

After the elucidation of the crystal structure of sanbornite, Douglass (1958) also questioned the occurrence of solid solution in BaSi_2O_5 . He doubted that the sanbornite structure could accommodate sufficient change in the BaO to SiO_2 ratio to account for the complete solid solution between $\text{BaO} \cdot 2\text{SiO}_2$ and $2\text{BaO} \cdot 3\text{SiO}_2$, as first reported by Escola (1922). The solid solutions reported to occur at the liquidus are with the high temperature form of BaSi_2O_5 rather than with sanbornite. However, the doubt raised by Douglass' work is probably still valid because of the similarity of the two powder patterns.

A re-examination of the sub-system $\text{BaO} \cdot 2\text{SiO}_2$ - $2\text{BaO} \cdot 3\text{SiO}_2$ has shown that there is actually little or no solid solution in the binary system but that other discrete phases occur. A complete discussion of this sub-system will appear in the Journal of Research of the National Bureau of Standards, **62**, May 1959; RP 2953.

REFERENCES

- AUSTIN, A. E. (1947), X-ray diffraction data for compounds in the systems $\text{Li}_2\text{O-SiO}_2$ and BaO-SiO_2 : *J. Am. Ceram. Soc.*, **30**, 218-220.
- BOWEN, N. L. (1918), Crystals of barium disilicate in optical glass: *J. Wash. Acad. Sci.*, **8**, 265-268.
- DOUGLASS, R. M. (1958), Crystal structure of sanbornite, BaSi_2O_5 : *Am. Mineral.*, **43**, 517-536.
- ESCOLA, P. (1922), The silicates of strontium and barium: *Am. J. Sci.*, [5] **4**, 331-375.
- LEVIN, E. M. AND UGRINIC, G. M. (1953). The system barium oxide-boric oxide-silica: *J. Research Nat. Bur. Standards*, **51**, 37-56.
- ROGERS, A. F. (1932) Sanbornite, a new barium silicate mineral from Mariposa County, California: *Am. Mineral.*, **17**, 161-172.

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MELTING OF CALCITE IN THE PRESENCE OF WATER

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In a recent note in this journal Paterson (1958) described the partial melting of calcite in the presence of water and carbon dioxide at temperatures "around 900° C. to 1000° C." at a total pressure of 50 bars. The ratio of water vapor to carbon dioxide in the system was not known.

This note is to point out that a program designed to throw light on the origin of carbonatites has been underway for more than two years. The authors are investigating the phase relations in the system $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$ as part of the overall program on carbonatites and calcite has

been partially melted at 740°C . in the presence of water vapor at a pressure of 1000 bars. In compositions on the CaO side of the calcite-water join in the system $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$, melting begins at $675 \pm 5^{\circ}\text{C}$. at the same pressure. The joins calcite-water, magnesite-water, and dolomite-water are being studied and, to illustrate the general nature of our results, we will describe briefly the phase relations in a portion of the system $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$ as deduced from runs completed in the join $\text{CaCO}_3-\text{H}_2\text{O}$. These data were presented at the Annual Meeting of the Geological Society of America, St. Louis, Missouri, 1958 (Tuttle and Wyllie, 1958).

Runs were made in small sealed platinum capsules containing measured quantities of water and calcite, the calcite being in the form of a single cleavage rhomb. A preliminary isobaric equilibrium diagram for this join at a pressure of 1000 bars is given in Fig. 1A. The diagram is based on 200 runs determined in the temperature interval from 600°C . to 1200°C . and in the composition range from 10 to 100 weight per cent

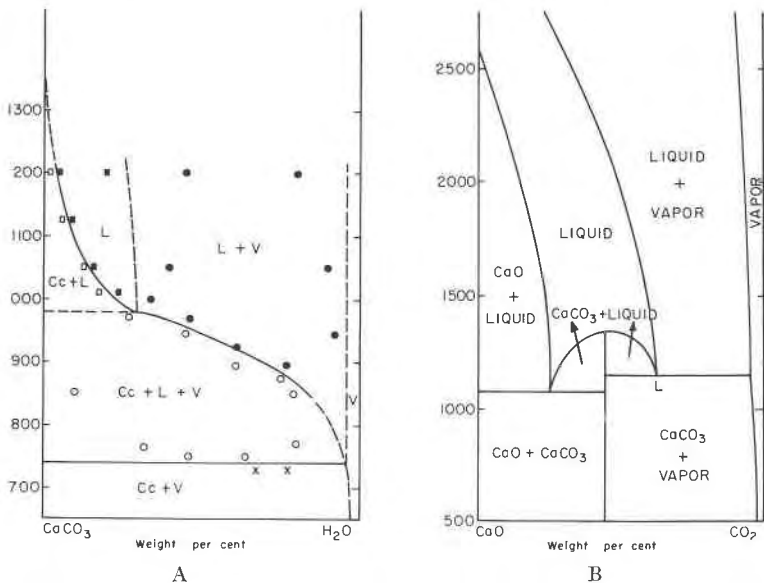


FIG. 1. (A) Isobaric equilibrium diagram for the join calcite-water of the ternary system $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$ at 1000 bars pressure. Cc—calcite; L—liquid; V—vapor. The diagram shows the phase fields intersected by the join at this pressure. When liquid and vapor co-exist their compositions do not lie in the plane of the section (See Fig. 2).

(B) Schematic isobaric equilibrium diagram for the system $\text{CaO}-\text{CO}_2$ at 1000 bars pressure. This is believed to represent the probable phase relations, although the positions of the isobaric invariant lines $\text{CaO}+\text{liquid}+\text{CaCO}_3$ and $\text{CaCO}_3+\text{liquid}+\text{vapor}$ are not yet known.

calcite. The liquid developed along this join quenches to a white compacted powder, which is quite distinct from the transparent cleavage fragment initially sealed into the capsule. The powder consists of a mixture of dendritic calcite and $\text{Ca}(\text{OH})_2$ (portlandite), the proportions of which indicate the composition of the liquid. Much information was obtained from the physical character of the platinum capsules and of the charges within the capsules at the end of each run.

At a pressure of 1000 bars calcite begins to melt at 740°C ; a small amount of calcite dissociates, thus releasing carbon dioxide to the vapor phase, and liquid develops from the CaO , CaCO_3 and water vapor. Only a trace of liquid is developed at this temperature and for charges containing less than 30 weight per cent water, the presence of liquid was not established. Within the three-phase region CaCO_3 +liquid+vapor the proportion of liquid developed at any temperature increases with increasing water content; for a charge of fixed composition the proportion of liquid increases with increasing temperature.

Whenever vapor and liquid co-exist, their compositions do not lie on the join. For this reason it is difficult to discuss the phase relationships without reference to the ternary system $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$. Vapor is apparently absent between 980°C . and 1200°C . for compositions containing less than 30 weight per cent water, and this part of the join is binary. As shown in Fig. 1A, a one-phase field of liquid is intersected by the join in this region.

As an aid to understanding the experimental results in the ternary system $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$, a schematic isobaric section through the PTX model of the binary system $\text{CaO}-\text{CO}_2$ is shown in Fig. 1B. These are the probable phase relations at 1000 bars. At this pressure calcite melts congruently and the congruent liquid must be heated well above the melting temperature before a vapor phase appears. It should be noted that two three-phase univariant surfaces are intersected at this pressure, one representing the equilibrium CaO +liquid+ CaCO_3 and the other CaCO_3 +liquid+vapor. The univariant surfaces intersect the isobaric section in straight invariant lines. As water is added to the binary system at constant pressure these invariant three-phase lines move into the isobaric three-dimensional ternary model and generate three-phase spaces which are bounded by three surfaces representing two-phase equilibria. For example, the invariant line CaCO_3 +liquid+vapor becomes a three-phase space bounded by the surfaces CaCO_3 +liquid, CaCO_3 +vapor, and liquid+vapor. The solid phases do not change in composition, but the compositions of the liquid and vapor become ternary. Each of the stability fields shown in the isobaric section of Fig. 1B also extends into the isobaric prism when water is added as a third

component, and each becomes a space separated by the curved surfaces which are generated by the field boundaries of Fig. 1B as they move into the solid model.

It is convenient to visualize the phase relations in the ternary isobaric prism by passing isothermal planes through the model. The isothermal intersection of a three-phase space is a triangle, with the composition of each phase given by the apices, and the intersections of the curved surfaces separating the one and two-phase spaces are curved lines.

Using the information obtained for the join $\text{CaCO}_3\text{-H}_2\text{O}$, it is possible to sketch the isobaric isothermal planes for the system $\text{CaO-CO}_2\text{-H}_2\text{O}$ (Fig. 2). The three-phase triangle calcite+liquid+vapor is bordered by two-phase fields of calcite+vapor, calcite+liquid, and liquid+vapor (Fig. 2B). A one-phase field of liquid, extending from the liquid corner

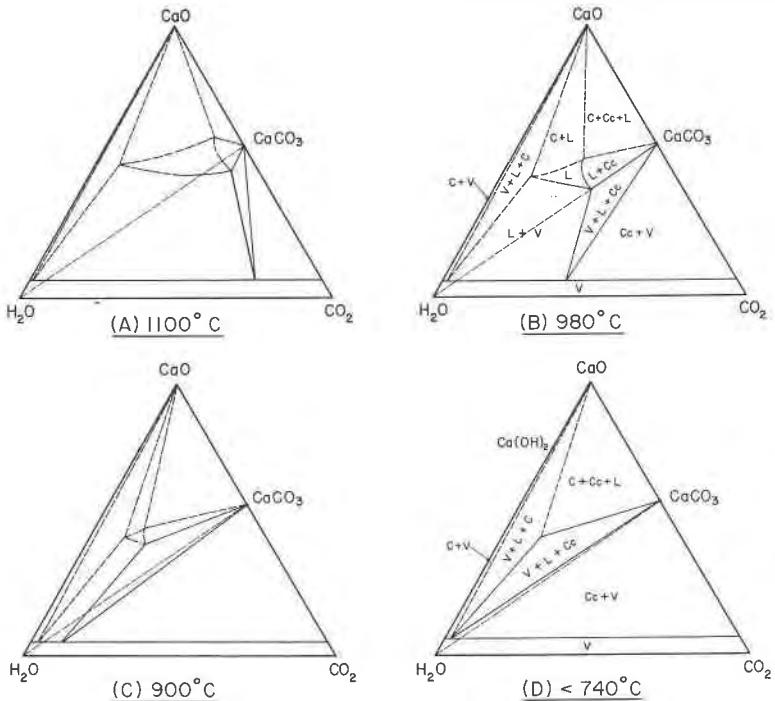


FIG. 2. Schematic isobaric isothermal planes in the system $\text{CaO-CO}_2\text{-H}_2\text{O}$ deduced from data determined for the join calcite-water. C— CaO ; Cc— CaCO_3 ; L—liquid; V—vapor. For compositions on the join calcite-water, melting begins at 740°C . when the calcite-vapor side of the three-phase triangle calcite+liquid+vapor crosses the join. The ternary isobaric invariant temperature illustrated in (D) is $675 \pm 5^\circ\text{C}$.

of the three-phase triangle, intersects the calcite-water join for temperatures above 980° C. At 980° C. (Fig. 2B) the calcite-liquid side of the three-phase triangle crosses the calcite-water join, and at lower temperatures the vapor deficient region of the ternary system is completely within the area $\text{CaO-CaCO}_3\text{-H}_2\text{O}$. The liquid corner of the three-phase triangle is the locus of a liquidus field boundary which passes from a point in the binary system CaO-CO_2 (such as L in Fig. 1B) across the calcite-water join at about 30 weight per cent water at 980° C, (Fig. 2B) to the ternary isobaric invariant point indicated in Figure 2D. Here the last trace of liquid disappears. The temperature of this point is $675 \pm 5^{\circ}$ C. at 1000 bars pressure and $650 \pm 5^{\circ}$ C. at 2000 bars pressure. In addition to the three-phase triangle calcite+liquid+vapor, there must be two other three-phase triangles in the system, $\text{CaO+calcite+liquid}$ and CaO+liquid+vapor , which meet at the ternary isobaric invariant point as shown in Fig. 2D. Below the invariant point the three triangles are replaced by one triangle in which the phases CaO+calcite+vapor are stable. The successive positions of the vapor corners of the three-phase triangles are not known, but with decreasing temperature they must change from pure carbon dioxide to almost pure water. At 1000 bars pressure portlandite becomes stable in the binary system $\text{CaO-H}_2\text{O}$ below 750° C. (Majumdar and Roy, 1956), so there must be a three-phase triangle $\text{CaO+Ca(OH)}_2\text{+vapor}$ in the space shown as CaO+vapor in Fig. 2D. This need not concern us in the present discussion.

The temperature of beginning of melting of calcite for any composition on the join calcite-water is the temperature at which the join intersects the three-phase region calcite+liquid+vapor. This temperature is just above the isobaric ternary invariant point in the system if the relationships are as shown in Fig. 2D; it is believed to be the best interpretation of the available data. The phase relations within the ternary system can be determined more accurately when runs for other joins are completed. The intersection of the join $\text{CaCO}_3\text{-H}_2\text{O}$ with the three-phase triangle $\text{CaCO}_3\text{+liquid+vapor}$ at 900° C. (Fig. 2C) shows how rapidly the proportion of liquid decreases as the percentage of water in the charge decreases. This probably explains why the presence of liquid at 750° C. was not established for charges containing less than 30 weight per cent water. At 750° C. the calcite-vapor side of the three-phase triangle must be almost coincident with the join $\text{CaCO}_3\text{-H}_2\text{O}$.

The vapor phase in Paterson's experiments consisted of a mixture of carbon dioxide and water in unknown proportions. Melting would begin when the three-phase triangle calcite+liquid+vapor crosses the line

joining calcite to the composition of the vapor in the pressure vessel. This temperature would be lowered as the proportion of water in the vapor is increased. The phase relationships in the ternary system corresponding to the beginning of melting in Paterson's experiments could correspond to the condition shown in Figs. 2B or 2C which would represent a temperature well above the minimum liquidus temperature in the ternary system $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$ at the same pressure. Paterson concluded that calcite, in the presence of water and carbon dioxide at a total pressure of 50 bars, will melt some three to four hundred degrees below the melting point in the presence of carbon dioxide alone. Liquid develops at considerably lower temperatures (650°C.) at 2000 bars pressure within the system $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$.

The presence in many natural carbonate rocks of additional components such as alkalis would probably lower the melting temperatures further and increase the amount of liquid developed at low temperatures. Some carbonate liquids can be quenched to a glass by extremely rapid cooling, but in nature such rapid cooling is unlikely and evidence of melting in rocks will be difficult to find.

The presence of even a trace of interstitial liquid in a rock will greatly modify its physical character and hasten the attainment of chemical equilibrium. The partial melting of carbonates in the presence of water vapor at temperatures as low as 650°C. and at pressures reached at relatively high levels in the earth's crust has important petrological implications in regard to:

(1) Emplacement of carbonatites. Many field geologists have long been convinced that carbonatites were emplaced as liquid magmas. Previous experimental data has suggested that the existence of carbonatite liquids in nature was unlikely, but present results prove that carbonatite magmas can exist at moderate temperatures and pressures.

(2) Deformation of limestones. The development of a small quantity of intergranular liquid in massive limestone would greatly facilitate its deformation.

(3) Contact metamorphism of limestones. PT conditions at many igneous contacts must be suitable for the development of liquid in limestones. Moreover, there would sometimes be a continuous supply of water and other volatile materials passing from the igneous magma through the aureole; this would produce more melting than could occur in a closed system. The presence of liquid in an impure limestone would aid recrystallization and growth of new minerals.

The carbonate dikes and carbonatite-like bodies associated with the skarn zones of limestone "granite" contacts may also represent intrusion

of carbonate liquid. Burnham (1958) has described dike-like masses of carbonate-microcline-oligoclase-quartz which grade outward from the contact to carbonate veins enclosing euhedral crystals of epidote.

REFERENCES

- BURNHAM, C. WAYNE (1958), Contact Metamorphism at Crestmore, California. *Bull. Geol. Soc. Am.* In Press.
- MAJUMDAR, A. J., AND ROY, R. (1956), The System $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$. *Jour. Amer. Ceram. Soc.*, **39**, 434-442.
- PATERSON, M. S. (1958), The Melting of Calcite in the Presence of Water and Carbon Dioxide. *Am. Mineral.*, **43**, 603-606.
- TUTTLE, O. F., AND WYLLIE, P. J. (1958), Calcite-Water Join in the System $\text{CaO-CO}_2\text{-H}_2\text{O}$. Abstract. *Bull. Geol. Soc. Am.*, **69**, 1655-1656.

Note added in press: Study of the system $\text{CaO-CO}_2\text{-H}_2\text{O}$ has now been completed. The general relations deduced above have been confirmed experimentally at 1000 bars pressure, but some modifications are required because it was discovered that portlandite does not dissociate, but melts at 835 C., and calcite melts incongruently, rather than congruently. Detailed results will be published shortly.

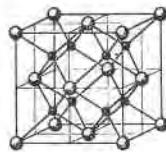
M.S.A. MEMBERSHIP NOTICE

The Council authorized the preparation of an attractive notice to advertise membership in our Society (*Am. Mineral.*, **43**, 1958, 350). The



MINERALOGY

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Anyone interested in mineralogy, petrology, crystallography and allied sciences may become a member of the Mineralogical Society of America. The *American Mineralogist*, the bimonthly journal of the Society, which averages about 200 pages each number, is free to members. The annual dues are \$4.00; there is no initiation fee. To obtain a membership application blank, see _____ or

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reproduction presented herewith does not do full justice to the 9 by 12 inch form on heavy stock, since it fails to show that the name and seal of our Society are done in red overprint. It is hoped that those in colleges or universities or industrial laboratories or in other callings where a suitable bulletin board is available will drop a postal to the undersigned or the Treasurer requesting a copy for posting. The notice has a blank line on which it is intended will appear the name of a local individual who will be glad to sponsor new members. Membership forms are available from the Treasurer or any member of the membership Committee. One of the better ways to advance the mineralogical sciences is by the wider dissemination of our journal; thus please cooperate.

The teaching profession should be interested in the following quotation paraphrased from a portion of a recent letter from Professor R. A. Hoppin: "It is good to get students interested in the *American Mineralogist*; they too can find much in it that will be useful. Once they get the habit of receiving it, they are very apt to continue their subscription on leaving school. On the other hand once outside the catalytic effect is gone in most cases and they probably won't be interested in starting a new subscription. I know that I felt a certain pride the first time I received a professional journal. I started two publications under student rates. I have continued getting them although I doubt that I would have subscribed to them later at the regular rate."

D. JEROME FISHER, *Chairman*
Membership Committee
(see page 459, this issue)

(Note by editor: Drs. D. J. Fisher and A. A. Levinson are responsible for the design of the membership notice.)

INTERNATIONAL MINERALOGICAL ASSOCIATION

The first general meeting of the IMA since its foundation last year in Madrid, will be held in Zürich, Switzerland, from Monday, August 31 to Thursday, September 3, 1959, and will have a full program. This includes meetings of the Commissions dealing with Abstracts, Mineral Data, Museums, and New Minerals, most of which will be assembled for the first time. The business meeting of delegates (at which representatives from at least 16 nations are expected) will have to deal with certain extensions and modifications of the constitution, prepared by the Executive Committee at a meeting held in Zürich from January 19 to 22, 1959 and attended by five members (Amoros, Fisher, Onorato, Parker, Wickman).

Two symposia will be held during the general meeting. The first of these (September 1 and 2) will deal with *Alpine Fissure Minerals* [Speakers: Epprecht, (Zürich), Fagnani, (Milan), Grigoriev, (Lenin-

grad), Laves, (Zürich), Lietz, (Hamburg), Lovering, (Denver), and Parker, (Zürich)]. The second (September 3, Chairman: Professor M. J. Buerger) will have *Twinning* as its topic [Speakers: Amoros, (Madrid), Buerger, (Cambridge, Mass.), Curien, (Paris), Donnay, (Baltimore), Holser, (La Habra, Cal.), Ito, (Tokyo), and a Russian speaker].

Two concurrent field excursions are planned from Friday, September 4 until Monday, September 7 (inclusive). Of these the "*East*" *Excursion* under the leadership of Professors Staub and Burri and others will visit the Göschener Alps (Granites of the Aar Massif), the mineralized marbles of Castione, the Region of San Bernardino and Maloja in the Engadin, the granite of Val Bregaglia (Bergell) with pegmatites and injection phenomena, and finally the manganese ore deposits of Falotta with characteristic minerals such as tinzenite (Mn-axinite), etc.

The "*West*" *Excursion* to be led by Professor Ernt Niggli (Bern) and others will go from Zürich via Luzern and the Grimsel Pass (granites, gneisses, etc. of the Aar Massif) to Binn (rare sulfosalts in dolomite), thence to Andermatt and Val Maighels (garnetiferous lime-silicate rocks), Sedrun (Alpine fissure mineral deposits), and the Lukmanier Pass (metamorphic rocks and minerals).

Attendance at the symposia will be open to all, as will participation in the excursions, though priority in registering for the latter must be given to the delegates and others attending the General meeting in an official capacity. A more detailed program will be obtainable in the near future from the Secretary of the IMA, Professor J. L. Amoros, Museo de Ciencias Naturales, Castellana 84, Madrid, Spain.

FREQUENCY CONTROL SYMPOSIUM

The 13th annual Frequency Control Symposium, sponsored by the Signal Research and Development Laboratory, will be held May 12-14 at the Berkeley-Carteret Hotel, Asbury Park, New Jersey. A total of 62 technical papers will be presented.

The sessions will be concerned with the fundamental properties of quartz, piezoelectric resonators, crystal measurements, stable oscillator circuits, ultra precision crystals, crystal standards, frequency synthesis and measurements, precision filters, atomic and molecular beam devices, and gas cells.

CONFERENCE ON APPLICATIONS OF X-RAY ANALYSIS

The eighth annual conference on Applications of X-Ray Analysis, sponsored by the Metallurgy Division of the Denver Research Institute of the University of Denver, will be held August 12-14 at the Stanley Hotel, Estes Park, Colorado. The deadline for titles and author information is May 1, 1959. Conference Chairman: William M. Mueller, Denver Research Institute, University of Denver, Denver 10, Colorado.

ERRATUM

In the January-February, 1959 issue of *The American Mineralogist*, page 5, the *d* spacing for *hkl*=411 (Table 1) should read 1.299 instead of 1.229.