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The Calcite-Aragonite Transition, Reinvestigated

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Abstract. The calcite-aragonite equilibrium has been investigated between 200 and 600° C both in a carefully calibrated hydrothermal apparatus and in a piston-cylinder device of high precision. The equilibrium pressure is 5 kb at 180° C, 7 kb at 300° C, 9 kb at 400° C, and 11 kb at 480° C.

The calcite-aragonite transition boundary which has been bracketed is continuously curved between 300 and 500° C and is more or less straight above and below this temperature range. It is shown that the calcite I-calcite II reaction is probably a second (and not a first) order transition.

The experimental result shows that aragonite may already be formed out of calcite at a depth of 15 km if the temperature is not much higher than 100° C. The calcite-aragonite and the albite-jadeite-quartz curves intersect at about 750° C and 20 kb. There is a P-T-field (up to 3.5 kb broad) where aragonite and albite coexist.

Introduction

The calcite-aragonite equilibrium has been of great interest to both field geologists and experimental petrologists. In contrast to calcite, aragonite is never found as a primary mineral in rocks formed at high temperatures nor in rocks which underwent mediumgrade or highgrade metamorphism. Aragonite is usually regarded as an indicator of high pressure (at low temperatures), providing that it is formed in its stability field. (It will be shown that the pressure need not be very high to reach the aragonite stability field.) The rocks of the "glaucophane schist facies" (Turner, 1968) (the Glaucophane-Lawsonite Facies" of Winkler, 1967) are reliable indicators of high-pressure (and low-temperature) metamorphism. If aragonite has been formed under the conditions of this facies, it has most probably grown in its stability field.

Aragonite as a widespread metamorphic mineral was first observed in Californian glaucophane schists in 1962 (Brown, Fyfe and Turner; Coleman and Lee; McKee). In these schists aragonite usually occurs with jadeite and quartz. This means that the pressure not only reached the stability field of aragonite but also that of the assemblage jadeite + quartz. In some places, however, aragonite has been produced at pressures too low to decompose albite into jadeite + quartz (Ernst, 1965; Ghent, 1965). (The relative position of the jadeite-quartz-albite and calcite-aragonite curves is discussed below.)

Metamorphic aragonite has also been observed in the glaucophane schists of the Mihaliccik district (Turkey) by Cogulu (1967). A new occurrence of metamorphic aragonite in glaucophane schists was recently discovered in North

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Calabria (South Italy) by Hoffmann (1970). In this locality, aragonite occurs in the form of small, commonly untwinned grains; sometimes it forms small veins. The aragonite usually comprises less than 2% of the whole rock. Calcite is even less common than aragonite in these schists, and occurs in small veins only.

Aragonite has also observed by Vance (1968) to be a widely distributed mineral in the rocks of the lower-grade portion of the prehnite-pumpellyite facies of Northwest Washington. Vance concludes that this aragonite is either metastably formed or that the experimental data reflect metastable equilibrium. We want to show that there probably is a real stability curve fixed by experimental data.

Metamorphic aragonite is obviously more common than was thought some years ago, and more rocks containing metamorphic aragonite will undoubtedly be discovered during the next years. The interpretation of these rocks needs a well established calcite-aragonite equilibrium curve.

The first experiments with calcite and aragonite as starting material were performed to check a newly installed piston-cylinder apparatus. Therefore we needed the comparison of hydrothermal and piston-cylinder runs. The calcite-aragonite reaction was the only suitable one for this purpose.

After having done the first experiments, we decided to reinvestigate the whole calcite-aragonite transition curve and to check the existence of a triple point between aragonite, calcite I and calcite II, as was first suggested by Boettcher and Wyllie (1968). Such a triple point would mean that the calcite I-calcite II transition is of first order. If the calcite I-calcite II transition were of second order, it would be represented by a curved portion of the calcite-aragonite equilibrium curve.

Previous Work

Almost everyone who has worked with a high-pressure apparatus has investigated the calcite-aragonite transition boundary. Some of the results achieved before 1969 are shown in Fig. 1. Simple squeezer results are not considered since they would cover the entire P-T diagram. Fig. 1 shows that there were no data at all in the critical range of 200 to 400° C and that no consistent data existed above 400° C when we started calcite-aragonite experiments in 1968.

Earlier papers have already been discussed by Boettcher and Wyllie (1968). In order to avoid repetition of this discussion, we recommend this paper.

Boettcher and Wyllie (1968) have bracketed the calcite-aragonite transition boundary between 400 and 800° C. Their runs were conducted in a single-stage piston-cylinder apparatus. The samples were brought cold to final nominal pressure and then heated. A pressure correction of minus 7–10% (depending on the temperature applied) was made for friction (this value was determined using, as a standard, the Bi I-Bi II transition at 25.4 kb and 25° C). We are not sure if this correction was necessary. The procedure used by Boettcher and Wyllie is not a true piston-in procedure demanding a negative correction. Indeed, the uncorrected curve would agree perfectly with the transition boundary we have bracketed.

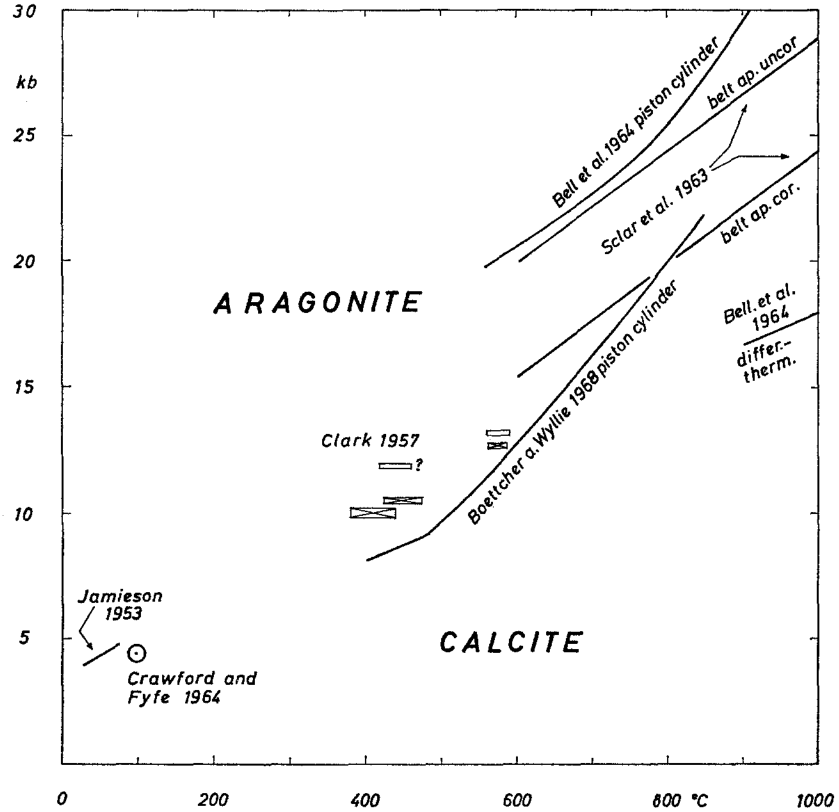

Fig. 1. Selection of experimental results published before we began investigating the calcite-aragonite transition

Boettcher and Wyllie used the point determined by Crawford and Fyfe (1964) at 100° C to provide the extension of their calcite-aragonite curve to lower temperatures. This combination led them to establish a change in slope in the region of 9.4 kb and 480° C. Taking into account the experimental results of Boeke (1912) and of Bridgman (1939), they interpreted the point at 9.4 kb and 480° C as a triple point between the three phases, calcite I, calcite II, and aragonite. This would mean that the calcite I-calcite II transition is of first order. Boettcher and Wyllie also considered that the calcite-aragonite transition could be of second order. In their Fig. 2 they show the possible error in the extrapolation of their calcite-aragonite curve to lower temperatures. The broad field of uncertainty indicated in that figure suggests that the order of the calcite I-calcite II transition had not been satisfactorily demonstrated.

The experimental results of Goldsmith and Newton (1969) and of Newton, Goldsmith and Smith (1969) will be discussed below.

There have been various attempts to calculate the calcite-aragonite transition boundary. These calculations have been compiled and discussed by Zimmermann

(1969). Zimmermann demonstrated that it is not possible to calculate a reliable calcite-aragonite equilibrium curve; on the basis of thermodynamic calculations, he predicts a curved calcite-aragonite transition boundary for higher temperatures.

Starting Material and Experimental Methods

A mixture of 75 weight % aragonite and 25 weight % calcite was used as starting material. (A mixture of 50/50 would have been preferable, but having started with that composition we decided to continue with it). The calcite was reagent pure crystalline $CaCO_3$ of Merck (Darmstadt/Germany) and the aragonite was sedimentary (metastably formed) aragonite from Eisenerz, Austria. This aragonite contains 0.12% MgO. TiO_2, FeO, MnO, and Sr_2O_3 could not be detected in wet chemical analysis. The average grain size was 0.02–0.05 mm. More than 95% of the starting material was larger than 10 micrometer and smaller than 50 micrometer. All runs were made in welded gold tubes, with 20 to 30 mg starting material used in each. The calcite-aragonite mixture was dried at 110° C in the case of "dry" runs; no special care was taken to prevent the absorption of water during the preparation of the samples. 10 to 20% of water was added in the case of "wet" runs. The quenched charges were examined optically and by x-ray methods. Besides the formation of sharp edges and margins and slight enlargement of the crystals in the case of wet runs, no other changes could be detected optically. The composition of the quenched charges was determined by scanning from 25° to 30° 2θ with an x-ray defractometer. In this region there are two aragonite peaks: (111) at $2\theta = 26.2$ and (021) at $2\theta = 27.2$, and one calcite peak (104) at $2\theta = 29.4$. (The material was ground for 20 to 30 sec before x-raying. The ground material was mounted on a glass slide with acetone.) The area of the two aragonite peaks was compared with the area of the calcite peak. An alteration of less than 10% is indicated as "no change". The results of the runs (alteration of starting material) are given in the Table[1] and shown graphically in Figs. 2–5.

Chromel-alumel thermocouples were used in all runs for temperature measurements. In the case of the cold-seal runs, an exterior thermocouple was placed ca. 10 mm from the sample. The difference between the temperature of the exterior thermocouple and that of the capsule was determined by calibrating the bombs with sheathed thermocouples under run conditions. All temperatures listed in the Table[1] are accurate to ±10° C (also in case of piston-cylinder runs). No correction was made for pressure on the emf of the thermocouples.

The pressure of the cold-seal runs was measured with hydraulic gauges and with a manganin coil or with a high-pressure Baldwin cell. The gauges, the manganin coil and the high-pressure cell are calibrated with a Kistler piezo-quartz pressure cell. The pressure values given in the Table[1] for cold-seal runs are accurate to within ±200 bars.

The pressure values given for the piston-cylinder runs are uncorrected data of the nominal pressure. The runs were conducted in a calibrated hydraulic ram. The calibrated ram is guaranteed to perform accurately within ±1% of the given value. The calibration was checked several times during those months in which the piston-cylinder runs were conducted, and was always confirmed. The nominal pressures given in the Table[1] for piston-cylinder runs are accurate to within ±1% of the given value.

The cylinder of the piston-cylinder apparatus used has a diameter of 22 mm. NaCl was used as the pressure transmitting medium, see Fig. 6.

Experimental Results

The points plotted in Figs. 2 and 3 do not show error limits of P and T. The pressures given are accurate to within ±200 bars and the temperatures to within ±10° C, as mentioned above.

The hydrothermal curve is well bracketed below 450° C and above 300° C, (see Fig. 2). In this region experimental results are entirely consistent. At 5.5 kb

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[1] The Table has been omitted in order to save space. This table can be requested from the authors.

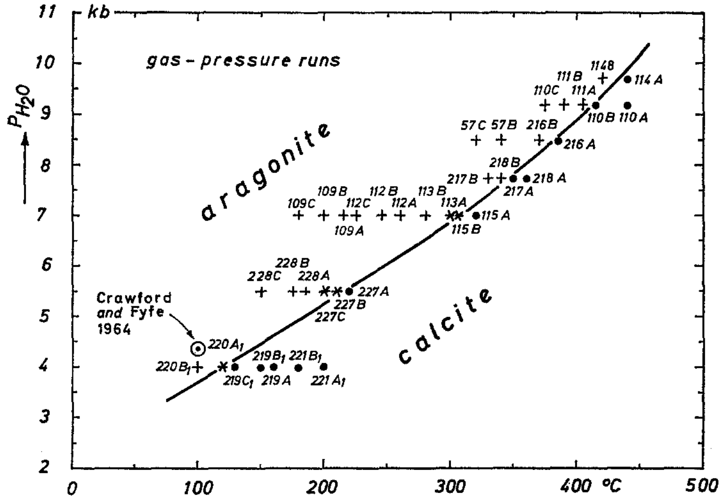

Fig. 2. Results achieved in a gas-pressure apparatus

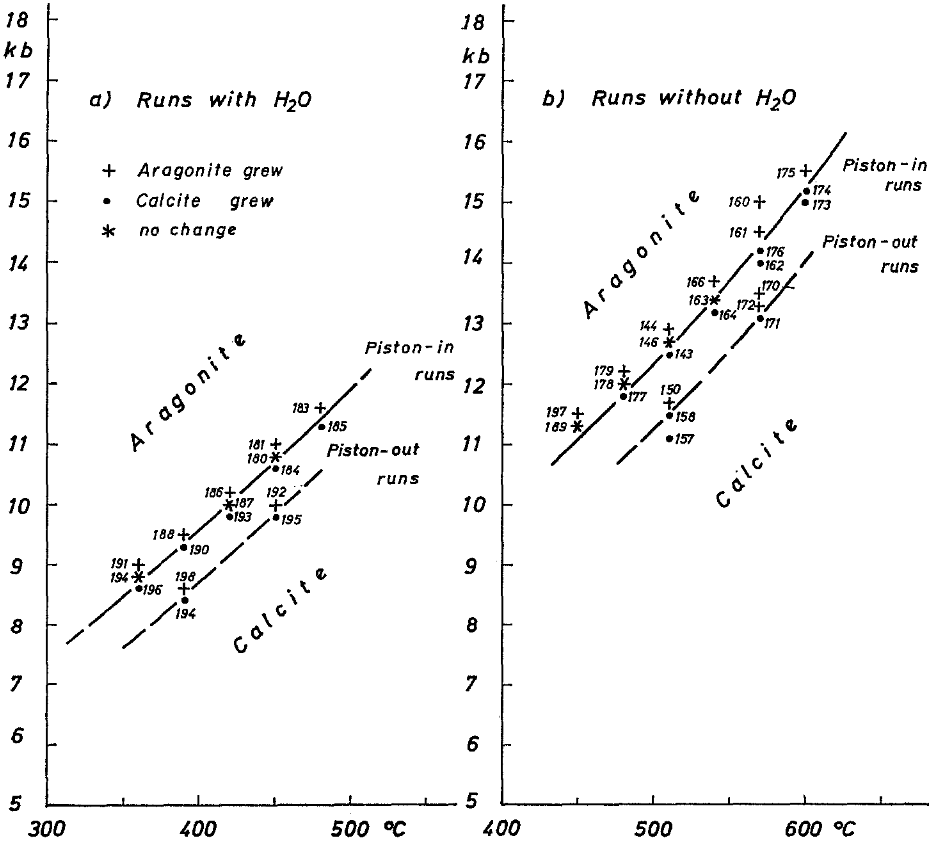

Fig. 3. Piston-cylinder results

the transition boundary lies between 220° C (sample 227 A) and 185° C (sample 228 A). It is difficult to limit this bracket more precisely, because of the low reaction rate at those temperatures. Sample 227 C_1 (see table) is the result of a run containing 0.2 m $CaCl_2$. As noted above, this may not represent a bracket of true stability.

At 4 kb the calcite-aragonite transition was found to occur at 120° C in 0.2 m calcium chloride solutions. The extrapolation of these data to 100° C gives a difference of 0.7 kb in comparison to the determination of Crawford and Fyfe at that T. (In Figs. 2 and 4 our transition boundary is drawn through points 227 B and 220 A_1. This increases the difference somewhat between our results and those of Crawford and Fyfe). The experimental data below 6 kb are not completely satisfactory. More experiments in this range will be conducted with pure water and with $CaCl_2$-bearing solutions of various concentrations. So far it can only be stated that the calcite-aragonite equilibrium curve lies above point 219 A (4 kb and 160° C).

The results of the piston-cylinder runs are shown in Fig. 3. The equilibrium could not be quenched above 500° C in the case of wet runs and not above 600° C in the case of dry runs. (The average cooling rate down to 200° C was 25° C/sec.) We are certain that the data given show true changes in the starting material at the given run conditions and not during quenching. In order to reach this conclusion, we conducted a series of runs with various combinations of heating, pressure admittance, quenching methods and with differing run times. (The data of these runs are not given in this paper.) The experiments were conducted at P-T conditions where no misleading results could have been obtained.

The pressure difference between the piston-in curve and the piston-out curve is 0.8–0.9 kb in the case of the wet runs. In the case of the dry runs, the difference is 1.1–1.2 kb. This difference of about 1 kb represents the sum of double friction plus strength of our piston-cylinder apparatus in the P-T region investigated. The actual equilibrium boundary is expected to lie between the piston-in curve and the piston-out curve. The pressure on the sample cannot be lower than the nominal pressure in the case of the piston-out runs and cannot be higher than the piston-in pressure providing there is no "pressure peak" or "overpressure" in the central part of the furnace we have used (a sketch of this furnace is shown in Fig. 6.) There is, as yet, no possibility of measuring directly the sample pressure in a piston-cylinder apparatus at higher temperatures. Information about the exact sample pressure can only be gained by comparing results achieved in a piston-cylinder apparatus with results bracketed in a carefully calibrated hydrothermal apparatus. The gas-pressure results and the pistoncylinder results both for p-in, p-out, wet and dry runs bracketing the calcite-aragonite inversion are presented in Fig. 4.

All curves shown in Fig. 4 are consistent. There is a small difference between the curves for wet and dry runs. So far, we have no satisfactory explanation for this observation. It should be noted that the gas-pressure curve lies nearer to the piston-out curve than it does to the piston-in curve of the piston-cylinder runs. This means either that the friction built up in piston-in runs is larger than the friction occurring in piston-out runs or that the strength of the NaCl used behaves differently in piston-in and piston-out runs.

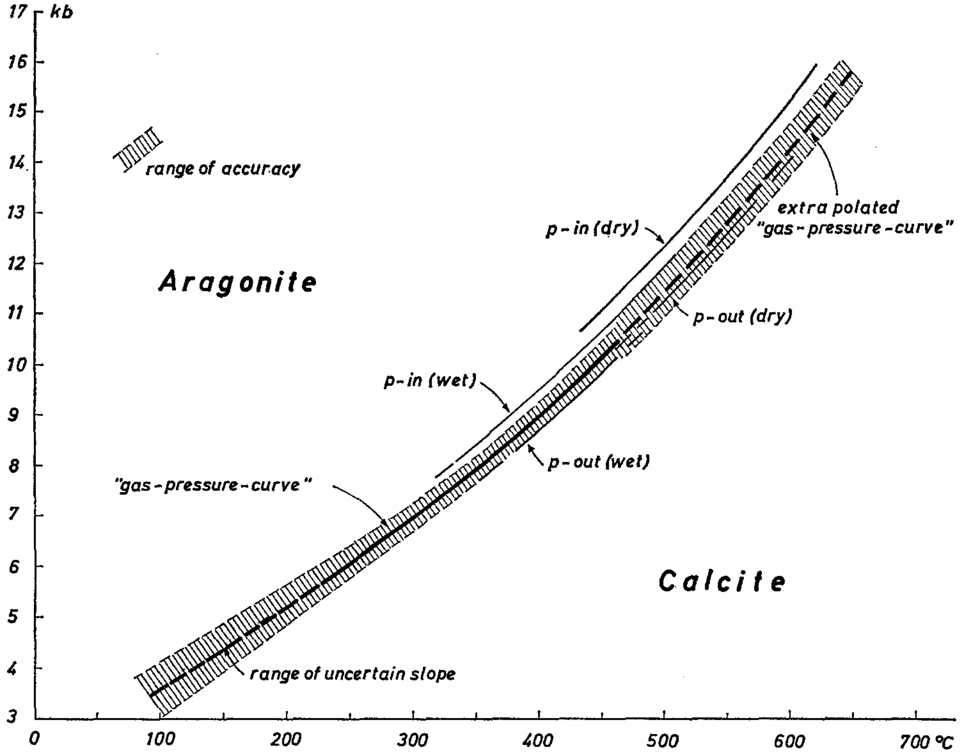

Fig. 4. Composition of piston-cylinder and gas-pressure runs

According to the results shown in Fig. 4, we state following "standard procedures" with following ranges of accuracy for our NaCl cell: In case of a piston-in run, we apply a correction of −0.7 kb. The estimated range of accuracy is ± 0.5 kb. In case of a piston-out run, we make a correction of +0.5 kb and the estimated range of accuracy is ± 0.5 kb. The given ranges of accuracy will probably be valid up to 900° C and 20 kb.

Above 300° C (there being no exact information about the precise slope and shape of the calcite-aragonite curve below 300° C) the calcite-aragonite transition boundary is continuously curved. The curvature is more marked between 350 and 400° C than at other temperatures. It is not possible to connect the experimental data by one of two straight lines. According to Zimmermann (1969) the calcite-aragonite transition boundary should be almost a straight line below 300° C. This prediction is consistent with our experimental results.

Discussion

While the experiments reported in this paper were being conducted, new calcite-aragonite data were published by Goldsmith and Newton (1969). The results of these authors are included in Fig. 5. The maximum difference between the curve Goldsmith and Newton have bracketed and ours is less than 1 kb. The estimated

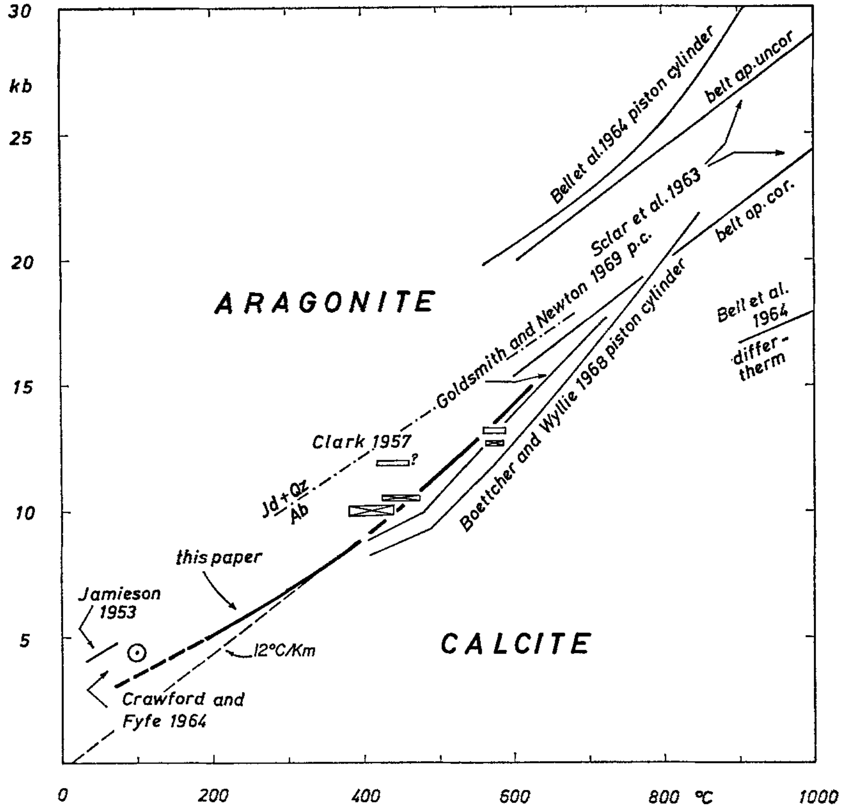

Fig. 5. Selection of experimental results including the recent experiments of Goldsmith and Newton and our transition curve. The albite ⇌ jadeite + quartz euqilibrium curve determined in the same apparatus (unpublished data) is also shown

uncertainty of the sample pressure of both curves is ± 500 bars. This means that the calcite-aragonite curve we have bracketed is consistent with that of Goldsmith and Newton.[2]

Contrary to the suggestions of Boettcher and Wyllie and of Goldsmith and Newton, we do not have any evidence of a calcite I-calcite II-aragonite triple point in the P-T region we have investigated. If there is a calcite I-calcite II transition, it is probably not of first order. The calcite-aragonite transition boundary we have bracketed is continuously curved between 300 and 500° C and is more or less straight above and below this temperature range.

Aragonite can only be formed from (pure, unstrained) calcite in those regions where the geothermal gradient is less than 12° C/km (see Fig. 5). At low temperatures the pressure necessary to transform calcite into aragonite is not as high as was hitherto thought. If the temperature of the rock is about 100° C, the approximate equilibrium pressure is 3.5 ± 0.5 kb. A depth of 10–15 km would be

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[2] Goldsmith and Newton applied the same procedure as Boettcher and Wyllie, but without any negative pressure correction.

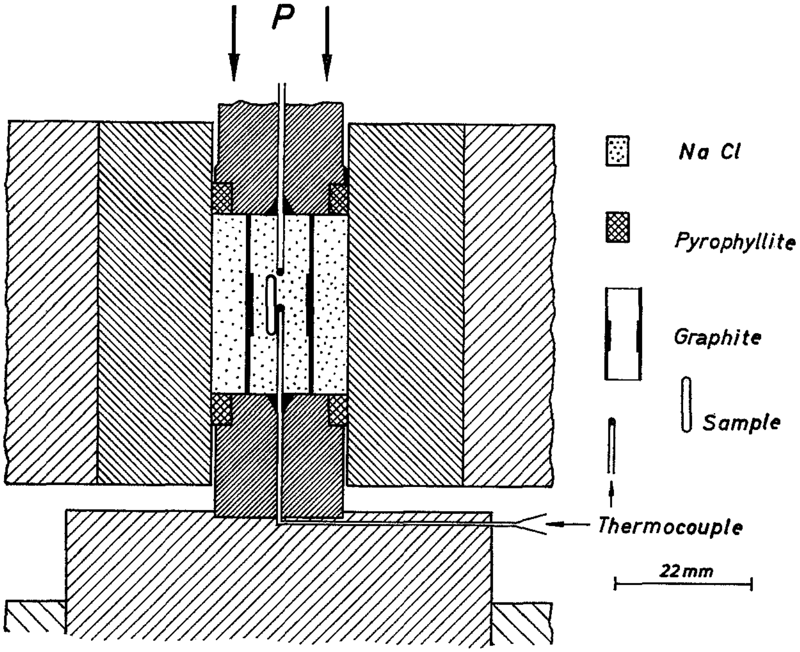

Fig. 6. Sketch of the high-pressure cell we used for the piston-cylinder runs. The thermocouple was always a NiCr-Ni one. The diameter of the cell is 22.0 mm. The core consisted of tungsten carbide. The surface of the boring was always well polished

sufficient to create a pressure high enough to reach the stability field or aragonite. At 180° C (300° C, 400° C) the approximate equilibrium pressure is 5 kb (7 kb, 9 kb).

We are convinced that it is not particularly useful to compare reaction times observed in experiments with those nature needs for mineral reactions. But the experimental results show that the presence of water very much accelerates the reaction, especially at low temperatures. Metamorphic aragonite can only reach the surface if it remains dry and if it enters the stability field of calcite at relatively low temperatures. (At 440° C and 9.2 kb e.g. dry aragonite is completely transformed into calcite during a run time of only 40 hours, see run No. 110 A_1.)

Newton, Goldsmith and Smith (1969) have shown that aragonite can grow at very low pressures from strained calcite. They observed that aragonite grows before strain is released from calcite. (Newton *et al.* have convincingly demonstrated an effect one should always be aware of while thinking about mineral reactions.) But it has not jet been proven that the prehnite-pumpellyite facies rocks of N. W. Washington where both aragonite and strained calcite occur (see Vance, 1968, and Newton, Goldsmith and Smith, 1969) are necessarily low pressure formations.

The calcite-aragonite transition boundary most probably represents the lowest pressure boundary at which aragonite can be stable at any given temperature. Addition of $MgCO_3$ to the pure system $CaO-CO_2$ moves the calcite-aragonite boundary to higher and not to lower pressures, see Goldsmith and Newton (1969). Froese and Winkler (1966) have shown that the amount of Sr in metamorphic aragonites is insufficient to cause a significant lowering of the pressure of the calcite-aragonite equilibrium. This will probably also be the case with other cations.

The calcite-aragonite and the albite-jadeite-quartz curves do not intersect below 600° C (see Fig. 5: The albite-jadeite-quartz curve is the dash-dotted curve in Fig. 5). This curve is based on unpublished data achieved with the piston-cylinder apparatus used for the calcite-aragonite runs. Extrapolation of the calcite-aragonite and albite-jadeite-quartz curves suggests an intersection at about 750° C. This means that there is a pressure field about 3 kb wide where both albite and aragonite are stable phases. That aragonite can be formed at pressures where albite is not yet decomposed to jadeite + quartz has already been described by Ernst (1965) and Ghent (1965) from Franciscan blueschists.

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References

Bell, P. M., England, J. L.: High-pressure differential thermal analysis of a fast reaction with CaO_3. Carnegie Inst. Wash. Year Book **63**, 176–178 (1964).

Boeke, H. E.: Die Schmelzerscheinungen und die umkehrbare Umwandlung des Calciumcarbonats. Neues Jahrb. Mineral. Geol. **1**, 91–212 (1912).

Boettcher, A. L., Wyllie, P. J.: The calcite-aragonite transition measured in the system CaO-CO_2-H_2O. J. Geol. **76**, 314–330 (1968).

Bridgeman, P. W.: The high pressure behaviour of miscellaneous minerals. Amer. J. Sci. **237**, 1–9 (1939).

Brown, W. H., Fyfe, W. S., Turner, F. J.: Aragonite in California glaucophane schists, and the kinetics of the aragonite-calcite transformation. J. Petrol. **3**, 566–582 (1962).

Clark, S. P.: A note on calcite-Aragonite equilibrium. Am. Mineralogist **42**, 564–566 (1957).

Cogulu, E.: Etude pétrographique de la région de Mihaliccik (Turquie). Schweiz. Mineral. Petrog. Mitt. **47**, 683–824 (1967).

Coleman, T. G., Lee, D. E.: Metamorphic aragonite in the glaucophane schists of Cazadero, California. Am. J. Sci. **260**, 577–595 (1962).

Crawford, W. A., Fyfe, W. S.: Calcite-aragonite equilibrium at 100° C. Science **144**, 1569–1570 (1964).

Ernst, W. G.: Mineral paragenesis in Franciscan metamorphic rocks, Panoche Pass, California. Geol. Soc. Am. Bull. **76**, 879–913 (1965).

Froese, E., Winkler, H. G. F.: The system $CaCO_3$-$SrCO_3$ at high pressures and 500° C to 200° C. Can. Mineralogist 8, 551–566 (1966).

Ghent, E. D.: Glaucophane-schist facies metamorphism in the Black Butte Area, Northern Coast Ranges, California. Am. J. Sci. **263**, 385–400 (1965).

Hoffmann, C.: Die Glaukophangesteine und ihre stofflichen Äquivalente in Nordcalabrien (Süditalien). Contr. Mineral. and Petrol. **27**, 283–320 (1970).

Jamieson, J. C.: Phase equilibrium in the system calcite-aragonite. J. Chem. Phys. **21**, 1385–1390 (1953).

McKee, B.: Aragonite in the franciscan rocks of the Pacheco Pass area, California. Am. Mineralogist **47**, 379–387 (1962).

Newton, R. C., Goldsmith, J. R., Smith, J. V.: Aragonite crystallization from strained calcite at reduced pressures and its bearing on aragonite in low-grade metamorphism. Contr. Mineral. and Petrol. **22**, 335–348 (1969).
Sclar, C. B., Carrison, L. C., Schwartz, C. M.: The calcite-aragonite transition and the calibration of a belt-type apparatus between 15 and 35 kb, 700° to 1400° C. Am. Soc. Mech. Engineere Paper 62-WA-248, 7 p (1962).
Simmons, G., Bell, P.: Calcite-aragonite equilibrium. Science **139**, 1197–1198 (1963).
Turner, F. J.: Metamorphic petrology. New York: McGraw Hill Book Co. 1968.
Vance, J. A.: Metamorphic aragonite in the prehnite-pumpellyite facies, Northwest Washington. Am. J. Sci. **266**, 299–315 (1968).
Winkler, H. G. F.: The genesis of metamorphic rocks, 2nd ed. Berlin-Heidelberg-New York: Springer 1967.
Zimmermann, H. D.: Gleichgewichtsbedingungen der Reaktion Albit⇌Jadeit + Quarz und Calcit⇌Aragonit: Dissertation, Göttingen 1969.

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