

The Crystal Structure of the Zeolite Offretite, $K_{1.1}Ca_{1.1}Mg_{0.7}[Si_{12.8}Al_{5.2}O_{36}].15.2H_2O$

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The crystal structure of offretite (hexagonal, $a=13.291$, $c=7.582$ Å) from Mt. Simouise, France, has been refined in the space group $P\bar{6}m2$ to a residual of 0.108. The frame structure proposed by Bennett & Gard [*Nature, Lond.* (1967) **214**, 1005] was confirmed. It comprises alternating double and single rings of six tetrahedra centred on (0,0,0) and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ respectively, forming columns with two types of cavity, one similar to those found in cancrinite, the other in the centre of the double ring. The columns are cross-linked to enclose channels *ca.* 6.9 Å wide, parallel to *c*, and cavities similar to those in gmelinite, with 'windows' 3.6 Å diameter. Each cancrinite-type cavity contains a K^+ ion that cannot be replaced with an NH_4^+ ion at 80°C. During synthesis, the cancrinite cage probably collects round the K ion to form a precursor of erionite or offretite. A few (0.14) double rings contain a Ca ion. Most (0.82) gmelinite-type cavities contain an Mg ion coordinated to five water molecules. A feasible arrangement was deduced for the Ca ions and water molecules that occupy seven-tenths of the volume of the channels. 5.4 out of 15.2 H_2O per unit cell were not located; they are probably in random sites or are mobile. (Si, Al)–O distances suggest that most of the 5.2 Al atoms are located in the 12 tetrahedra of the double ring; this implies a high degree of local ordering, and the space group $P\bar{6}m2$ is probably an average one. Disorder comprising intergrowth with erionite is discussed as this places limits on refinement, and also constricts the channels. Consideration of the unit-cell dimensions of zeolites with frames comprising rings of six tetrahedra showed that the ratio nac^{-1} , where *n* is the number of rings in the *c*-period, can be used to indicate the presence of double rings only, single rings only, or both, in frame structures of this type.

Introduction

Offretite was discovered by Gonnard (1890, 1891) in the basalt of Mt. Simouise, Montbrison, Loire, France, where it occurred in cavities as hexagonal prisms with optically positive elongation. Hey & Fejer (1962) stated that its X-ray powder photographs were identical with those of erionite (hexagonal, $P6_3/mmc$, $a=13.25$, $c=15.10$ Å) and that the name 'erionite' (Eakle, 1898) should be discarded in favour of 'offretite', which would have clear priority. No decision was reached by the Commission on New Minerals and Mineral Names of the International Mineralogical Association on the validity of these names (*Miner. Mag.*, 1967). However, Bennett & Gard (1967) showed by single-crystal electron and X-ray diffraction that the *c*-period of offretite is half that of erionite, and that the two minerals are distinct but closely related species. Harada, Iwamoto & Kihara (1967) appear to have reached the same conclusion independently. Bennett & Gard proposed a structure for the aluminosilicate frame of offretite, which is confirmed in the present study, with space group $P\bar{6}m2$, in which rings of six (Si,Al) O_4 tetrahedra are stacked in the sequence *AABAAB* . . . , compared with *AABAAC* . . . for erionite (Staples & Gard, 1959; Kawahara & Curien, 1969), where rings *A* are centred on (0,0,*z*), *B* on $(\frac{1}{3}, \frac{2}{3}, z)$ and *C* on $(\frac{2}{3}, \frac{1}{3}, z)$ axes. Bennett & Gard (1967) and Gard & Tait (1971) found that, on electron-diffraction patterns of all the samples of synthetic 'erionite'

that they examined, the odd-*l* reflexions, if present, were elongated or streaked in the c^* direction, indicating varying degrees of disorder between the two structures. Some particles of natural offretite, but not erionite, also show stacking disorder. Mt. Simouise is the only known locality for offretite; twelve other natural specimens examined in this laboratory were fully-ordered erionite.

Sheppard & Gude (1969) have listed chemical analyses and optical properties of offretite and samples of erionite from eleven different localities. They stated that erionite has optically positive and offretite negative elongation; this confirms published optical data for erionite (e.g. Staples & Gard, 1959) but contradicts Gonnard's observation that offretite has positive elongation. Sheppard & Gude also commented on the narrow range of potassium content indicated by the analyses; all but one specimen (from Mazé, Japan; Harada *et al.*, 1967) had rather more than two K atoms in each unit cell of erionite, or double cell of offretite. They also showed that the Al:Si ratio is higher for offretite than for any of the erionite samples analysed, and that offretite contains no sodium. Published cation exchange studies (Eberley, 1964; Peterson, Helfferich & Blytas, 1965; Sherry, 1970) have shown that, although all other cations are exchangeable, a residue of at least two K^+ ions in each unit cell of erionite or Zeolite T (Breck & Acara, 1960) – a disordered synthetic erionite – cannot be replaced at temperatures below 300°C; at higher temperatures, loss of K^+ is accompanied by a reduction in Si:Al

ratio, and probably involves partial disruption of the frame.

Disordered synthetic offretite has been identified as an impurity in samples of Zeolite L (Breck & Acara, 1962; Breck & Flanigen, 1968) by Kerr, Gard, Barrer & Galabova (1970). It occurs as hexagonal prisms growing out of platy aggregates of Zeolite L. Barrer & Villiger (1969) showed that Zeolite L contains columns identical to those in offretite; evidently some columns extend from the Zeolite L into the prism of offretite and hold the two phases together. Fully ordered offretite has now been synthesized in a number of laboratories (see *e.g.* Aiello & Barrer, 1970; Gard & Tait, 1971; Whyte, Wu, Kerr & Venuto, 1971), using tetramethylammonium (TMA) hydroxide as one of the bases in the parent gel (Barrer & Denny, 1961; Rubin, 1968). It comprises elongated cylinders with rounded ends, and can be distinguished from disordered intergrowths of erionite and offretite by the complete absence of reflexions doubling the *c* spacing, or any streaks parallel to c^* , from the electron-diffraction patterns. Aiello, Barrer, Davies and Kerr (1970) found that one K^+ and one $(Me_4N)^+$ could not be exchanged for other cations in their $K_2(Me_4N)_2$ offretite. They suggested that one K^+ was locked in the double-six ring of tetrahedra, and one TMA ion in the gmelinite-type cavity (see below for definition of these cavities), while the replaceable ions were sited with K^+ in the cancrinite-type cavity and TMA^+ in the wide channel. We thought it unlikely that K^+ in a cancrinite-type cavity would be exchangeable, so (0001) projections of the electron density of a natural erionite and its NH_4^+ -exchanged form were compared. The peak height at (0,0,*z*) was unchanged, proving that the K^+ was *not* replaced by NH_4^+ .

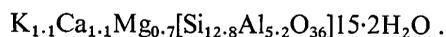
Structure determination and refinement

Offretite

The crystal used for structure analysis was a regular hexagonal prism, *ca.* 0.4 mm long and 0.12 mm wide, removed from a cavity in part of Gonnard's original specimen, BM68970, kindly provided by Dr M. H. Hey of the British Museum (Natural History). Unit-cell dimensions measured on X-ray rotation photographs (see Gard & Tait, 1971, Fig. 2, p. 491) agreed with those accurately determined by Sheppard & Gude (1969) with powder diffractometry, and their values were used as follows:

$$a = 13.291 \pm 0.002, c = 7.582 \pm 0.006 \text{ \AA}.$$

There were no systematically absent reflexions, but faint streaks parallel to c^* were present on the rotation photographs, indicating some disorder. Atomic cell contents calculated from Ingram's analysis quoted by Sheppard & Gude corresponded to



Intensity data were collected with a Hilger Automatic Linear Diffractometer using $Mo K\alpha$ radiation. Inspection of typical sets of 6 or 12 equivalent reflexions revealed no signs of trigonal symmetry, so results were averaged to give the data for 363 independent reflexions, representing the zero and six layers of the reciprocal lattice rotated around the *c* axis. As no heavy atoms were present, absorption corrections were considered unnecessary, and were not applied. An Elliott 803 computer and, later, an I.C.L. 4/50 computer were used for data reduction and refinement of the structure, with programs kindly supplied by Dr F. R. Ahmed and his collaborators of the National Research Council, Canada, and adapted by Mr J. S. Knowles of the Department of Computing, University of Aberdeen. Form factors (atomic scattering amplitudes) for Si^{2+} , O^- , K^+ , Ca^{2+} and Mg^{2+} were taken from *International Tables for X-ray Crystallography* (1962).

The frame structure for offretite proposed by Bennett & Gard (1967), with atomic coordinates adapted from those of Staples & Gard (1959) for erionite, gave a value for *R* of 0.34. This confirmed the general validity of the structure and provided a basis for refinement in the non-centrosymmetrical space group $P\bar{6}m2$. The frame can conveniently be considered in terms of the various cavities among which the cations and water molecules are distributed (see Fig. 1). The entire frame is composed of the type of cage found in cancrinite (Pauling, 1930*a*; Jarchow, 1965), each cage being joined through bridges of six oxygen atoms to two identical cages to form columns parallel to *c*. Two types of cavity are present in the columns, one in each cancrinite cage, and one in each double-six ring of twelve (Si,Al) O_4 tetrahedra; the latter is often referred to as the hexagonal prism. Each column is cross-linked to three others forming single rings of six tetrahedra, between which lie larger cavities with their axes on $(\frac{1}{3}, \frac{2}{3}, z)$, similar to, but not identical with, those in gmelinite (Fischer, 1966). There are also wide channels with their axes along $(\frac{2}{3}, \frac{1}{3}, z)$; if disorder of the erionite type is completely absent, these channels run the full length of the crystal parallel to *c*.

A three-dimensional electron density distribution slightly modified most of the atomic coordinates, and displayed a number of new peaks, the largest of which was at (0, 0, $\frac{1}{2}$); the peak height, the distance from the six O(2) frame atoms, and the cation exchange data already discussed were all in accordance with the presence of one K^+ in the centre of each cancrinite-type cavity. Other peaks at $(\frac{1}{3}, \frac{2}{3}, 0)$ and $(\frac{2}{3}, \frac{1}{3}, 0.354)$ were provisionally interpreted as Ca^{2+} and Mg^{2+} respectively, with partial occupancies estimated from the peak heights. The distances of water molecules that subsequently appeared, however, suggested that these atoms should be interchanged, and refinement later proceeded with Mg(1) in the centre of the gmelinite cavity, and Ca(1) on the axis of the wide channel.

Individual isotropic temperature factors were ini-

tially fixed at 2.0, but were later refined. Several cycles of least-squares refinement using Cruickshank's (1965) weighting scheme were alternated with three-dimensional electron density distribution and difference syntheses in order to locate new peaks. At several stages of the refinement, parameters of the K^+ and frame atoms, and sometimes also of the Mg and Ca(1), were temporarily fixed while the parameters and occupancies of the other atoms were subjected to least-squares

refinement. Minor peaks as they appeared were included one at a time as water molecules. The residual improved rather sporadically. The layer scaling was adjusted at one point after analysis of $|F_o|$, $\sin^2 \theta$ and l -index.

A persistent small peak on the axis of the cavity in the double ring eventually settled to a twofold site that was too close to the O(2) atoms for K^+ or a water molecule. It was therefore interpreted as a Ca(2) atom of 0.07 occupancy. Five water molecules coordinated

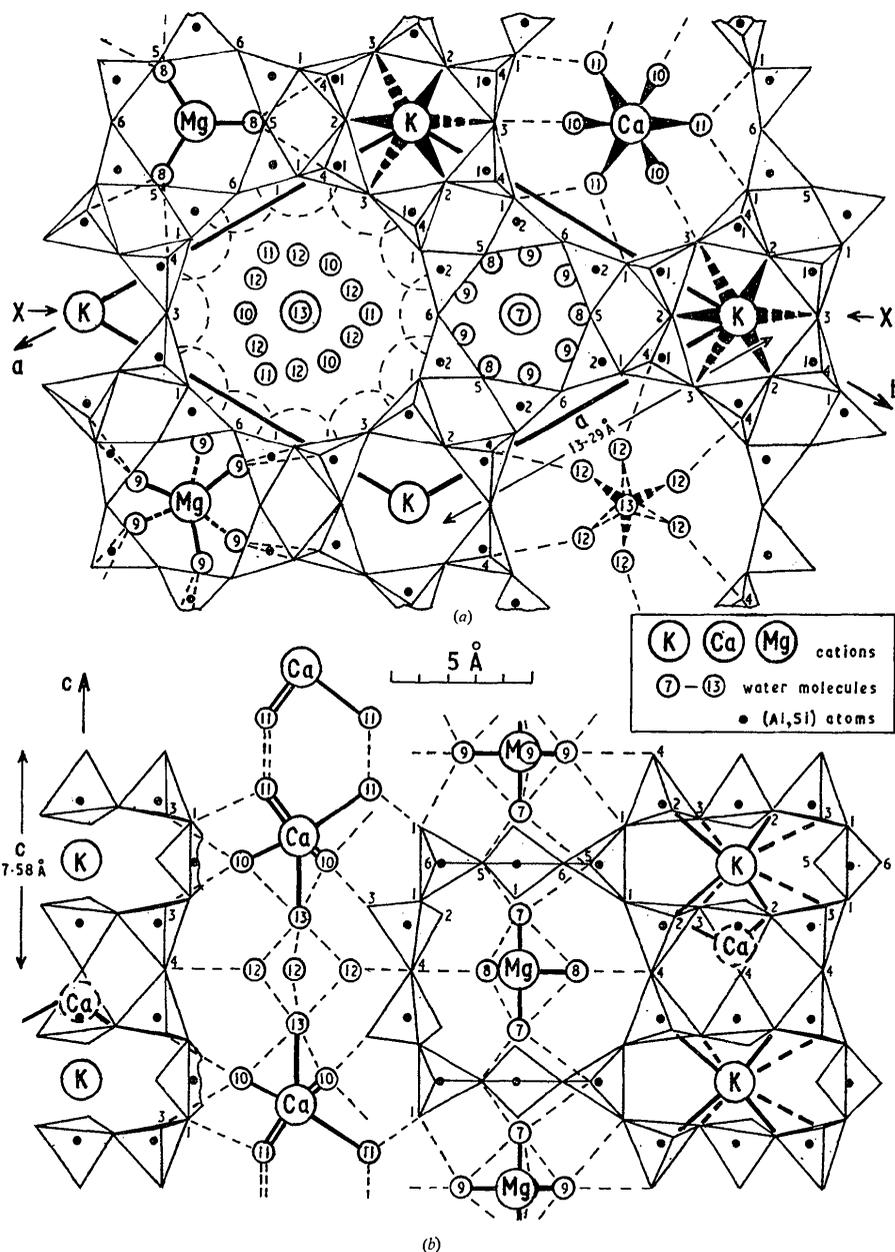


Fig. 1. Projections of the structure of offretite (a) on (0001), (b) of section X-X on (11 $\bar{2}$ 0). Each cancrinite-type cavity contains one K^+ ion. The wide channel and gmelinite-type cavity in the centre of (a) show projections of all the Fourier peaks, while other cavities show separately the structural arrangements discussed in the text. (b) shows the arrangement of Ca^{2+} ions and water molecules that apparently fills about seven tenths of the volume of the channels. Broken circles in (a) represent oxygen atoms, indicating the free space in one of the channels. Thin broken lines show possible hydrogen bonds.

to Mg in the gmelinite-type cavity at H₂O(7) and H₂O(8) established themselves early, but *R* improved distinctly with addition of the sixfold H₂O(9) site. Part of the final electron density map for the level *z*=0 in Fig. 2 shows the peaks for Mg²⁺, H₂O(8) and H₂O(9). In the wide channel, three H₂O(10) and three H₂O(11) molecules may be regarded as being octahedrally coordinated to the Ca(1) ion. Other peaks at H₂O(12) and H₂O(13) appear to overlap H₂O(11) and Ca(1) respectively, but all of these sites are only partially occupied. These overlaps necessarily apply restrictions that forbid the presence of certain atoms in adjacent sites, a factor that assisted interpretation. Refinement appeared complete at *R*=0.108, but the seven reflexions shown in Table 1(a) had $||F_o| - |F_c|| / |F_o| \geq 0.25$;

Table 1. Observed and calculated structure factors

(a) For seven (out of 363) reflexions with $||F_o| - |F_c|| / |F_o| \geq 0.25$

hk.l	F _o	F _c	F _o - F _c	ΔF/ F _o
30,1	34.33	23.28	11.05	32%
30,2	24.98	3.59	21.39	85
30,3	68.04	50.73	17.31	25
50,6	26.93	2.89	24.04	89
11,0	38.40	53.13	14.73	38
32,0	26.36	14.30	12.06	46
55,5	24.18	2.47	21.71	90

R=0.096 excluding these reflexions. All observed and calculated structure factors and phase angles are listed in Table 1(b). A difference map for the seven reflexions alone revealed no new peaks and suggested no modifications to existing ones. On a final electron density map for all reflexions, the minimum value was -4.4

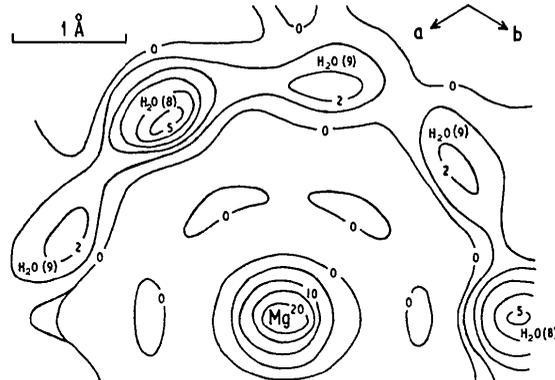


Fig. 2. Part of the electron density map of offretite for *z*=0, showing the Mg²⁺ ion at $(\frac{1}{2}, \frac{1}{2}, 0)$ and its coordinated H₂O(8) and (9) molecules (compare Figs. 1 and 4). Contours are spaced 1 e.Å⁻³, except around the Mg²⁺ peak, where they are 5 e.Å⁻³ apart. The axes shown do not intersect at the origin.

Table 1 (cont.)

(b) Observed and calculated structure factors (all × 10) and phase angles

L	FO	FC	ALPHA	L	FO	FC	ALPHA	L	FO	FC	ALPHA	L	FO	FC	ALPHA	L	FO	FC	ALPHA
3	171	153	230.25	0	1528	1450	0.37	0	960	936	4.22	0	153	166	325.84	0	237	271	132.59
1	347	294	164.05	1	70	59	241.27	1	125	115	26.00	1	114	110	149.18	1	117	107	210.04
2	372	405	165.08	2	182	271	268.56	2	88	91	212.03	2	88	91	212.03	2	140	131	38.65
3	644	643	179.89	3	674	675	171.96	3	130	84	274.09	3	304	245	111.92	3	172	222	241.16
4	615	642	111.29	4	565	575	111.29	4	184	184	35.22	4	210	211	164.31	4	126	220	112.98
5	159	170	23.20	5	311	301	347.26	5	311	301	347.26	5	114	142	210.03	5	100	156	172.54
6	230	256	5.39	6	173	143	330.80	6	173	143	330.80	6	173	143	330.80	6	152	158	76.80
7	105	101	45.51	7	105	101	45.51	7	105	101	45.51	7	105	101	45.51	7	105	101	45.51
8	177	165	144.62	8	177	165	144.62	8	177	165	144.62	8	177	165	144.62	8	177	165	144.62
9	560	627	19.81	9	560	627	19.81	9	560	627	19.81	9	560	627	19.81	9	560	627	19.81
10	398	274	40.44	10	398	274	40.44	10	398	274	40.44	10	398	274	40.44	10	398	274	40.44
11	408	384	91.01	11	408	384	91.01	11	408	384	91.01	11	408	384	91.01	11	408	384	91.01
12	205	175	45.51	12	205	175	45.51	12	205	175	45.51	12	205	175	45.51	12	205	175	45.51
13	124	139	112.54	13	124	139	112.54	13	124	139	112.54	13	124	139	112.54	13	124	139	112.54
14	207	261	134.09	14	207	261	134.09	14	207	261	134.09	14	207	261	134.09	14	207	261	134.09
15	410	74	9.95	15	410	74	9.95	15	410	74	9.95	15	410	74	9.95	15	410	74	9.95
16	331	114	118.00	16	331	114	118.00	16	331	114	118.00	16	331	114	118.00	16	331	114	118.00
17	109	9	142.44	17	109	9	142.44	17	109	9	142.44	17	109	9	142.44	17	109	9	142.44
18	285	237	159.65	18	285	237	159.65	18	285	237	159.65	18	285	237	159.65	18	285	237	159.65
19	103	111	324.95	19	103	111	324.95	19	103	111	324.95	19	103	111	324.95	19	103	111	324.95
20	430	385	198.40	20	430	385	198.40	20	430	385	198.40	20	430	385	198.40	20	430	385	198.40
21	537	484	203.49	21	537	484	203.49	21	537	484	203.49	21	537	484	203.49	21	537	484	203.49
22	761	788	250.98	22	761	788	250.98	22	761	788	250.98	22	761	788	250.98	22	761	788	250.98
23	286	267	255.89	23	286	267	255.89	23	286	267	255.89	23	286	267	255.89	23	286	267	255.89
24	81	90	152.01	24	81	90	152.01	24	81	90	152.01	24	81	90	152.01	24	81	90	152.01
25	503	535	165.51	25	503	535	165.51	25	503	535	165.51	25	503	535	165.51	25	503	535	165.51
26	215	202	30.98	26	215	202	30.98	26	215	202	30.98	26	215	202	30.98	26	215	202	30.98
27	7	8	111.51	27	7	8	111.51	27	7	8	111.51	27	7	8	111.51	27	7	8	111.51
28	151	169	84.07	28	151	169	84.07	28	151	169	84.07	28	151	169	84.07	28	151	169	84.07
29	477	490	177.20	29	477	490	177.20	29	477	490	177.20	29	477	490	177.20	29	477	490	177.20
30	116	114	283.11	30	116	114	283.11	30	116	114	283.11	30	116	114	283.11	30	116	114	283.11
31	65	52	178.03	31	65	52	178.03	31	65	52	178.03	31	65	52	178.03	31	65	52	178.03
32	228	243	12.21	32	228	243	12.21	32	228	243	12.21	32	228	243	12.21	32	228	243	12.21
33	113	91	207.54	33	113	91	207.54	33	113	91	207.54	33	113	91	207.54	33	113	91	207.54
34	240	256	350.07	34	240	256	350.07	34	240	256	350.07	34	240	256	350.07	34	240	256	350.07
35	111	121	10.87	35	111	121	10.87	35	111	121	10.87	35	111	121	10.87	35	111	121	10.87
36	108	162	209.81	36	108	162	209.81	36	108	162	209.81	36	108	162	209.81	36	108	162	209.81
37	409	427	58.98	37	409	427	58.98	37	409	427	58.98	37	409	427	58.98	37	409	427	58.98
38	82	127	10.36	38	82	127	10.36	38	82	127	10.36	38	82	127	10.36	38	82	127	10.36
39	175	184	279.88	39	175	184	279.88	39	175	184	279.88	39	175	184	279.88	39	175	184	279.88
40	74	118	267.65	40	74	118	267.65	40	74	118	267.65	40	74	118	267.65	40	74	118	267.65
41	409	404	190.89	41	409	404	190.89	41	409	404	190.89	41	409	404	190.89	41	409	404	190.89
42	151	169	84.07	42	151	169	84.07	42	151	169	84.07	42	151	169	84.07	42	151	169	84.07
43	477	490	177.20	43	477	490	177.20	43	477	490	177.20	43	477	490	177.20	43	477	490	177.20
44	116	114	283.11	44	116	114	283.11	44	116	114	283.11	44	116	114	283.11	44	116	114	283.11
45	65	52	178.03	45	65	52	178.03	45	65	52	178.03	45	65	52	178.03	45	65	52	178.03
46	228	243	12.21	46	228	243	12.21	46	228	243	12.21	46	228	243	12.21	46	228	243	12.21
47	113	91	207.54	47	113	91	207.54	47	113	91	207.54	47	113	91	207.54	47	113	91	207.54
48	240	256	350.07	48	240	256	350.07	48	240	256	350.07	48	240	256	350.07	48	240	256	350.07
49	111	121	10.87	49	111	121	10.87	49	111	121	10.87	49	111	121	10.87	49	111	121	10.87
50	108	162	209.81	50	108	162	209.81	50	108	162	209.81	50	108	162	209.81	50	108	162	209.81
51	409	427	58.98	51	409	427	58.98	51	409	427	58.98	51	409	427	58.98	51	409	427	58.98
52	82	127	10.36	52	82	127	10.36	52	82	127	10.36	52	82	127	10.36	52	82	127	10.36
53	175	184	279.88	53	175	184	279.88	53	175	184	279.88	53	175	184	279.88	53	175	184	279.88
54	74	118	267.65	54	74	118	267.65	54	74	118	267.65	54	74	118	267.65	54	74	118	267.65
55	409	404	19																

$e.\text{\AA}^{-3}$, while minimum and maximum values on a difference map were -1.7 and $+1.7 e.\text{\AA}^{-3}$, respectively.

NH_4 -erionite

As only a few prisms of offretite were available, erionite was used in this experiment. Intensity data have been collected for a crystal of erionite from Maz , Niigata Pref., Japan (Harada *et al.*, 1967), kindly provided by Dr Harada, and a structure analysis is in progress. Preliminary three-dimensional Fourier synthesis has confirmed the frame and indicated one K^+

in each cancrinite-type cavity, as for offretite; a very small peak was also present inside the double ring. Some crystals of this material were refluxed with saturated NH_4NO_3 solution at 80°C for 14 days, then washed thoroughly and dried. $hk.0$ intensities were estimated visually on zero-layer Weissenberg photographs using $\text{Cu K}\alpha$ radiation. (0001) projections of the natural and NH_4 -exchanged erionites are compared in Fig. 3. They show clearly that the peaks due to the frame atoms and the K^+ are virtually identical, proving that this K^+ cannot be replaced with NH_4^+ at 80°C .

Description of the structure

Atomic coordinates, isotropic temperature factors and occupancies are listed in Table 2, and interatomic distances in Tables 3 and 4. Projections on (0001) and (1120), in Fig. 1, show the disposition of cations and water molecules in the various cavities in the frame. Each cancrinite-type cavity contains one K^+ , coordinated to six O(2) atoms at 2.96\AA disposed at the corners of a trigonal prism, and six O(3) atoms at 3.33\AA , similarly arranged. This K^+ is locked in the cavity and is not exchangeable. There are two Ca(2) sites inside the double-six ring, 2.51\AA from three O(2) atoms and 2.79\AA from the K^+ ion. The rather close approach of the K and Ca(2) ions is apparently permitted by the screening action of the six O(2) and O(3) atoms. The Ca(2) sites are separated by 2.00\AA , too close for occupation of both sites in the same cavity, so the effective occupancy is doubled to 0.14 on a single site in each cavity.

The centre of the gmelinite-type cavity has Mg^{2+} with fairly high occupancy, 0.82, coordinated to five water molecules, comprising two $\text{H}_2\text{O}(7)$ on the trigonal axis, and a planar triad that can take up three alternative positions on the $\text{H}_2\text{O}(8)$ and sixfold $\text{H}_2\text{O}(9)$ sites, re-

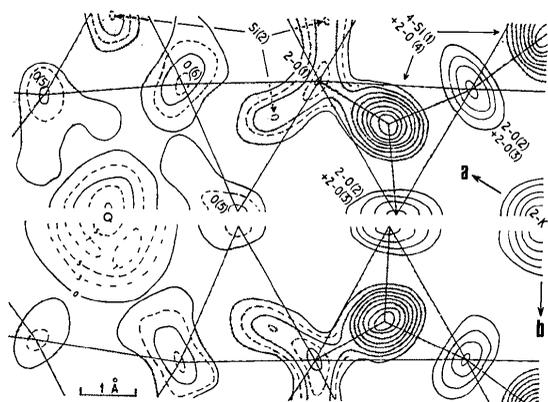


Fig. 3. (0001) electron density projections of (a) erionite from Maz , Japan, and (b) its NH_4 -exchanged form. Contours in solid lines are spaced $10 e.\text{\AA}^{-3}$; those in broken lines are spaced $5 e.\text{\AA}^{-3}$, except where otherwise indicated. Negative contours (minimum $-18 e.\text{\AA}^{-3}$) are not shown. The number and type of all atoms contributing to each peak are indicated. The only significant difference is the reduction of electron density around point Q ($\frac{2}{3}, \frac{1}{3}, z$), the axis of the large cavity, where the cations have been replaced with NH_4^+ . The density at the origin is unchanged, however, showing that the K^+ ions in the cancrinite-type cavities have not been replaced.

Table 2. Fractional atomic coordinates, isotropic temperature factors ($B=8\pi^2u$ in \AA^2) and fractional occupation factors, with *e.s.d.*'s on the last digit in parentheses

	Symmetry*	x/a	y/b	z/c	B	Occupancy
K	1(b)	0	0	$\frac{1}{2}$	2.2 (1)	1
Ca(1)	2(i)	$\frac{2}{3}$	$\frac{1}{3}$	0.377 (5)	3.3 (2)	0.39 (3)
Ca(2)	2(g)	0	0	0.13 (1)	4.0 (3.0)	0.07 (3)
Mg	1(c)	$\frac{1}{3}$	$\frac{2}{3}$	0	1.8 (2)	0.82 (6)
Si(1)	12(o)	0.0027 (5)	0.2342 (4)	0.2085 (7)	0.88 (3)	1
Si(2)	6(m)	0.0930 (6)	0.4251 (5)	$\frac{1}{2}$	0.68 (3)	1
O(1)	12(o)	0.029 (1)	0.351 (1)	0.329 (2)	2.29 (9)	1
O(2)	6(n)	0.101 (2)	0.202 (2)	0.257 (4)	2.2 (1)	1
O(3)	6(n)	0.255 (2)	0.127 (3)	0.293 (4)	3.3 (2)	1
O(4)	6(l)	0.012 (2)	0.267 (2)	0	1.5 (1)	1
O(5)	3(k)	0.230 (3)	0.460 (3)	$\frac{1}{2}$	1.5 (2)	1
O(6)	3(k)	0.075 (2)	0.537 (2)	$\frac{1}{2}$	2.0 (2)	1
$\text{H}_2\text{O}(7)$	2(h)	$\frac{1}{3}$	$\frac{2}{3}$	0.261 (5)	1.7 (2)	0.90 (8)
$\text{H}_2\text{O}(8)$	3(j)	0.243 (6)	0.486 (6)	0	1.7 (4)	0.34 (6)
$\text{H}_2\text{O}(9)$	6(l)	0.16 (1)	0.52 (1)	0	2.6 (8)	0.14 (5)
$\text{H}_2\text{O}(10)$	3(k)	0.485 (6)	0.242 (8)	$\frac{1}{2}$	4.0 (5)	0.58 (8)
$\text{H}_2\text{O}(11)$	6(n)	0.562 (7)	0.438 (7)	0.172 (9)	4.7 (5)	0.47 (5)
$\text{H}_2\text{O}(12)$	6(l)	0.53 (3)	0.35 (3)	0	3.0 (1.0)	0.17 (4)
$\text{H}_2\text{O}(13)$	2(i)	$\frac{2}{3}$	$\frac{1}{3}$	0.24 (2)	1.6 (5)	0.30 (8)

* Number of equivalent positions and Wyckoff symbol for $P\bar{6}m2$.

Table 3. *Interatomic distances and angles, with e.s.d.'s in parentheses*

Distances of cations to frame oxygens and water molecules, and of possible H-bonds, are given. * indicates distances too short for simultaneous occupation of both sites; † indicates distances too long for H-bonding. Tetrahedral (Si, Al)-O and O-O distances are given in Table 4.

K-O(2)	2.96 (3) Å
K-O(3)	3.33 (3)
K-Ca(2)	2.79 (11)
Ca(2)-O(2)	2.51 (5)
Ca(2)-O(3)	3.17 (5)
Ca(2)-Ca(2)	2.00 (15)
Mg-H ₂ O(7)	1.98 (4)
Mg-H ₂ O(8)	2.08 (7)
Mg-H ₂ O(9)	2.14 (17)
H ₂ O(7)-H ₂ O(8)	2.88 (5)
H ₂ O(7)-H ₂ O(9)	2.92 (13)
H ₂ O(8)-H ₂ O(9)	1.43 (21)*
H ₂ O(8)-H ₂ O(9)	2.73 (17)*
H ₂ O(9)-H ₂ O(9)	2.72 (27)*
H ₂ O(9)-H ₂ O(9)	1.50 (22)*
H ₂ O(7)-O(5)	2.99 (4)
H ₂ O(7)-O(6)	3.48 (3)†
H ₂ O(8)-O(4)	2.99 (8)
H ₂ O(9)-O(1)	3.24 (10)
H ₂ O(9)-O(4)	2.95 (15)
Ca(1)-Ca(1)	1.86 (5)*
Ca(1)-H ₂ O(10)	2.29 (9)
Ca(1)-H ₂ O(11)	2.87 (9)
Ca(1)-H ₂ O(13)	1.02 (13)*
Ca(1)-H ₂ O(13)	2.89 (13)
Ca(1)-H ₂ O(12)	3.47 (27)
H ₂ O(11)-H ₂ O(11)	2.61 (11)
H ₂ O(13)-H ₂ O(12)	2.69 (36)
H ₂ O(13)-H ₂ O(10)	2.86 (11)
H ₂ O(13)-H ₂ O(11)	2.47 (10)*
H ₂ O(12)-H ₂ O(12)	3.39 (63)†
H ₂ O(11)-H ₂ O(10)	3.37 (10)†
H ₂ O(12)-H ₂ O(11)	1.66 (25)*
H ₂ O(12)-H ₂ O(11)	3.50 (40)†
H ₂ O(10)-O(3)	3.08 (9)
H ₂ O(10)-O(1)	3.40 (9)†
H ₂ O(11)-O(1)	3.03 (9)
H ₂ O(11)-O(6)	3.38 (9)†
H ₂ O(12)-O(4)	3.22 (47)

Si-O-(Si, Al) and O-(Si, Al)-O angles, with e.s.d.'s in parentheses.

Si(1)-O(2)-Si(1)	141.7 (1.9)°
Si(1)-O(3)-Si(1)	132.5 (2.0)
Si(1)-O(4)-Si(1)	151.7 (1.4)
Si(1)-O(1)-Si(2)	144.1 (1.0)
Si(2)-O(5)-Si(2)	151.6 (2.2)
Si(2)-O(6)-Si(2)	165.4 (1.5)
O(1)-Si(1)-O(2)	107.7 (1.1)
O(1)-Si(1)-O(3)	102.5 (1.2)
O(1)-Si(1)-O(4)	108.9 (0.9)
O(2)-Si(1)-O(3)	107.8 (1.5)
O(2)-Si(1)-O(4)	109.8 (1.2)
O(3)-Si(1)-O(4)	119.4 (1.3)
O(1)-Si(2)-O(1)	108.9 (1.1)
O(1)-Si(2)-O(5)	110.7 (1.3)
O(1)-Si(2)-O(6)	106.6 (1.0)
O(5)-Si(2)-O(6)	113.1 (1.4)

Table 4. *Tetrahedral (Si, Al)-O and O-O distances for offretite (this investigation, with e.s.d.'s on the last digit in parentheses), erionite (Kawahara & Curien, 1969) and Zeolite L (Barrer & Villiger, 1969), compared with distances assuming that all Al atoms are in Si(1) sites, i.e. in the double-six rings*

	Offretite	Erionite	Zeolite L
Si(1)-O(1)	1.69 (1) Å	1.59 Å	1.74 Å
Si(1)-O(2)	1.61 (3)	1.61	1.62
Si(1)-O(3)	1.72 (3)	1.68	1.64
Si(1)-O(4)	1.63 (1)	1.60	1.70
Mean Si(1)-O (Si _{0.63} Al _{0.37})-O*†	1.66	1.66	1.67 ₅ 1.66
Si(2)-O(1)†	1.59 (1)	1.65	1.53
Si(2)-O(5)	1.64 (4)	1.61	1.64
Si(2)-O(6)	1.63 (3)	1.59	1.72
Mean Si(2)-O†	1.61	1.62 ₅	1.60
Si-O*	1.61	1.61	1.61
Overall mean (Si, Al)-O† (Si _{0.75} Al _{0.25})-O*†	1.64 ₅ 1.64 ₅	1.62 1.64 ₅	1.65 1.64 ₅
	Offretite	Zeolite L	
O(1)-O(2)	2.66 (3) Å	2.71 Å	
O(1)-O(3)	2.66 (4)	2.76	
O(1)-O(4)	2.70 (2)	2.67	
O(2)-O(3)	2.69 (4)	2.68	
O(2)-O(4)	2.65 (3)	2.81	
O(3)-O(4)	2.89 (4)	2.76	
Mean O-O for Si(1)O ₄	2.71	2.73	
O-O for (Si _{0.63} Al _{0.37})O ₄ *	2.71	2.71	
O(1)-O(1)	2.59 (2)	2.55	
O(1)-O(5)†	2.66 (4)	2.61	
O(1)-O(6)†	2.58 (2)	2.64	
O(5)-O(6)	2.72 (5)	2.65	
Mean O-O for Si(2)O ₄ †	2.63	2.62	
O-O for SiO ₄ *	2.63	2.63	

* Calculated from values given by Smith & Bailey (1963) for mean (Si, Al)-O distances in frame structures.

† Two Si(2)-O(1) distances are included for calculation of the mean Si(2)-O, two each of O(1)-O(5) and O(1)-O(6) distances for the mean O-O distance in Si(2)O₄, and two each of the Si(1)-O distances for the overall mean (Si, Al)-O distance.

‡ The overall mean (Si, Al)-O distance is in accordance with the presence of 4.5 Al atoms (*i.e.* 25%) in the 18 tetrahedra; if restricted to the 12 Si(1) sites, 4.5 Al atoms would occupy 37% of these sites.

lated by rotations of *ca.* 40° around the Mg ion. Elongations of the peaks on the electron density map in Fig. 2 suggest that this triad has some rotary oscillation. Six very weak peaks suggest possible H₂O sites in cavities from which Mg is absent. H₂O(7) has a higher occupancy (0.90) than the Mg ion, but the sum of occupancies of each H₂O of the triad is only 0.61. Fig. 4(a) is a stereoscopic drawing of the oxygen atoms enclosing half of a gmelinite-type cage, with the Mg and the water triad in the preferred H₂O(8) position; one H₂O(9) site is shown unshaded. This gives an indication of the free space inside the cavity. The H₂O(8) and H₂O(9) sites appear to be equilibrium positions decided by hydrogen bonding to frame oxygen atoms. Obviously, H₂O(9) is the most mobile of the contents; escape of H₂O(8) through a window must be preceded

by a shift to an H₂O(9) site. The H₂O(7) is more firmly bonded to three O(5) atoms, and remains in most of the cavities even in the absence of Mg; loss of H₂O(7) must in any case be preceded by movement of the Mg ion.

As might be expected, the contents of the wide channel are not as clear as those of the smaller cavities, but some structural arrangements are strongly indicated. The two adjacent Ca(1) sites across the H₂O(10) triad are too close, 1.86 Å, for simultaneous occupation in the same unit cell, so effective occupancy would be doubled to 0.78 for the available sites. Ca(1) is octahedrally coordinated to three H₂O(10) and three H₂O(11); the H₂O(10)–Ca(1) distance of 2.29 Å is rather short, but the coordinates were confirmed in spite of attempts to vary them. This short distance is in accordance with OH[−] ions rather than H₂O molecules, but the chemical analysis does not support this interpretation, as the number of Al atoms already exceeds the total positive charge due to non-tetrahedral cations. Six H₂O(11) in adjacent octahedra could associate by hydrogen bonding to form a trigonal prism; the high occupancy suggests that this prism could exist independently. A plausible grouping of the remaining water molecules is shown in Fig. 1(b). Only H₂O(13) lies within H-bonding distance of H₂O(12) without overlapping, suggesting the presence of the trigonal bipyramid shown; the base comprising three H₂O(12) can take two positions related by rotation of *ca.* 50°, doubling the effective occupancy to 0.34. This bipyramid could only occur in the absence of Ca(1) from a volume equivalent to a whole unit cell; this is quite feasible, as six out of ten unit cells must be devoid of Ca. H₂O(13) is also within bonding distance of a Ca(1) site and its three associated H₂O(10) molecules, increasing the coordination of this Ca(1) to seven H₂O.

On this basis, out of ten unit cells, about three would be occupied by the trigonal bipyramid, and four by

two Ca octahedra linked through the trigonal prism H₂O(11). Many of the water molecules are within H-bonding distance of frame oxygen atoms; some such bonds are shown in Fig. 1. These groupings are tentative suggestions, and some differences might be implied if the structure analysis were continued in a space group of lower symmetry.

Atomic cell contents detected in this structure analysis amount to $K_{1.0}Ca_{0.92}Mg_{0.82}(Si,Al)_{18}O_{36} \cdot 9.8H_2O$. The equivalent number of monovalent cations outside the tetrahedra is 4.5, close to that of 4.7 for Ingram's analysis, although the proportions differ slightly. The crystal used in this analysis may not be chemically identical with that of Ingram's sample. 5.4 out of 15.2 water molecules have not been detected. They are probably mobile or randomly distributed in the sections of the wide channels occupying the three out of ten unit cells devoid of the structures shown in Fig. 1(b), or in the gmelinite-type cavities from which Mg is absent. The streaking parallel to *c**, already mentioned, indicates some stacking disorder that disturbs the *AABAAB*... sequence, introducing irregularity of the water sites at these points. Any substitution of the larger K ions for Ca(1), or Ca for Mg, to correspond more closely to the chemical analysis, would also cause some disorder.

Some indication of the sites of the tetrahedral Al atoms is given by consideration of the (Si,Al)–O distances listed in Table 4. Smith & Bailey (1963) gave values of 1.61 Å for Si–O and 1.75 Å for Al–O distances, and found that the proportion of Al atoms in a frame structure could be deduced within ± 5% from the mean (Si,Al)–O distance. For offretite, the overall mean distance is 1.645 Å, which corresponds to 4.5 Al out of 18 (Si,Al) atoms, rather less than that indicated by the chemical analysis, but very close to the equivalent number of non-tetrahedral cations. The mean Si(2)–O distance is almost exactly 1.61 Å, while the mean Si(1)–O dis-

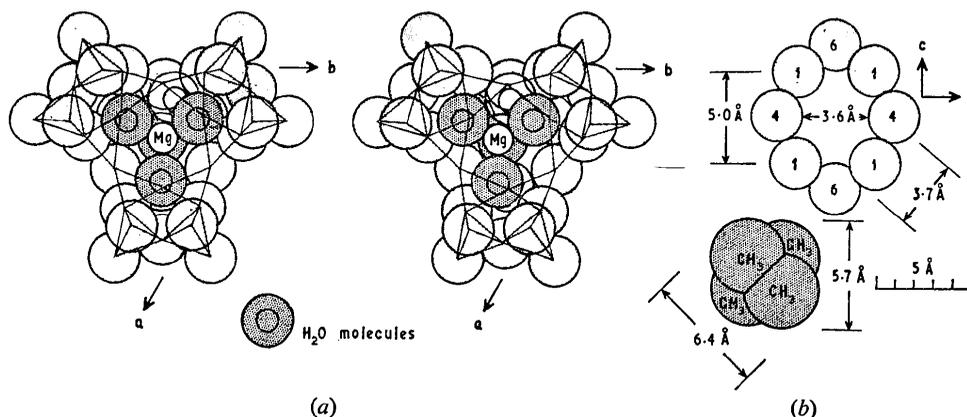


Fig. 4. (a) Stereoscopic drawing of half of a gmelinite-type cage in offretite, containing an Mg²⁺ ion coordinated to H₂O(7) below (the other one above is omitted) and to three H₂O(8) molecules. Loss of an H₂O(8) through a window must be preceded by movement to an H₂O(9) site, one of which is shown unshaded. (b) Oxygen atoms bordering a window in a gmelinite-type cage, and (below left) a tetramethylammonium (TMA) cation, with their critical dimensions. The TMA could occupy the gmelinite cavity during growth of the crystal, but it is too large to pass through the window.

tance of 1.661 Å corresponds to the presence of 4.4 Al atoms in the 12 Si(1) sites of the double ring. Most, if not all, of the Al atoms, therefore, occupy Si(1) sites. Application of Loewenstein's (1954) rule that Al atoms do not occupy adjacent tetrahedra in aluminosilicate frame structures would then imply a high degree of local ordering. The possible effects of such ordering are discussed below.

Discussion

Disorder indicated by streaks parallel to c^* in diffraction patterns could be due to one or more of several factors. A single fault equivalent to rotation of 60° around c would change the *ABAAB*... sequence to *AABAABAACAAC*..., with interchange of the axes of the wide channels and gmelinite-type cages. A double fault would introduce a thin layer of erionite into the structure, and change the sequence to *AABAABAACAABAAB*.... Barrer & Villiger (1969) have suggested the possibility of a different type of disorder, with the sequence *ABAABBABBA*..., in which the double and single rings are interchanged, amounting to inclusion of a unit cell of gmelinite. The first two types of break in the regular sequence would restrict the channels with 'windows' similar to those in erionite, *ca.* $4.7 \times 3.5 \text{ \AA}$, but the last named would apply no such restriction. Faults of these three types extend in the (0001) plane right across the crystal; a low concentration of faults should therefore be sufficient to register as streaks on electron-diffraction patterns, as the effects would reinforce each other across the entire crystal. On the other hand, local ordering of Al atoms in Si(1) sites, and of cations and water molecules, although potentially capable of producing multiple unit cells, would not usually extend far in any direction. They would merely generate background fog rather than coherent diffraction effects. The streaks parallel to c^* are therefore predominantly due to irregularities in the stacking sequence of the frame. To some extent, they will affect the observed structure factors and increase the residual R .

If the Al atoms were locally ordered, the coordinates for some of the frame oxygens would merely indicate average positions. Lack of extended Al ordering and stacking faults are both equivalent to twinning of small domains of lower symmetry. The space group $P\bar{6}m2$ is therefore probably an average one, which might explain the poor correlation between $|F_o|$ and $|F_c|$ for the seven reflexions listed in Table 1. Ideally, the analysis should be continued in a space group of lower symmetry, but to do so would require collection of intensity data from a crystal exhibiting trigonal symmetry. In the somewhat similar case of ettringite, Moore & Taylor (1970) were able to find a trigonal crystal and achieve a more complete structure analysis. The chances of finding a suitable crystal of such a rare mineral as offretite seem remote. In spite of these limitations, however, the present analysis has revealed a number of interesting features.

This study of offretite, that of Kawahara & Curien (1969) on erionite, the comparison of erionite and NH_4 -erionite described above, and the published cation exchange data already mentioned, all indicate that each cancrinite-type cavity contains one K ion that cannot be removed or replaced without disrupting the frame. This is hardly surprising, as the 'window' between the cavity and the channel has a minimum free diameter of only 0.44 Å. This explains the narrow range of K content in erionite and offretite noted by Sheppard & Gude (1969, Fig. 2, p. 879), as there is a minimum value independent of subsequent changes in cation environment. The Mg content is higher than that of all the erionites quoted by the same authors; this may be due to selective migration of Mg and its coordinated water to the gmelinite-type cavity.

Either a TMA or a K ion appears to be an essential ingredient of gels from which offretite, erionite or their intergrowths crystallize (see *e.g.* Breck & Acara, 1960; Aiello & Barrer, 1970). There is a strong possibility, therefore, that in the absence of TMA ions each cancrinite cage 'collects' around the K ion as a precursor to crystallization, and the frame is subsequently built up by condensation of these cancrinite cages. The strong attraction between the K^+ ion and those oxygen atoms that are bonded to a tetrahedral Al atom (because of their negative charge) would favour their taking up O(2) and O(3) sites, nearest the K ion. This would explain the concentration of Al atoms in the double-six ring, as the single rings have no atoms in O(2) or O(3) sites. Table 4 shows that Zeolite L, which has columns identical to those in offretite, also appears to have the Al atoms concentrated in the double-six ring, but that Kawahara & Curien's analysis of erionite did not reveal any signs of differentiation between sizes of the tetrahedra.

Bennett & Gard predicted that a fully-ordered synthetic offretite should be capable of sorbing larger molecules than would erionite. Aiello *et al.* (1971) and Whyte, Wu, Kerr & Venuto (1971) have confirmed this prediction by showing that their synthetic H-offretites can sorb cyclohexane, with a critical dimension of 6.0 Å, *m*-xylene (7.1 Å), but not 1,3,5-trimethylbenzene (8.3 Å). Comparison of the scale drawings in Fig. 4 of the gmelinite-type cage, one of its windows, and the TMA ion (assuming a C-N distance of 1.47 Å and van der Waals radius of 2.0 Å for the methyl group) supports the assumption of Aiello *et al.* that a TMA ion could occupy a gmelinite-type cavity but not escape from it without decomposition. The Fourier maps in Fig. 2, however, prove that the exchangeable K ion cannot be sited in the cancrinite-type cavity. The only site permitted for this K ion by spatial considerations appears to be near the window of a gmelinite-type cage, where it would be screened from the TMA ion in that cage by the frame oxygen atoms, and presumably from the other TMA ion by some of the water molecules present in each unit cell.

Robson, Hamner & Arey (1971) have shown that,

because of their longer cavities, some disordered synthetic 'erionites' are superior to the natural mineral as selective cracking catalysts for straight-chain paraffins. Assessment of the nature of these synthetic intergrowths is technically important. X-ray powder diffraction tends to underestimate the proportion of erionite because of gross line broadening, and more direct information can be obtained by inspection of electron-diffraction patterns of single particles. Some examples and interpretations have been given by Gard & Tait (1971) and Gard (1971). Attempts are now being made to develop a satisfactory quantitative procedure.

It is interesting to compare the unit cell of offretite with those of other zeolites with frames comprising rings of six (Si,Al)O₄ tetrahedra stacked in various sequences. Table 5 lists some published data, including those for the two erionites with the highest and lowest Si:Al ratios quoted by Sheppard & Gude (1969). The ratios nac^{-1} fall into three distinct groups, depending on the presence of single rings, double rings, or both. There is a simple explanation for these groupings. Where single rings only are present, one edge of each tetrahedron is vertical, or nearly so, and the c -period is a multiple of the length of this edge. In the double rings, this edge is inclined, and the base of each tetrahedron is more nearly normal to the c axis, reducing the c period and increasing the a -axial length. In idealized structures of regular tetrahedra, nac^{-1} can readily be shown to be 4.73 for single rings alone, and ca. 5.5 for double rings alone with one tetrahedral edge inclined at 21° to the c axis. Assuming a similar orientation for tetrahedra in the double rings of the erionite group, the idealized value of nac^{-1} would be

5.21, close to the actual values. In spite of the difference in Si:Al ratios, the two erionites have the same value, 5.28, for nac^{-1} . The structures of the zeolites quoted differ considerably from the idealized arrangements assumed here, but nac^{-1} is nearly constant within each group, suggesting that this ratio could be used to give a reliable indication of the presence of double and single rings of six tetrahedra in similar structures.

Determination of the structure of gmelinite appears to have presented Fischer (1966) with problems similar to those encountered during this study of offretite. Rotation photographs of gmelinite showed streaks parallel to c^* , indicating intergrowth with chabazite; this seems to be one of the factors that limited the analysis to a residual of 0.17. The contents of the wide channel and the other cavities are quite different in the two zeolites, in spite of strong resemblances between the frame structures. In gmelinite, two cations are located on the axis of the double ring of tetrahedra, near the planes of the O(2) atoms, but the 'gmelinite-type' cavity and the wide channel appear to be devoid of cations. Structure analysis of an Mg-exchanged gmelinite would be interesting, as it would show whether an Mg ion would prefer the same site as it occupies in offretite, with water molecules coordinated in a similar manner.

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Table 5. Relations between unit cells of zeolites with frames comprising rings of six (Si,Al)O₄ tetrahedra stacked in various sequences

Zeolite	Stacking sequence (1)	n (2)	Ring types (3)	Hexagonal		cn^{-1} (Å)	nac^{-1}
				a (Å)	c (Å)		
Cancrinite (4)	BC	2	S	12.72	5.19	2.59	4.91
Sodalite (5)	ABC	3	S	12.53	7.68	2.56	4.90
Offretite (6)	AAB	3	D+S	13.291	7.582	2.53	5.26
Erionite (7)	AABAAC	6	D+S	13.25	15.10	2.52	5.28
Erionite (8)	AABAAC	6	D+S	13.214	15.041	2.51	5.28
Levyne (9)	AABCCABBC	9	D+S	13.32	22.51	2.50	5.33
Gmelinite (10)	BBCC	4	D	13.75	10.05	2.51	5.47
Chabazite (11)	AABBCC	6	D	13.78	15.03	2.51	5.50

- (1) Sequence of rings of six tetrahedra in c direction. A, B, C , indicate centre of ring on $(0, 0, z)$, $(\frac{1}{3}, \frac{2}{3}, z)$, $(\frac{2}{3}, \frac{1}{3}, z)$ respectively.
- (2) n = number of rings of six tetrahedra in each c period.
- (3) S = single rings only; D = double rings only; D + S = equal numbers of double and single rings.
- (4) Pauling (1930a); Jarchow (1965).
- (5) Pauling (1930b); Shishakova & Dubinin (1965); Löns & Schulz (1967). Cubic, $a = 8.87$ Å; the hexagonal dimensions are for the equivalent rhombohedral cell with c_{hex} parallel to $[111]_{\text{cub}}$.
- (6) Sheppard & Gude (1969).
- (7) From Durkee, Oregon; Staples & Gard (1959): low Si:Al.
- (8) From Tecopa, California; Sheppard & Gude (1969): high Si:Al.
- (9) Barrer & Kerr (1959).
- (10) Fischer (1966).
- (11) Dent & Smith (1958); Smith, Rinaldi & Glasser (1963).

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