary study in this system and found that CdCO_3 did not have an exact calcite-type structure, and that this structural difference could not be detected by powder X-ray diffraction method.

The solubility of CdCO_3 in aragonite was determined by running a series of compositions, $\text{Ca}_{98.5}\text{Cd}_{1.5}$, $\text{Ca}_{97.5}\text{Cd}_{2.5}$, $\text{Ca}_{96}\text{Cd}_4$, and $\text{Ca}_{95}\text{Cd}_5$, at two temperatures, 550° and 650°C , and four pressures, 15, 20, 25, and 30 kbar. Results obtained indicate that the solubility is both temperature- and pressure-dependent. At 550°C , aragonite can take 1.5 mole percent CdCO_3 into its solid solution at 15 kbar, and the amount increases to 2.5 mole percent at 30 kbar, while at 650°C , a pressure of 20 kbar is necessary for aragonite to take 1.5 mole percent CdCO_3 . Sample of $\text{Ca}_{98.5}\text{Cd}_{1.5}$ produced the two-phase assemblage of aragonite- and calcite-type phases at 15 kbar.

In nature, intermediate phases of this system have not been observed to exist. Otavite, in a few known occurrences (Ramdohr and Strunz, 1941; and Johan, 1962), was found as a secondary mineral in close association with smithsonite.

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