Studies on the zeolites. Part VII.[1] *'Clinoptilolite', a silica-rich variety of heulandite.*

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IN 1890, L. V. Pirsson[2] described under the name of mordenite a crystalline mineral, isomorphous with heulandite, occurring in a highly weathered amygdaloidal basalt in the Hoodoo Mts., Wyoming. His analysis (1, table I) showed that the mineral had a composition near that of the original mordenite of H. How (1864) and his assumption that it represented a platy-crystalline phase of that normally fibrous mineral was generally accepted.

More recently, T. L. Walker and A. L. Parsons[3] have suggested the identity of How's fibrous mordenite with ptilolite, which is known as well-developed crystals crystallographically quite different from those of Pirsson's mineral. The latter, in this case, cannot be mordenite. W. T. Schaller,[4] who differentiates between ptilolite and mordenite, regards Pirsson's material as an independent species; neglecting its obvious affinities to heulandite, noticed by Pirsson, he proposes for it the very inappropriate name of clinoptilolite, and regards it as having the same fixed composition as ptilolite, namely $(Ca,Na_2,K_2)O.Al_2O_3.10SiO_2.7H_2O$.

Recently M. N. Bramlette and E. Posnjak[5] have described a zeolite from Dome, Arizona, which gives analytical figures near Pirsson's material, but distinctly lower in silica. Its optical properties agree with those of Pirsson's material, as determined by Pirsson and

[1] Part VI. Edingtonite. Min. Mag., 1934, vol. 23, p. 483.

[2] L. V. Pirsson, Amer. Journ. Sci., 1890, ser. 3, vol. 40, p. 232.

[3] T. L. Walker and A. L. Parsons, Univ. Toronto Studies, Geol. Ser., 1922, no. 12, p. 61. [M.A. 2-55.]

[4] W. T. Schaller, Amer. Min., 1932, vol. 17, p. 128; also in abstract in Amer. Min., 1923, vol. 8, p. 93, and quoted in C. S. Ross and E. V. Shannon, Proc. U.S. Nat. Mus., 1925, vol. 64, p. 3. [M.A. 5-147, 2-301; Min. Mag. 20-450.]

[5] M. N. Bramlette and E. Posnjak, Amer. Min., 1933, vol. 18, p. 167. [M.A. 5-357.]

amplified by E. S. Larsen. Bramlette and Posnjak therefore class their material as clinoptilolite, but they observe that as they were unable to distinguish between Debyeograms of their material, Pirsson's material, and heulandite it will be necessary to consider further the relation between clinoptilolite and heulandite. This the present authors have done, and conclude that there can be no doubt that 'clinoptilolite' is merely a high-silica heulandite. The identification is based mainly on an X-ray study of single crystals.

No specimen of 'clinoptilolite' was available in the British Museum collection, but Prof. W. E. Ford very kindly loaned us the type specimen, no. 5268, from the Brush collection of the Sheffield Scientific School, Yale University, U.S.A. A small crystal detached from this was examined optically with results in close agreement[1] with Larsen's, then mounted and an X-ray rotation photograph taken about the a-axis. This proved to be completely identical with a photograph of a heulandite crystal about the a-axis. Long exposure photographs were also taken with iron radiation. The greater resolution thus obtained failed, however, to reveal any differences between heulandite and 'clinoptilolite'.

Now long exposure rotation photographs of small single crystals of natrolite, mesolite, and scolecite, three zeolites possessing very closely related crystal structures, are easily distinguished whether copper or iron radiation be used.[2] We therefore conclude that 'clinoptilolite' and heulandite must be members of an isomorphous series.

If they were independent species there should be differences in the optical properties greater than can be accounted for by the difference in composition. But the difference in the optical properties of ordinary heulandite and 'clinoptilolite', though considerable, is just about what one may expect from the effect of an increase in silica on the optics of thomsonite,[3] namely a decrease of about 0·01 in the refractive index for replacement of CaAl by NaSi in a unit cell of 80 oxygen atoms, together with a marked decrease in the greatest refractive index relatively to the other two[4] (actually the decrease is enough to change the optic sign).

[1] The present authors find n 1·48 approx., birefringence low, extinction undulatory, Bx_o (?) $\perp$ b (010), probably optically negative.

[2] Part V of this series, Min. Mag., 1933, vol. 23, p. 421; compare W. H. Taylor, Zeits. Krist., 1933, vol. 84, p. 373. [M.A. 5-354.]

[3] Part II of this series, Min. Mag., 1932, vol. 23, p. 51.

[4] It appears probable from the data so far available that in many zeolites the birefringence is largely due to polarization by the charged aluminium atoms, and

In chemical composition, both Pirsson's material and Bramlette and Posnjak's agree with silica-rich heulandite.[1] Heulandite shows marked variations in composition, the silica content ranging from 53 to 61 %; the 'clinoptilolites' show 66 % and 64 % silica in the two published analyses. The oxygen content for both heulandite[2] and 'clinoptilolite' is 72 atoms per unit cell, and the two analyses, recalculated into atomic proportions on this basis, are reproduced in table I.

TABLE I. Chemical composition (atomic ratios per 72 oxygen atoms) and optical properties of high-silica heulandites ('clinoptilolites').

	1.	2.
Si	30·04	29·26
Al	5·96	6·84
Ca	0·54	1·18
Na	2·00	3·48
K	2·06	0·78
H_2O	20·34	21·64
Ca+Na+K	5·00	5·44
Sp. gr.	2·14	—
Oxygen atoms per unit cell ...	73·1*	—

1. Hoodoo Mts., Wyoming; L. V. Pirsson, 1890. Ax. pl. and $a \perp b(010)$, $\gamma : a = 15°$, birefringence low (Pirsson). α 1·476, γ 1·479, 2V small, negative, $\beta \perp b$ (010), extinction on b 34° (E. S. Larsen, determined on original material, quoted by W. T. Schaller, loc. cit.).

2. Dome, Arizona; M. N. Bramlette and E. Posnjak, 1933. n 1·480, birefringence low, extinction undulatory, $\gamma \perp b$ (010), 2V large, negative (?).

* Taking Wyart's figures for heulandite (loc. cit.) for the cell sides; this procedure is justified by the complete identity of rotation photographs of heulandite and 'clinoptilolite'.

The unit cell formula of heulandite appears from the data so far available to be essentially $Na_xCa_yAl_{x+2y}Si_{36-(x+2y)}O_{72}\cdot 24H_2O$, where $(x+y)$, the number of cations per unit cell, is variable, ranging from

their replacement by silicon appears as a rule to decrease the birefringence very markedly.

[1] W. T. Schaller, as quoted by Bramlette and Posnjak, considers that the differences in chemical composition between the Arizona and Wyoming material are unimportant. In the present authors' opinion, the differences are well outside the probable experimental error; moreover, Schaller does not give any grounds for his statement that the Arizona material contained 5 % of clay. The analysis itself affords no internal evidence of impurity; and even 5 % of clay would not account for the differences.

[2] For the unit cell contents of heulandite, compare J. Wyart, Compt. Rend. Acad. Sci. Paris, 1930, vol. 190, p. 1564. [M.A. 4–369.] The figures there given are half the unit cell contents, the end-centred cell containing two 'structural units'.

4 to 6, and $(x+2y)$, the number of aluminium atoms per unit cell, ranges from 8 to 10 in most heulandites. In the 'clinoptilolites', the aluminium content falls as low as 6 atoms per unit cell, while the cation content is within the above range of 4–6 atoms. The water content, in both 'clinoptilolites' and ordinary heulandite, generally falls considerably below 24 molecules per unit cell; this is probably due to the high vapour-pressure of the quasi-saturated zeolite at room-temperatures. Similar behaviour has been observed in the case of edingtonite.

Since the minerals examined by Pirsson and by Bramlette and Posnjak are essentially high-silica heulandites, without any simple relation to mordenite or ptilolite,[1] the name 'clinoptilolite' is unsuitable and should not be used.

[1] X-ray photographs of mordenite and ptilolite are quite different from those of heulandite, and appear to be identical; the name mordenite has priority.