## Synthetic soda-free thomsonite.

JULIAN R. GOLDSMITH, Ph.D.

Department of Geology, University of Chicago.

[Taken as read June 12, 1952.]

**X**-RAY powder photographs reveal thomsonite as the principal product of some low-temperature hydrothermal experiments. Glasses of three compositions were used as starting materials; one of the composition of anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>), one of a gallium-containing anorthite<sup>1</sup> (Ca<sub>4</sub>[Ga<sub>3</sub>Al<sub>5</sub>]Si<sub>8</sub>O<sub>32</sub>) in which  $\frac{3}{5}$  of the Al is replaced by Ga, and a glass of the oxide composition of zoisite minus the water (4CaO.3Al<sub>2</sub>O<sub>3</sub>.6SiO<sub>2</sub>).

The Na:Ca and Al:Si ratios in natural thomsonite vary between the extremes expressed in the formulae  $Na_3Ca_9Si_{19}Al_{21}O_{80}.24H_2O$  and  $Na_7Ca_5Si_{23}Al_{17}O_{80}.24H_2O$  according to A. N. Winchell,<sup>2</sup> and M. H. Hey.<sup>3</sup> E. T. Wherry,<sup>4</sup> on the basis of the available analytical data, regarded thomsonite to be of fixed composition ( $NaCa_2Al_5Si_5O_{20}.6H_2O$ ) and noted that the name comptonite had priority for a supposedly soda-free or soda-poor 'variety'. Hey's later X-ray, optical, and chemical data disprove Wherry's views, and for the most part support Winchell's suggestions as to solid solution in thomsonite, chiefly that of concurrent Na-Ca and Al-Si interchanges as in the plagioclase felspars. In 1924 Gordon<sup>5</sup> proposed a compositional range for thomsonite with  $CaAl_2Si_2O_8.3H_2O$  as an end-member, but Winchell (1925) discards Gordon's formulations as being very unlikely as regards solid-solution possibilities.

The synthetic products here produced from the several glasses are soda-free; the glasses were melted from reagent-grade oxides and reacted hydrothermally with distilled water in stainless steel pressure vessels.

<sup>1</sup> J. R. Goldsmith, Gallium and germanium substitutions in synthetic feldspars. Journ. Geol. Chicago, 1950, vol. 58, pp. 518-536. [M.A. 11-326.]

<sup>2</sup> A. N. Winchell, A new theory of the composition of the zeolites. Amer. Min., 1925, vol. 10, pp. 88–97, 166–174. [M.A. 3–13.]; Elements of optical mineralogy. Fourth edition, 1951, pt. 2. [M.A. 11–463.]

<sup>3</sup> M. H. Hey, Studies on the zeolites. Part II. Thomsonite (including faroelite) and gonnardite. Min. Mag., 1932, vol. 23, pp. 51-125.

<sup>4</sup> E. T. Wherry, Note on the composition of thomsonite. Amer. Min., 1923, vol. 8, pp. 121-125. [M.A. 2-302.]

<sup>5</sup> S. G. Gordon, The composition of thomsonite. Proc. Acad. Nat. Sci. Philadelphia, 1924, vol. 76, pp. 103-107. [M.A. 2-528.] If one uses Winchell's formulation, but replaces all Na by Ca (and adjusts the Al:Si ratio to fit), the formula reduces to  $Ca_3Al_6Si_4O_{20}$ .  $6H_2O$ . The precise compositions of the synthetic products cannot be stated with certainty, and it is not definitely known that the material in question can be represented by the above formula. If the Al:Si ratio remained 1:1, as it was in the original batch ingredients, the soda-free nature would necessitate a greater number of vacant cation sites than are evident from the structural determination of Taylor et al.<sup>1</sup> The structure was determined on the basis of a unit cell containing four molecules of



FIG. 1. X-ray diffraction powder photographs, Cu-Ka radiation, 57.3 mm. diameter camera.

Upper photograph: thomsonite from Table Mt., Colorado. Lower photograph: synthetic soda-free, Ga-bearing thomsonite ( $\frac{3}{8}$  of the Al replaced by Ga).

 $NaCa_2Al_5Si_5O_{20}$  (plus water), whereas if this fixed Al:Si ratio is maintained in the soda-free thomsonite, the formula would be  $Ca_{2\frac{1}{2}}Si_5Al_5O_{20}$ (plus water). This would correspond to anorthite  $+H_2O$  in composition, which is the end-member suggested by Gordon.

To determine precisely the composition would require synthesis of crystals sufficiently large so that the absence of extraneous phases could be established. This was not attempted; in fact, the material here described was so very fine-grained that ordinary optical examination was fruitless.

The  $H_2O$  content of the synthetic products is unknown, as are the pressure, temperature, and composition limits of the thomsonite stability field. It is perhaps of interest to note that if the composition is correctly expressed by the formula  $Ca_3Al_6Si_4O_{20}.6H_2O$ , the Al:Si ratio is 1.5; this is rather unusual in network silicates, as this ratio, particularly in natural minerals, ordinarily fails to exceed unity.

<sup>1</sup> W. H. Taylor, C. A. Meek, and W. W. Jackson, The structures of the fibrous zeolites. Zeits. Krist., 1933, vol. 84, pp. 373-398. [M.A. 5-354.]

## 954 J. R. GOLDSMITH ON SYNTHETIC SODA-FREE THOMSONITE

Fig. 1 shows X-ray powder diffraction photographs of a natural thomsonite and of a synthetic soda-free, gallium-bearing product. As would be expected, the unit cell of the latter is somewhat larger than that of normal thomsonite. This material was crystallized at 245° C. and at 8000 psi (H<sub>2</sub>O pressure), somewhat above the temperatures used for the Ga-free thomsonite syntheses. Unless the composition of this compound is the same as anorthite (plus water), an extraneous phase or phases should be present. For example, if the composition were Ca<sub>3</sub>Al<sub>6</sub>Si<sub>4</sub>O<sub>20</sub>. 6H<sub>2</sub>O (including the Ga with the Al), excess SiO<sub>2</sub> (unless leached out of the sample) would be present after crystallization from a composition initially that of anorthite. No diffraction lines other than those belonging to the thomsonite pattern are apparent on the film from which the photograph of fig. 1 was made. Although even a moderately small content of crystalline SiO<sub>2</sub> might be expected to yield lines in this film, the absence of these lines, although suggestive, does not prove that the composition is equivalent to a hydrated anorthite.

Acknowledgement.—Thanks are due to Dr. M. H. Hey for his examination of the powder pattern of the Colorado thomsonite, and for his comments on the composition and properties of thomsonite.

This work was done in conjunction with a research programme financed in part by the Geophysics Branch of the Office of Naval Research, U.S.A.