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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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$_2$CO$_3$ 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 ±5°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 2θ=40.26° (a=2.1648 Å, 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.](image-url)
718°C. This temperature of transformation agrees fairly well with reported data (MacDonald, 1956; Clark, 1957; Boettcher and Wyllie, 1962; 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 Ca$_{90}$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

![Variation of lattice parameters of the calcite-type solid solutions in the system CaCO$_3$-CdCO$_3$.](image)
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Iaw, 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 CdCO₃ 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 CdCO₃ in aragonite was determined by running a series of compositions, Ca₉₈₅Cd₁₅, Ca₉₅₅Cd₂₅, Ca₉₄Cd₄, and Ca₉₃Cd₅, at two temperatures, 550°C 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 CdCO₃ 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 CdCO₃. Sample of Ca₉₅₅Cd₂₅ 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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