

THE AMERICAN MINERALOGIST, VOL. 44, MARCH-APRIL, 1959

## POLYMORPHISM IN BARIUM DISILICATE

ROBERT S. ROTH AND ERNEST M. LEVIN, *National Bureau of Standards, Washington, D. C.*

The question of polymorphism in barium disilicate has recently been discussed in this journal by R. M. Douglass (1958). Although Rogers (1932) postulated dimorphism of  $\text{BaSi}_2\text{O}_5$  in order to reconcile his optical data with those of Bowen (1918) and Escola (1922), Douglass found no evidence of polymorphism in his own experiments. Douglass compared his indexed  $x$ -ray diffraction powder pattern of the mineral sanbornite with the pattern published by Austin (1947) for  $\text{BaO} \cdot 2\text{SiO}_2$ . He correlated the (112/004) doublet of sanbornite occurring at  $3.422 \text{ \AA}$  with the  $3.55 \text{ \AA}$  peak in Austin's pattern. However, if a calculation of Austin's pattern is made, it can be seen that the  $3.55 \text{ \AA}$  peak is well beyond the limit of error of any  $d$  spacing which can belong to the sanbornite structure.

Douglass (1958) further states that: "An uninterpreted powder pattern for  $\text{BaO} \cdot 2\text{SiO}_2$  given by Levin and Ugrinic (1953) contains many lines for which there are no corresponding calculated spacings" and concludes that "in the material of Levin and Ugrinic the preponderant phase was not  $\text{BaSi}_2\text{O}_5$  of sanbornite structure."

In the present study the material used by Levin and Ugrinic was re-examined. Using a modern high angle diffractometer it was found to have an  $x$ -ray diffraction pattern essentially the same as that reported in 1953. However when the material was reheated at temperatures below about  $1350^\circ \text{ C.}$  for many hours it slowly transformed to a low temperature form. This phase has an  $x$ -ray powder pattern the same as that reported by Douglass (1958) for sanbornite. Material having the sanbornite structure slowly inverted above about  $1350^\circ \text{ C.}$  to the high- $\text{BaSi}_2\text{O}_5$  form. This form is characterized especially by the diffraction peak at about  $3.55 \text{ \AA}$  or  $25.1^\circ 2\theta$  for  $\text{CuK}\alpha$  radiation.

Therefore polymorphism in barium disilicate has been definitely established. The phase transformation takes place at about  $1350^\circ \text{ C.}$  and is sluggish but reversible. The indices of refraction of the two polymorphs differ by less than two thousandths. Thus the two forms can only be distinguished with confidence by the  $x$ -ray diffraction method. The  $x$ -ray patterns reported by Austin (1947) and by Levin and Ugrinic (1953) represent the high temperature form of  $\text{BaSi}_2\text{O}_5$ . The pattern of sanbornite given by Douglass (1958) is the first  $x$ -ray pattern of the low temperature form of  $\text{BaSi}_2\text{O}_5$  to be published.

After the elucidation of the crystal structure of sanbornite, Douglass (1958) also questioned the occurrence of solid solution in  $\text{BaSi}_2\text{O}_5$ . He doubted that the sanbornite structure could accommodate sufficient change in the  $\text{BaO}$  to  $\text{SiO}_2$  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  $\text{BaSi}_2\text{O}_5$  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  $\text{Li}_2\text{O}-\text{SiO}_2$  and  $\text{BaO}-\text{SiO}_2$ : *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,  $\text{BaSi}_2\text{O}_5$ : *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.

THE AMERICAN MINERALOGIST, VOL. 44, MARCH-APRIL, 1959

## MELTING OF CALCITE IN THE PRESENCE OF WATER

P. J. WYLLIE AND O. F. TUTTLE, *College of Mineral Industries, The Pennsylvania State University*

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  $\text{CaO}-\text{MgO}-\text{CO}_2-\text{H}_2\text{O}$  as part of the overall program on carbonatites and calcite has