

magma at the time of phenocryst formation (i.e. near liquidus conditions), has a higher carbon dioxide content than is apparent from study of the vent gases, where water is the dominant volatile species.

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## Thermal decomposition of okenite from India

AMIDST a wide variety of fibrous zeolites occurring in druses and cavities of basaltic lava flows referable to the Deccan Traps of India, okenite is widespread in all the three zeolite zones, namely the laumontite, scolecite, and heulandite zones identified by Sukheswala *et al.* (1974) in the western region of this volcanic province. In spite of its wide occurrence in India and other parts of the world, including Disko Island (Greenland), Crestmore (California), Scawt Hill (Northern Ireland), literature relating to the dehydration and thermal decomposition of okenite is lacking. The present study was undertaken on Indian material from Bombay, Nasik, and Poona in order to fill this lacuna and supply basic DTA curves for the mineral. In this attempt the effects were recorded by continuous heating up to 1000 °C using a Mom Derivatograph OD Type 102 (System Paulik, Paulik and Erdy) in which DTA, DTG, and TG curves are simultaneously recorded.

Okenite commonly occurs as delicate fibres aggregating into spherical globules ranging from a few mm to 4 cm in diameter, in association with other cavity minerals (fig. 1). In the Poona region it is commonly associated with quartz, chalcedony, apophyllite, stilbite, and heulandite; in the Nasik region it occurs with scolecite, laumontite, stilbite, and apophyllite; and in the Bombay region it is accompanied by laumontite, quartz, calcite,

prehnite, mordenite, apophyllite, and rare babingtonite. At times it is seen to grow over gyrolite. Chemical analyses are given in Table I.

In hand specimen okenite closely resembles mordenite, but it may be easily distinguished microscopically by its higher refractive indices ( $\alpha = 1.540$ ,  $\gamma = 1.542$ ). However, in the present studies the identity of the study material was confirmed from the X-ray powder diffraction patterns using Cu K $\alpha$  radiations and Ni filter.

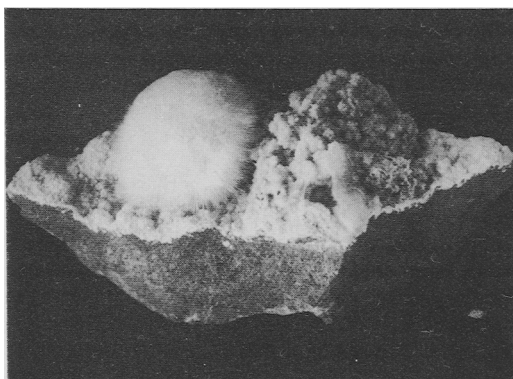


FIG. 1. Fibrous aggregate of okenite from Bombay (2/3 natural size).

TABLE I. Chemical analyses (wt. %) of okenite from India

	1	2	3	4	5	6
	Bombay	Nasik	Poona	Bombay	Bombay	Poona
SiO <sub>2</sub>	53.66	53.20	53.88	53.88	54.28	54.04
Al <sub>2</sub> O <sub>3</sub>	0.16	0.18	0.16	0.08	0.20	0.12
Fe <sub>2</sub> O <sub>3</sub>	—	—	—	0.01	—	—
FeO	—	—	—	—	—	—
MgO	—	—	—	—	—	—
CaO	27.58	27.72	27.56	27.61	27.53	27.20
SrO	—	—	—	0.21	—	—
Na <sub>2</sub> O	1.16	0.87	1.02	0.12	1.20	0.90
K <sub>2</sub> O	0.05	0.04	0.04	0.06	0.04	0.03
H <sub>2</sub> O	17.20	18.12	17.16	18.02	17.34	17.46
Total	99.81	100.13	99.82	99.99	100.59	99.75

1, 2, 3. Analyses by present authors following Shapiro and Brannock (1962). 4. Analysis from Christie (1925). 5, 6. Analyses from Sukheswala *et al.* (1974).

**Thermal effects.** Representative samples of okenite from the three zeolite zones were crushed to grains smaller than 63 nm and were subjected to continuous heating up to 1000 °C with a heating rate of 10 °C per minute in air using Pt crucibles and Al<sub>2</sub>O<sub>3</sub> as inert reference. The DTA curves obtained in these recordings are reproduced in fig. 2 and the results tabulated in Table II. It may be seen that, in the lower temperature ranges, three distinct endothermic maxima appear at 100 °C, 190 °C, and 370 °C. In the upper temperature range a strong and sharp exothermic peak at 890 °C appears without a corresponding change in weight.

**Discussion.** In all the analysed samples the DTA and DTG patterns are highly similar and reproducible. The first peak at 100 °C is obviously due to loss of adsorbed water and the two major endothermic peaks around 190 °C and 370 °C represent loss of structural water in two steps of approximately equal amounts. The rate of water loss in the second step is rather slower, indicating that the water is more firmly held in the structure. The sharp exothermic peak at 890 °C, characteristic of all analysed samples, together with X-ray diffractograms taken at 1000 °C, clearly indicate that conversion of anhydrous okenite to wollastonite and cristobalite begins at 855 °C, with a maximum at 890 °C and completion at about 915 °C. Heller's X-ray studies (Gard and Taylor, 1956) indicated conversion to oriented wollastonite and unoriented cristobalite at 730 °C, but the present investigation shows that this temperature was too low an estimate.

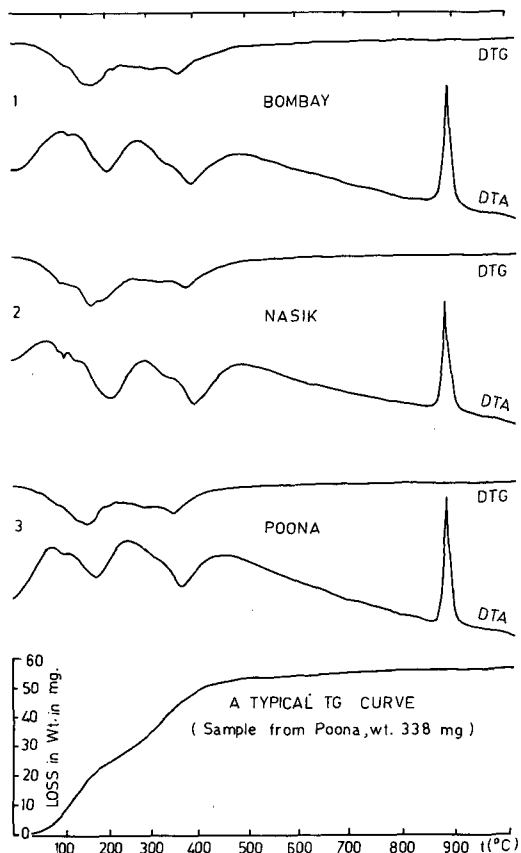


FIG. 2. DTA and DTG curves of okenite from India.

TABLE II. DTA and dehydration data on okenite from India

Locality	Endothermic reaction (°C)	Exothermic reaction (°C)	Dehydration	
			0-200 °C	0-500 °C
Bombay	100, 197, 376	890	35.3	88
Nasik	98, 188, 368	890	39.65	88.23
Poona	100, 190, 370	890	42.66	93

In conclusion it may therefore be remarked that the DTA curves of okenite may serve as excellent identification characteristics, and that the precise range of temperature of transformation of okenite to wollastonite and cristobalite is from 855 °C to 915 °C.

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## Further evidence for the instability of $\text{LiMnSi}_2\text{O}_6$ at low pressure

SPODUMENE and spodumenes with Al replaced by Fe, Cr, V, Sc, In, and Ga have been synthesized at various temperatures and pressures. Brown (1971) synthesized Fe, Cr, V, and Sc spodumenes by firing pelletized silica, lithium carbonate, and metal oxide mixes at 850 to 1000° but failed to produce Al, Mn, or Ga spodumenes. He suggested no  $\text{LiMnSi}_2\text{O}_6$  exists because spontaneous distortion caused by the pyroxene structure does not correspond to that required by  $\text{Mn}^{3+}$  due to the Jahn-Teller effect. This follows the argument presented by Strens (1965) to account for failure to hydrothermally synthesize  $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  garnet at 2-3 kb and 530-600°, and is supported by the occurrence of non-cubic henritermierite with hydrogarnet composition  $\text{Ca}_3(\text{Mn}_{1.5}\text{Al}_{0.5})(\text{SiO}_4)_2$

(OH)<sub>4</sub> (Gaudefroy *et al.*, 1969) and by the doubtful validity of blythite.

However, reviewing garnets, Geller (1967) noted germanate garnets  $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$  and  $\text{Cd}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$  had been synthesized and  $\text{Mn}^{3+}$  had been substituted for  $\text{Fe}^{3+}$  to  $\text{Y}_3(\text{Mn}_{0.1}\text{Fe}_{1.9})\text{Fe}_3\text{O}_{12}$  in YIG, suggesting  $\text{Mn}^{3+}$  may enter sites lacking suitable distortion. For spodumene, Leckebusch *et al.* (1974) found  $\text{Mn}^{3+}$  in reddish violet varieties but  $\text{Mn}^{2+}$  in reddish yellow spodumenes.

These and other reports on  $\text{Mn}^{3+}$  in blanfordites suggest  $\text{Mn}^{3+}$  may enter the pyroxene structure, and successful syntheses of Al spodumene hydrothermally (reviewed by Stewart, 1978) indicate Brown's failure to obtain  $\text{LiMnSi}_2\text{O}_6$  may be because of the technique and conditions used and