A heulandite with excess water

By WILLIAM S. WISE

Department of Geology, University of California,
Santa Barbara, California

[Read 9 March 1967]

Summary. A heulandite from Nelson Creek, Skamania County, Washington, has 30 H_2O per unit cell instead of the normal 24; the excess water is lost on gentle heating. The b and c cell-dimensions are also rather larger than normal. Normal heulandite also occurs in the same area.

IN his well-known series, 'Studies on the Zeolites' (1930 to 1935), M. H. Hey contributed significantly to the understanding of various zeolite minerals. Of equal importance he refined their dehydration and rehydration behaviour. Instead of the simple and often misleading temperature *vs.* weight loss curves Hey (1932–35) showed that dehydration of zeolites is best studied in terms of temperature and water-vapour pressure. From these data plots of the water content of the unit cell *vs.* temperature were calculated.

After observing the dehydration and rehydration of several different zeolites Hey (1935, p. 104) concluded that 'it is impossible for any set of equivalent water positions to be quite fully occupied, even when the zeolite is in contact with water . . .'. He further commented: 'In many zeolite structures there are cavities which might be occupied by water molecules but are not. Presumably the heats of hydration for these groups of lattice positions would be so small that at all accessible water vapour pressures the positions must remain practically empty.'

In this paper a heulandite is described in which cavities or channels normally unoccupied by water contain nearly six molecules of water, giving a unit cell content of nearly 30 instead of the usual near 24.

X-ray and chemical data. During investigation of zeolitic alteration of lower Tertiary rocks in southern Washington an unusual heulandite was found.[1] The X-ray powder pattern of the sample is similar to that yielded by heulandite but all reflections have consistently higher *d*-spacings (see table I). The cell dimensions calculated from these data

[1] The outcrop is located along the north shore of the Columbia River, just west of the mouth of Nelson Creek, SE. ¼, sect. 36, township 3 N., range 7½ E., Skamania County, Washington.

TABLE I. Lattice spacings of two heulandites from Skamania County, Washington

	Heulandite*		Water-rich heulandite†	
hkl‡	d	I	d	I
020	8·97 Å	10	9·15 Å	50
002	7·97	3		
10$\bar{1}$	6·81	2		
022	5·96	1		
031	5·59	1		
11$\bar{2}$	5·266	2		
112	5·124	2	5·31	6
013	5·092	2		
130	4·656	3	4·66	26
10$\bar{3}$	4·366	1	4·27	6
004, 132	3·971	6	4·058	100
042	3·884	3	4·005	10
123	3·827	1		
14$\bar{1}$	3·711	1	3·736	9
21$\bar{1}$	3·560	1	3·497	3
051, 11$\bar{4}$	3·466	1		
220	3·426	2	3·398	16
114	3·396	2		
202	3·337	1		
22$\bar{2}$	3·168	3	3·187	21
222	3·132	2	3·103	6
143	3·076	1		
044	2·961	5	3·035	46
12$\bar{5}$, 035	2·794	3	2·885	4
16$\bar{1}$	2·725	2	2·777	19
006	2·660	1		
25$\bar{1}$	2·565	1		
15$\bar{4}$, 251	2·5205	1		
11$\bar{6}$	2·488	1		
116	2·453	1		
145	2·43	1D		
055	2·37	1D		

Cell dimensions§

a	7·46±0·02 Å		a	7·35±0·08 Å
b	17·80±0·05 Å		b	18·25±0·08 Å
c	15·88±0·05 Å		c	16·26±0·08 Å
β	91° 25'±15'		β	92° 40'±20'
V	2108·1 Å³		V	2178·8 Å³

* A normal heulandite (not analysed) from Lower Tertiary volcanic breccias one mile east of the locality of the water-rich heulandite. The d-spacings were obtained from a powder photograph, using a camera with a radius of 114·59 mm, Cu-K radiation with Ni filter.

† The d-spacings were obtained from diffractometer patterns, using silicon as an internal standard (a 5·4306 Å).

‡ The indices are based on the I 2/m cell.

§ The heulandite cell dimensions were obtained from single-crystal precession photographs, and those of the water-rich heulandite were calculated from the powder data.

have b and c dimensions, and consequently the cell volume, significantly larger than normal heulandite.

In making the cell-volume calculations and indexing the powder pattern I have made use of the $I\ 2/m$ space group setting of Wyart (1933). Some confusion exists over the use of several settings and indexed diffraction patterns based on each. For clarity a brief discussion is inserted here.

Wyart (1933) chose a setting that followed earlier crystallographic work (see for example, the 'Goldschmidt Atlas', vol. 4). This setting[1] was selected because the symmetry is then pseudo-orthorhombic (β 91° 25'); the space group is $I\ 2/m$. Strunz and Tennyson (1956) proposed to redefine the setting in order to illustrate possible structural similarities with stilbite and epistilbite. This setting has the more conventional monoclinic space group $C\ 2/m$ and is the one used by Merkle and Slaughter (1965) in their structural determination of heulandite. Fig. 1 illustrates the relationships between the settings proposed by Wyart, Strunz, and Tennyson, and a possible third cell (A).

The index-transformation matrix from the Wyart setting to that of Strunz and Tennyson is $[\bar{1}01/0\bar{1}0/100]$, and to cell A $[101/010/100]$.

The calculated empirical cell-contents from a chemical analysis (table II) yield 29·56 water molecules per unit cell of 72 oxygen atoms. In order to verify the existence of 5·56 H_2O molecules more than the normal 24 per cell, the water content was calculated by making use of the well-known relation $D = M/NV$, where D = density (in gm/cm³), M = sum of the atomic weights of all the atoms in the unit cell (in gm), V = volume of the unit cell (in cm³), and N = Avogadro's number.

If M is split into two parts, $M = M_d + M_w$, where M_w is the total molecular weight of the water molecules in the cell and M_d is the sum of the atomic weights of all the other atoms, and D is measured, M_w and the number of water molecules (n) can be calculated:

$$n = (D_{\text{meas}} VN) - M_d/18{\cdot}015.$$

M_d is obtained from calculation on the chemical analysis (ignoring the measured H_2O+ and H_2O-) on the basis of 72 oxygen atoms per cell. The cell volume is determined from an X-ray powder pattern.

Applying this relation to the Washington heulandite, where $D_{\text{meas}} = 2{\cdot}19 \pm 0{\cdot}01$ gm/cm³ and $M_d = 2333{\cdot}31$ (from table II), the number of water molecules is $2{\cdot}19 \times 2178{\cdot}8 \times 10^{-24} \times 6{\cdot}02257 \times 10^{23} - 2333{\cdot}31/18{\cdot}015 = 30{\cdot}0$ molecules per unit cell.

Since the density was measured with large crystals in an air-comparison pycnometer, the greater water content is taken as the more reliable. This then yields the structural formula

$$Ca_{4{\cdot}05}Na_{0{\cdot}58}K_{0{\cdot}10}Mg_{0{\cdot}06}Al_{8{\cdot}73}Si_{27{\cdot}23}O_{72}\cdot 30H_2O.$$
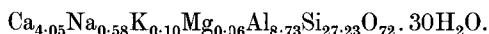
[1] Many workers using the $I\ 2/m$ cell have reversed the a and c axes from those of Wyart, in order to make $a > c$. See, for example, Smith (1963, p. 288), Hay (1963, p. 226), and Deer, Howie, and Zussman (1963, vol. 4, p. 375).
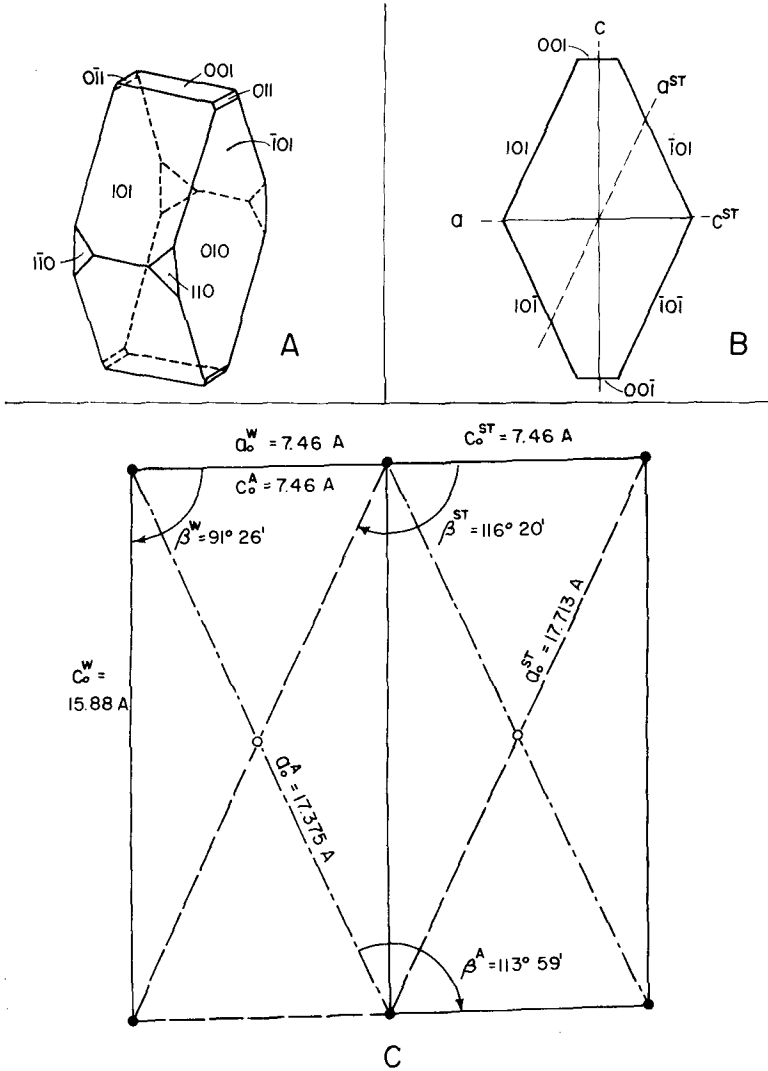
FIG. 1. Comparison of various settings of heulandite. A. The major forms of heulandite as used by Wyart (1933) and the majority of writers cited in the Goldschmidt Atlas. B. Section parallel to (010) through a heulandite crystal to show the relationship between the a and c axes of the Wyart cell ($I\ 2/m$) and the a and c axes of the Strunz and Tennyson (1956) cell ($C\ 2/m$), which are labelled a^{ST} and c^{ST}. C. Comparison of the $I\ 2/m$ cell (a^W and c^W axes), the $C\ 2/m$ of Strunz and Tennyson (1956) (a^{ST} and c^{ST}), and another possible $C\ 2/m$ cell (a^A and c^A axes). The b axes for all three settings are coincident.

To accommodate the six extra molecules there are 71 Å³ extra volume (table I); the *b* and *c* directions are extended 0·45 and 0·38 Å, respectively. This expansion is possibly accounted for by packing the extra water

TABLE II. Chemical analysis and calculation of empirical cell contents of water-rich heulandite from near Stevenson, Washington

				E	O	cell contents
			$\dfrac{Pm}{M}$	$\left(=\dfrac{FPm}{M}\right)$	$\left(=\dfrac{En}{m}\right)$	adjusted
SiO₂	57·14					to 72 O's
TiO₂	n.d.					
Al₂O₃	15·55	Si	0·9509	27·19	54·38	27·23 } 35·96
Fe₂O₃	tr.	Al	0·3051	8·72	13·08	8·73
FeO	tr.	Mg	0·0020	0·06	0·06	0·06
MnO	tr.	Ca	0·1414	4·04	4·04	4·05 } 4·79
MgO	0·09	Na	0·0204	0·58	0·29	0·58
CaO	7·93	K	0·0036	0·10	0·05	0·10
SrO	n.d.	H₂O+	1·6848	48·17	(24·09)	(24·12) } 29·56
Na₂O	0·63	H₂O-	0·3796	10·85	(5·43)	(5·44)
K₂O	0·17			Σ 71·90		
H₂O+	15·18					
H₂O-	3·42					
	100·11					

tr. trace
n.d. not detected
$\dfrac{Pm}{M}$ is atomic ratio, where P is wt % of oxide x_mO_n in analysis, and M is formula weight of oxide.
E is empirical cell contents. $F =$

$VD/1·6603S$, where S is the summation of wt % in analysis, V the cell volume in Å³, and D the density. Here $F = 28·594$.
Σ Total oxygen excluding oxygen of water.
Analyst: O. von Knorring

into normally unoccupied channels more or less parallel to the *a* direction, thereby expanding the lattice in the other two directions. Because one water molecule has a volume of about 30 Å³, much of the volume of the excess water is apparently taken up in existing space of the channels.

This extra water is lost on gentle heating, probably accounting for the slight deficiency of water in the analysis. Heating to 400° C causes so much structural collapse that no consistent interplanar spacings remain for X-ray diffraction. The normal heulandites reach this state on heating to 600° C (Mumpton, 1960).

Optical properties of the water-rich heulandites are: $\alpha = 1·487$; $\beta = 1·488$, $\gamma = 1·500$, all $\pm 0·001$, $2V\gamma = 35°$ to $45°$. The refractive indices are a little lower than the normal range of heulandites with similar calcium contents: $\alpha = 1·496–1·499$, $\beta = 1·497–1·501$, $\gamma = 1·501–1·505$, $2V\gamma = 0°$ to $48°$.

Conclusions. Channels parallel to the *a* crystallographic direction

(see fig. 1), normally contain little or no water molecules, though it is now apparent that several can be held in these positions. When this occurs, the cell is larger in the b and c directions and the refractive indices are lower. Although the physico-chemical conditions permitting the excess water to be retained are unknown, it is clear that the d-spacings of various reflections and optical data as parameters related to composition must be used with even more caution.

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