the whole range, occur naturally, though the scarcity of high cobalt members should be noted. The linearity of the series is also established, and the $d(511)$ Å spacing can be used to determine compositional variations of cobaltiferous pyrites, provided elements other than cobalt and iron do not enter the lattice. For practical purposes, nickel is the only other element likely to substitute, to any great extent.

For more detailed X-ray and chemical data, the reader should consult the author.

The electron probe scans revealed only minor variations in the distribution of iron and cobalt, and these could not be interpreted as banding, or a mechanical mixture of two phases, even on the finest scale.

All samples were completely optically homogeneous, showing no exsolution features.

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TRANSFORMATION OF ARAGONITE TO CALCITE UNDER HYDROTHERMAL CONDITIONS

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INTRODUCTION

Although numerous studies contributing to the knowledge of transformation rates for aragonite⇌calcite in dry environments have been published (*e.g.*, Kleber, 1940; Chaudron, 1952; Jamieson, 1953; MacDonald, 1956; Clark, 1957; Wray and Daniels, 1957; Brown *et al.*, 1962; Davis and Adams, 1965), data on reaction rates for the transition accomplished under hydrothermal conditions is nearly nonexistent. Brown

et al., (1962) have presented limited experimental data on the aragonite→ calcite transformation in liquid water, but inasmuch as such experimentation was only peripheral to their study, they did not pursue a systematic investigation of the reaction rates. A more detailed study of the transformation rates for aragonite→calcite under hydrothermal conditions, although not all-inclusive, is presented here.

Method of Investigation

The kinetics of the transformation of aragonite to calcite was studied by accomplishing the transformation in a closed hydrothermal system and determining the percent-of-conversion by X-ray diffraction analysis.

Source material. The white, fibrous aragonite (England) used in this study was obtained from Ward's Natural Science Establishment, Inc. Cubes measuring one cubic centimeter in volume were cut from this material using a diamond saw. This was done to eliminate any possible effect of varying size and shape of the material on the transformation rate. The absence of calcite in the X-ray diffractograms obtained on representative cubes simultaneously showed that the source material was free from calcite and that the cutting of the cubes and their being crushed for X-ray analysis did not induce a polymorphic transition.

Hydrothermal apparatus. The autoclave employed was of an improved design of the basic Morey pressure vessel developed by and commercially available from Tem-Pres, Inc. of State College, Penna. The vessel consisted of a thick-walled inconel container fitted with an SAE No. 4140 steel cap and a stainless steel plunger which permits a Bridgeman-type closure in addition to a gasket seal. The vessel was lined with 30-mil thick silver.

An electrical resistance, crucible-type, temperature-controlled furnace was used to maintain the autoclave at essentially constant temperature. Temperatures were measured by means of a calibrated chromel-alumel thermocouple inserted into the base of the autoclave at the level of the aragonite cube.

Experimental Procedure

Hydrothermal technique. The hydrothermal runs were carried out at 50° intervals over the temperature range 100° to 300°C. For those runs above 100°C a cube of aragonite was placed in the bottom of the reaction vessel which was then filled to 96.0, 91.4, 86.5, or 80.7 percent of the total free volume with deionized water when held at 150°, 200°, 250°, and 300°C, respectively. These percent-of-fill values are those which generate 800

bars pressure (Kennedy, 1950; the value for 150°C is extrapolated). The vessel was sealed and placed in a pre-heated furnace for a period of time; it was later removed, air-quenched, and cooled further by immersion in cold water. The partially transformed cube was then removed from the vessel and prepared for X-ray diffraction analysis. For the runs held at 100°C, the aragonite cubes were placed in a covered beaker of slowly boiling deionized water which was daily replenished.

Figure 1 shows the time and temperature of the individual runs. The time includes approximately three to four hours necessary for the auto-
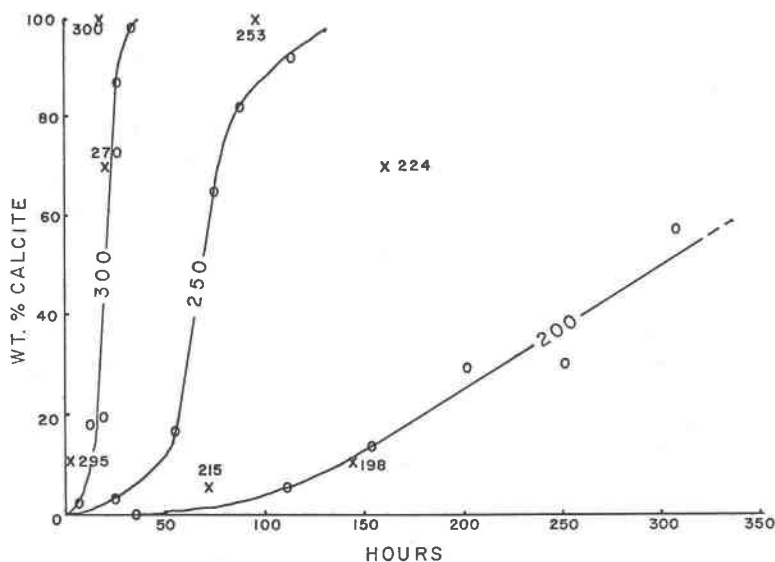

FIG. 1. Weight percent calcite formed vs. time for hydrothermal runs held at 200° to 300°C. Circles, authors' data; Xs, data of Brown *et al.* (1962).

clave, once placed in the preheated furnace, to attain the plotted temperature. The measured temperatures did not fluctuate greater than ±2°C. from the plotted values.

X-ray diffraction analysis. The partially transformed cubes were powdered by hand in a ceramic mortar and thoroughly mixed. Representative portions of this material were then examined on a Norelco diffractometer employing CuKα radiation. The intensities of the strongest diffraction peaks—for aragonite, {111}, and for calcite, {10.4}—were determined by subtracting the background counts measured adjacent to the respective peaks from the number of counts measured while scanning over each peak. The aragonite {111}/calcite {10.4} ratios were determined by

establishing an average of ten scans for each sample. These ratios were related to the weight percentages of aragonite and calcite in the samples by comparison with the intensity ratios obtained on a series of standards in which aragonite and calcite were mixed in 10 weight percent intervals between 10 and 90 weight percent of the total sample.

The aragonite used in the standards was powdered, unreacted aragonite from which the cubes were obtained. The calcite was obtained by placing some of the original aragonite in a furnace at 535°C for 13 hours; X-ray diffraction analysis of the material indicated that the aragonite had completely converted to calcite.

Results and Discussion

As might be expected, the transformation of aragonite to calcite initially occurred at the edges of the cubes and progressively extended inward towards the centers. In partially transformed cubes the outer portion was considerably softer than the core.

Curves denoting the rates of transformation for runs made at 200°, 250°, and 300°C are shown in Figure 1. The percentage of the sample converted to calcite is plotted against time. At each temperature there appears to be a period of time in which little or no reaction occurs in the aragonite. No reaction occurred in 2929 hours at 100°C or in 672 hours at 150°C. At higher temperatures this period is rapidly shortened (see Figure 1). After the reaction begins to affect the exterior of the cube, the rate of reaction increases and becomes linear until most of the cube is reacted. The data for 300° and 250°C suggest that the rate of reaction decreases again after approximately 85 to 90 percent of the cube has been transformed to calcite.

Variations in permeability of aragonite would doubtlessly affect the rate of transformation. This property was not measured on the material used in this study. However, the individual cubes were all cut from similar material and should have had essentially uniform permeability.

Earlier, Brown *et al.*, (1962) presented data for eight runs on the transformation of aragonite to calcite under hydrothermal conditions. In general, comparison of their results (superimposed on Figure 1) with those obtained in this study are in good agreement: their 198° run plots nearly on the 200° curve; the 215° and 224° runs plot essentially where curves at those temperatures could be constructed by interpolation from the curves established at 200° and 250°; and their 253° run plots on an extension of the linear portion of the 250° curve. The slope of the curve for the earlier authors' 295°–300° runs is identical with, although slightly displaced from, that established by the present authors. No claim is made that the results of the two studies should be identical—rather, with very

probable differences in size, volume, and permeability of the starting material and known differences in pressure, it is noteworthy that the rates established by the two studies are so comparable. The similarity suggests that these factors are secondary to the influences of temperature and the presence of water.

Davis and Adams (1965, Fig. 6, p. 441) show isochrons (lines of equal time) for 99 percent conversion of Kamsdorf aragonite to calcite, in which the transformation occurs in a *dry* environment. At 800 bars applied pressure—the same pressure attained in the hydrothermal runs—the time necessary for 99 percent conversion is given as approximately 2×10^{27} years at 100°C, 2×10^{20} years at 150°C, 2×10^{14} years at 200°C, 2×10^9 years at 250°C, and 2×10^5 years at 300°C. These values obviously are only semiquantitative, giving an order of magnitude for the time necessary. Nevertheless, these values do serve as a contrast when compared with extrapolated data of Figure 1 for conversion of aragonite to calcite in the presence of water and thereby proves the strong catalytic influence of water on the rate of transformation.

The experimental data thus far obtained on the transformation of aragonite to calcite under hydrothermal conditions suggests that aragonite in water saturated sediments could exist for thousands to perhaps a few million years at temperatures well under 100°C. However, during diagenesis of sediments containing aragonite, increase in temperature would result in the destruction of the aragonite, as is generally observed. In contrast, the observed presence of aragonite in highly metamorphosed rocks suggests two possibilities: either (1) the rocks were essentially nonporous and metamorphism was accomplished mainly without the aid of an aqueous phase or (2) the pressures attained were high enough so that the carbonate was in the aragonite stability field.

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ON THE CAUSE OF ASTERISM IN STAR CORUNDUM

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INTRODUCTION

It has been generally accepted that asterism in corundum (star rubies
and sapphires) is caused by needles or rutile (TiO_2) aligned along crystal-
lographic planes of the corundum (*e.g.* Webster, 1962). The evidence
given ty Tait (1955) was: (1) the presence of titanium, (2) the needle-
like habit, and (3) the square cross-section of the needles. Based on the
analogy with rutilated quartz, and by eliminating octahedrite and brook-
ite by the morphology, rutile was accordingly identified. This type of
evidence, however, is explained equally well by either TiO_2 or the com-
pound aluminum titanate Al_2TiO_5.

CORUNDUM GROWTH CONSIDERATIONS

The technique for the laboratory growth of star rubies and sapphire
has been revealed in patents by the Linde Division of the Union Carbide
Corp. (Burdick *et al.*, 1949, 1954). Corundum is grown by the Verneuil
technique with the addition of, preferably, 0.1 to 0.3 percent titanium
oxide in the feed powder. The corundum as grown is clear, but develops
asterism upon heat treatment at 1100 to 1500°C (Webster, 1962; Burdick
et al., 1949, 1954) due to precipitation of the excess titanium, the solu-
bility of which is exceeded at this temperature.

The phase diagram of the $Al_2O_3:TiO_2$ system has been studied by
Bunting (1933) and by Lang, Fillmore and Maxwell (1952). The relevant
parts of these studies are included in Figure 1. There is a slight uncer-
tainty as to whether Al_2TiO_5 melts congruently or incongruently near
1860°C in the shaded region, but this does not affect the present discus-
sion. Similarly, there may be other forms of Al_2TiO_5 besides the α form
which is stable above 1820°C, and the β form stable below 1820°C. Ac-