EXPERIMENTAL DETERMINATION OF CALCITE-ARAGONITE EQUILIBRIUM RELATIONS AT ELEVATED TEMPERATURES AND PRESSURES*

Gordon J. F. MacDonald, *Department of Geology and Geophysics, Massachusetts Institute of Technology, Cambridge, Mass.*

Abstract

Calcite-aragonite equilibrium relations have been investigated using the "simple squeezer" high pressure apparatus of Griggs and Kennedy. Samples of natural calcite and synthetic aragonite were subjected to pressures up to 30,000 bars in the temperature range 200° C. to 600° C. The equilibrium curve as determined by this study is given by the equation $P = 16T + 2400$, where P is in bars and T is in degrees Centigrade. Calcite inverts to aragonite at pressures greater than those given by this equation; aragonite inverts to calcite at lower pressures. The equilibrium curve determined by direct experiment is at a pressure about 1500 bars lower than the curve obtained by Jamieson based on a thermochemical study. The reason for this apparent discrepancy is not known, though several possibilities are discussed. These results confirm the metastability of aragonite at 25° C. and one bar.

The effect of other components on the equilibrium is considered. Thermodynamic arguments show that small amounts of $PbCO_3$, $SrCO_3$, etc., in natural aragonites will not stabilize aragonite relative to calcite. The geologic conditions controlling the deposition of aragonite are as yet uncertain.

Introduction

Two phases of $CaCO_3$, calcite and aragonite, are found in a wide range of geologic environments. The conditions under which aragonite forms in nature are a puzzling problem in many respects. Aragonite (density 2.95) is denser than calcite (density 2.71) and should thus be a higher pressure form of $CaCO_3$ than calcite. Natural aragonite on heating converts to calcite, the conversion being very rapid at temperatures above 400° C. This would indicate that calcite is a higher temperature form than aragonite, a conclusion substantiated by heat capacity measurements which show that calcite has a higher entropy than aragonite (Anderson, 1934). In addition, thermochemical studies of Backstrom (1925), Roth and Chall (1928), Kobayashi (1951 *a, b*) and Jamieson (1953) demonstrate that pressures on the order of several thousand bars would be required for the equilibrium formation of argonite at 25° C. Since aragonite is forming today in nature at or near atmospheric pressure, it has been

suggested that the presence of components other that $CaCO_3$, principally $SrCO_3$ and $PbCO_3$, "stabilize" natural aragonite relative to calcite.

The present study is concerned with the direct experimental determination of the calcite—aragonite equilibrium relations. Calcite has been converted to aragonite at high pressures; the reverse transition of aragonite to calcite has also been studied. The results establish the need of high pressures for the equilibrium formation of aragonite. On the basis of the experimental results on pure $CaCO_3$, theoretical calculations of the effect of other components on the stability of aragonite indicate that the percentages of these components found in natural aragonite are too small to account for an equilibrium formation of aragonite.

This investigation was further motivated by a desire to test the applicability of the "simple squeezer" to the study of solid-solid transitions. The "simple squeezer" is a high pressure apparatus designed by Professors Griggs and Kennedy and described by Griggs, Kennedy and Fyfe (1955). In the "simple squeezer" the pressure is not directly measured but is calculated from the force applied to the confining pistons. The sample between the pistons may not be under a hydrostatic pressure and the strain energy resulting from shearing the sample might conceivably affect the position of the equilibrium curve. The uncertainty in the pressure acting on the sample and the uncertainty of the effect of shear on the equilibrium relations made it desirable to compare the "simple squeezer" results on a solid-solid transition with results obtained by independent methods. The calcite-aragonite equilibrium was chosen for this purpose because Jamieson's (1953) careful thermochemical study provided an independent check on the results of the "simple squeezer," at least at relatively low pressures.

Experimental Details

Apparatus

The experimental work was carried out on the "simple squeezer." Since this high pressure system is being described in detail by Griggs and Kennedy elsewhere, the present description will outline only the major features of the apparatus. The confining pressure is produced by pressing two pistons together. The piston faces that come in contact have a diameter of $\frac{1}{4}$ inch. The pistons are pressed together by a commercial hydraulic jack, supported by a framework of plates and tie rods. The sample is placed between the piston faces and is separated from each face by a layer of platinum-10% rhodium foil. The foil is used to prevent adhesion of the sample to the piston faces. The pressure can then be raised by means of the jack, a gauge measuring the pressure on the hydraulic fluid in the jack. The sample is heated by an external furnace enclosing the

pistons and sample. The pistons used in the experiments described here were made of high-speed steel. These pistons were adequate for pressures up to 30,000 bars and temperatures up to 600° C.

The temperature was measured by placing a chromel-alumel thermocouple in a hole in one of the pistons. The tip of the thermocouple came within $\frac{1}{4}$ inch of the piston face. The temperature readings of this thermocouple were calibrated against the readings of a thermocouple placed between the piston faces in the normal position of the sample.

The pressure was determined from the readings on the jack pressure gauge and the area of the pistons. The areas of the piston faces were measured before and after a run. If the area changed significantly during the run, the run was discarded. Effects of friction within the jack were measured by a load cell calibration of the force acting on the pistons.

Materials used and identification

Natural calcite and artificial aragonite were used as starting materials. These were chosen since natural calcite containing only traces of components other than $CaCO_3$ is readily available, while analyzed natural aragonite was not available at the time of the investigation.

The calcite used was optical grade calcite from Chihuahua, Mexico. A spectrographic analysis of identical material has been published by Miller (1952) and this analysis shows that this calcite contains less than 0.1% $SrCO_3$, the major impurity, and less than 0.01% magnesium.

The aragonite was prepared using the method of Keyser and Dequeldre (1952). In this method 1N $CaCl_2$ is slowly mixed with 1N Na_2CO_3 at 100° C. The resulting precipitate is then thoroughly washed to remove the remaining NaCl. The resulting aragonite is extremely fine-grained. The x-ray pattern shows very much broadened lines. A fresh batch of aragonite was prepared for each day's runs, since it was observed that the artificial aragonite slowly converted to calcite on standing. The rate of conversion differed from one preparation to another, but in several batches of aragonite, calcite was detected in the x-ray pattern after the aragonite had aged for a period of a week.

The samples were identified by comparing the x-ray patterns obtained on a Norelco high-angle diffractometer with standard patterns of natural calcite and aragonite and artificial aragonite. Since the patterns are quite distinctive no difficulty was encountered in identifying relatively small amounts of either phase.

Procedure

A sample to be exposed to high pressures is placed on the platinum foil in the form of a dry powder with a small amount of water. The presence

of water does not appear to affect either the position of the equilibrium curve or the rate at which equilibrium is attained. An original thickness of powder of about .02 inch results in a wafer of about .005 inch thick in the center. The wafer tends to be disk-shaped, thicker in the middle and tapering to the edges.

The order of applying the pressure and temperature depends on whether aragonite or calcite is the initial material. If calcite is the original material, the temperature is first raised to the desired value and then the pressure is applied. In this way the sample is at a high pressure only at the desired temperature, and the high pressure form, in this case aragonite, can form only at the required temperature and not at some lower temperature. Similarly, if the original charge is aragonite, the pressure is first increased to the desired value and then the temperature is raised. The sample in this case is at a high temperature only at the pressure of the experiment, and the high temperature form, calcite, can form only at the given pressure. This careful cycling of the experiment is essential since the reaction proceeds rapidly. One hour is in general sufficient to convert calcite to argonite at 400° C. and 12,000 bars. Since raising the temperature to 400° C. takes about 15 minutes in the present apparatus, the sample has time to convert partially to aragonite at lower temperatures than 400° C. if the pressure were at or near 12,000 bars while the temperature is being raised.

After the sample is held at the required conditions of pressure and temperature for a suitable time, ranging from one to 17 hours, depending on the conditions of the experiment, the sample is quenched by releasing the pressure and placing the sample in water. In this way the pressure and temperature are reduced to room values in five seconds or less. This rapid quenching is essential in preserving any aragonite formed at high temperatures, since aragonite converts very rapidly to calcite at temperatures above 400–450° C.

RESULTS

The useful results of the experiments are summarized in Tables 1 and 2. These tables list temperature and pressure conditions of the experiment, length of time at these pressure-temperature conditions and results from *x*-ray examination of resulting products. About ten early runs are not included in this table since these runs were not properly cycled and therefore the results are inconsistent with those listed.

Most of the runs are of about an hour's duration. A few runs at lower temperatures were held at temperature and pressure for 10–20 hours to test whether or not the results obtained represented equilibrium or whether they were due to differences in reaction rates at high and low tem-

TABLE 1. RESULTS OF SUBJECTING CALCITE TO HIGH PRESSURES AND TEMPERATURES

Temperature °C.	Pressure, kilobars	Time, hours	Results of x-ray examination of products
250	6	10	calcite
300	6	1	calcite
360	6	1	calcite
250	8	10	weak aragonite and calcite
325	8	1	weak aragonite and calcite
340	8	1	aragonite and calcite
380	8	1	calcite
400	9	17	aragonite and calcite
430	9	1	calcite
430	10	1	aragonite and calcite
440	10	1	aragonite and calcite
450	10	1	aragonite and calcite
475	10	1	calcite
490	10	1.5	calcite
500	10	1	calcite
550	10	1	calcite
560	10	1	calcite
520	11	1	calcite
400	12	1	aragonite and calcite
450	12	1	aragonite and calcite
580	14	2.2	aragonite and calcite
300	15	1	aragonite and calcite
380	15	1	aragonite and calcite
400	15	1	aragonite and calcite
420	15	1	aragonite
440	15	1	aragonite and weak calcite
460	15	1	aragonite and weak calcite
470	15	1	aragonite and calcite
520	15	1	aragonite
450	20	1	aragonite and weak calcite
480	20	3.5	aragonite
490	30	.5	aragonite

perature. The longer runs gave results similar to those of the one-hour runs. This evidence, plus the fact that different starting materials give similar results, is taken as indicative that equilibrium was attained.

The points that were used to determine the equilibrium curve are shown in Fig. 1. Only those points near the curve are plotted. The remaining runs listed in Table 1 show that no other phases that can be quenched appear in the system for temperatures up to 600° C. and pressures up to 30,000 bars.

The uncertainties in the individual runs are estimated to be ±10° and ±500 bars. The uncertainty in the temperature is due to the difficulty

TABLE 2. RESULTS OF SUBJECTING ARAGONITE TO HIGH PRESSURES AND TEMPERATURES

Temperature, °C.	Pressure kilobars	Time, hours	Results of x-ray examination of products
500	8	1	calcite
550	8	1	calcite
400	10	1	aragonite
450	10	1.5	aragonite
500	10	1	calcite
550	10	1	calcite
600	10	1	calcite
550	11	1	calcite
500	12	1	aragonite
600	12	1	aragonite
600	14	1	aragonite
500	15	1	aragonite
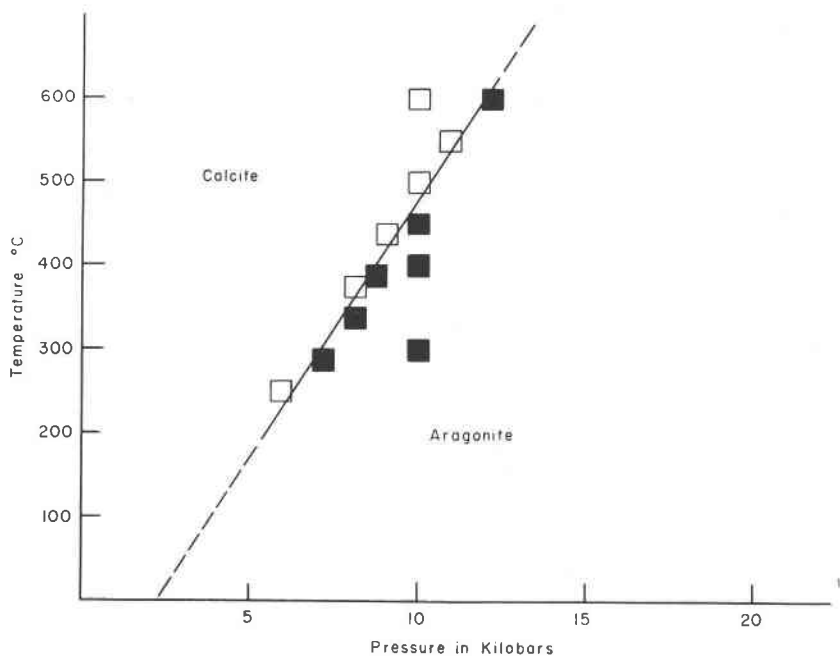
FIG. 1. Plot of runs used in determining calcite-aragonite equilibrium curve. Size of square is approximately proportional to the estimated error in the individual runs. One square may represent two or more runs.

in placing the thermocouple in the identical position relative to the sample. The pressure uncertainty is due to the scale of the pressure gauge on the jack and small fluctuations of the pressure during a run. This estimate of the uncertainty in pressure assumes that the pressure is uniform over the entire sample, an assumption that is certainly unjustified. A better estimate of the uncertainty in pressure is obtained by comparing results obtained by using two similar pieces of apparatus. Such a comparison indicates that the uncertainty in pressure may actually be as large as $\pm 10\%$ of the pressure.

The equation representing the equilibrium curve is $P = 16(\pm 3)T + 2400(\pm 1000)$ where T is in degrees Centigrade and P is in bars. The estimated uncertainties are derived by examining possible curves that could be drawn without contradicting the experimental determinations, taking into account the uncertainty in the individual points. The position of the curve is reasonably well determined at temperatures above 350° C., but the points at lower temperatures are not closely enough spaced to fix the boundary accurately. The boundary is assumed to be a straight line. The data are not of sufficient accuracy to show minor changes in slope of the equilibrium curve. In general the phase boundary should show curvature, the curvature depending on the differences of heat capacity, thermal expansion and compressibility of calcite and aragonite. Data available on these quantities show that the differences are indeed small.

THERMOCHEMICAL CONSIDERATIONS

Comparison with earlier results

The thermodynamic properties of calcite and aragonite have been extensively studied. Of particular interest is the work of Jamieson (1953) on the stability relations of aragonite and calcite at temperatures between 25° and 80° C. Jamieson determined the electrical conductivity of aqueous solutions in equilibrium with calcite and the conductivity of solutions in equilibrium with aragonite as a function of temperature and pressure. At equilibrium the solubilities of each phase in water should be equal and therefore the conductivities of the solutions should be equal. This method assumes that the unstable phase does not convert to the stable phase during the course of the experiment, and furthermore, that water does not enter into either solid phase.

On the basis of conductivity measurements at four temperatures between 25° and 80° C. and at various pressures, Jamieson obtained data from which he calculated the equilibrium curve shown in Fig. 2. Using the slope and position of the curve plus the densities of the two minerals, Jamieson obtained the change in entropy for the transition and the heat
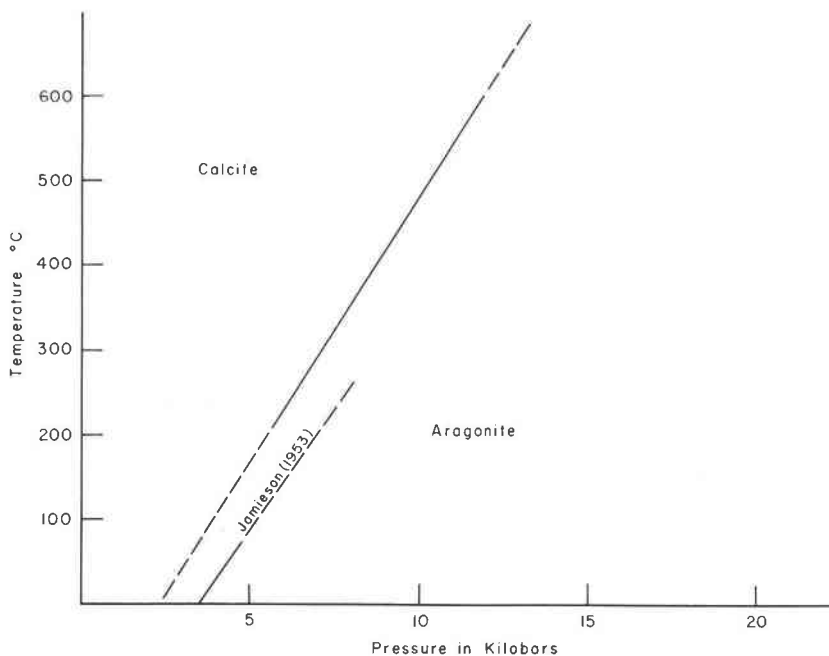
FIG. 2. Comparison of equilibrium curve obtained by Jamieson (1953) and the equilibrium curve obtained in the present study.

of transition at 25° C. and atmospheric pressure. These values are compared with the results of earlier workers in Table 3. Jamieson's value for the change in entropy is in agreeement with Anderson's values obtained by low temperature heat capacity measurements. Similarly, Jamieson's value for the heat of transition is in agreement with the heat of solution measurements of Roth and Chall. The equilibrium curve calculated using Anderson's and Roth and Chall's data would thus lie within a few hundred bars of the curve obtained by Jamieson.

TABLE 3. THERMOCHEMICAL QUANTITIES FOR THE TRANSITION ARAGONITE = CALCITE AT 25° AND ONE BAR

ΔS cal./deg. mole	ΔH cal./mole	ΔG cal/mole	Investigator
0.74	30	−180	Backstrom (1925)
	42		Roth and Chall (1928)
1.0 ±0.5			Anderson (1934)
1.1	62	−270	Jamieson (1953)
1.1 ±0.2	160±70	−160±70	MacDonald

The results of the present study are compared with those of Jamieson and earlier workers in Fig. 2 and Table 3. The slope of the equilibrium curve and consequently the entropy of the transition is in agreement with that of earlier workers. However, the equilibrium curve is at a pressure some 1500 bars lower than the curve obtained from Jamieson's data. There are several possible reasons for this discrepancy that should be examined. The mean pressure acting on the sample in the simple squeezer is calculated from the force acting on the piston, this force having been calibrated with a load cell. The actual pressure on the sample might be less than the calculated pressure if the opposing pistons came into contact. This would mean that the pressure would be over-estimated. The observed discrepancy could not be due to such errors, since the present curve lies at *lower* pressures than Jamieson's. The sample in the simple squeezer is under a non-uniform pressure. This shearing stress could affect the position of the equilibrium curve in the desired direction, provided that shear stabilizes aragonite relative to calcite. This possibility cannot at present be ruled out. Finally there is the possibility that Jamieson did not attain equilibrium in his experiments or that he was dealing with partially converted materials in certain of his runs. The agreement of Jamieson's results with those of earlier workers suggests that Jamieson was indeed dealing with equilibrium, but this earlier work should not be taken as decisive. The calculated position of the equilibrium curve depends on the heat of transition. This heat was determined by Roth and Chall by measurement of the heats of solution of the two minerals. Measurements of heats of solution of materials evolving a gas phase are notably difficult, and small errors in the heats of solution would lead to very large errors in the heat of transition.

The above discussion emphasizes the desirability of investigating the aragonite-calcite equilibrium directly in an apparatus in which the pressure is better known than in the simple squeezer, and where the sample is subjected to a uniform hydrostatic pressure. Only such measurements can clear up the discrepancy between the results obtained on the simple squeezer and those obtained from thermochemical data.

Effect of components other than $CaCO_3$ on calcite-aragonite equilibrium

The above results show that aragonite with a composition of $CaCO_3$ is unstable relative to calcite having the same composition at 25° C. and one bar. A measure of this instability at these conditions is the difference in Gibbs free energy of the two phases. The values listed in Table 3 show that at 25° C. and one bar aragonite has a free energy between 90 and 270 calories greater than calcite, depending on the method used to evaluate the free energy difference and taking into account the uncer-

tainties in the data of the present investigation. For the present discussion we will use a free energy difference of 200 ± 100 calories.

Natural aragonites that have formed at conditions near 25° C. and one bar have in general a more complicated composition than $CaCO_3$. It is interesting then to investigate the effects of components other than $CaCO_3$ on the relative stabilities of calcite and aragonite. A necessary condition for equilibrium between the two phases is that the chemical potential of $CaCO_3$ in calcite equal the chemical potential of $CaCO_3$ in aragonite. In general the chemical potentials will be a function of the composition of the phases as well as of temperature and pressure. The condition for equilibrium can then be written

$$\mu^A(T, P, x_1, \cdots, x_n) = \mu^C(T, P, x_1, \cdots, x_n)$$

where μ^A is the chemical potential of $CaCO_3$ in aragonite, and μ^C is the chemical potential of $CaCO_3$ in calcite. The chemical potentials can be written in the form

$$\mu = \mu^0(TP) + RT \ln x\gamma$$

where μ^0 is the chemical potential of the pure component $CaCO_3$ at a given temperature and pressure, x is the mole fraction of $CaCO_3$ in the solution and γ is the activity coefficient of $CaCO_3$ in the solution. The condition for equilibrium is then given by

$$\mu^{0A} + RT \ln x^A\gamma^A = \mu^{0C} + RT \ln x^C\gamma^C$$

which can be written as

$$\ln \frac{x^A\gamma^A}{x^C\gamma^C} = \frac{\mu^{0C} - \mu^{0A}}{RT} .$$

The difference in chemical potentials of the pure components, $\mu^{0C}-\mu^{0A}$, is just the difference in molar Gibbs free energy. At 25° C. and one bar this difference is -200 ± 100 calories. Substituting this value into the above relation we obtain

$$\frac{x^A\gamma^A}{x^C\gamma^C} = 0.71 \pm 0.15.$$

In order to interpret this result we need to assume something about the activity coefficients γ^A and γ^C. If we assume that $CaCO_3$ forms an ideal solution with other components such as $BaCO_3$, $PbCO_3$, $ZnCO_3$, etc. in both calcite and aragonite, the condition for equilibrium between calcite and aragonite at 25° C. and one bar is given by

$$x^A = 0.71(\pm 0.15)x^C.$$

The mole fraction of $CaCO_3$ in aragonite must be about 0.7 times the mole fraction of $CaCO_3$ in calcite for aragonite to be in equilibrium with calcite. This means that at least 30 mole per cent of components other than

$CaCO_3$ in aragonite are needed to "stabilize" aragonite relative to calcite. Natural aragonite contains at most 8–9 mole per cent of components such as $PbCO_3$, $SrCO_3$, $ZnCO_3$ (Palache, Berman and Frondel, 1951) and most natural aragonites contain much less, so that even considering the errors in the data, it appears very unlikely that aragonite is stabilized by forming solid solutions, provided such solutions are ideal. If the solutions are non-ideal then the activity coefficients are no longer equal to one. A value greater than one for γ^A would mean that even higher concentrations of components other than $CaCO_3$ would be needed to stabilize aragonite. In general an activity coefficient greater than one is associated with solutions having a positive heat of mixing. Solutions of the sort considered here generally have a positive heat of mixing (MacDonald 1954). A negative heat of mixing would favor the stabilization of aragonite by other components. This possibility is considered unlikely but cannot be ruled out except by actual measurements of the heats of mixing.

On the basis of the above thermodynamic argument it is concluded that the amounts of lead, strontium, zinc, etc., found in natural aragonites are not sufficient to stabilize aragonite relative to calcite.

Geologic Problems

The direct experimental study of the calcite-aragonite equilibrium relations confirms Backstrom's conclusion that aragonite near the surface of the earth is unstable relative to calcite. Theoretical considerations indicate that components such as $PbCO_3$, $SrCO_3$, etc., are ineffectual in stabilizing aragonite. This then leaves the major problem of determining what geologic conditions control whether aragonite or calcite is precipitated. One fascinating problem is why certain organisms precipitate aragonite and others calcite to form their shells or skeletons. Of particular interest is the role played by the organic membrane separating the organism from its environment. This membrane undoubtedly sets up an osmotic equilibrium which under certain conditions might lead to the precipitation of aragonite as a stable phase. A great deal of work on the mineralogy and chemistry of shells and conditions for growth of living organisms is needed before a thermodynamic attack on the problem would be profitable.

A further problem of interest is the effect, if any, of the calcite-aragonite transition on the mechanical properties of limestone. There is a definite possibility that plastic flow in limestone might be aided by such a polymorphic transition (Robertson, 1955). Griggs, Turner, Borg and Sosoka (1951) report studies on the deformation of Yule marble at 10,000 bars and 150° C. This is well within the field of stability of aragonite, but at this temperature the reaction would be relatively sluggish.

Similar experiments at 10,000 bars and 300° C. might be expected to show up any effects of the polymorphic transition on the mechanical properties of the marble.

The equilibrium curve shown in Fig. 2 could be interpreted as fixing the maximum pressure to which pure calcite marbles could have been subjected in regional metamorphism. Greater pressures than those given by the equilibrium curve would have resulted in aragonite. However, any aragonite that might have formed could have inverted to calcite at some later time in the history of the marble, erasing in such a process evidence of the original aragonite. The absence of aragonite in metamorphic rocks suggests that these may have formed at pressures lower than those of the equilibrium curve, but certainly nothing more definite can be said.

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