

MINERALOGICAL NOTES

SYNTHETIC ZEOLITES RELATED TO FERRIERITE AND YUGAWARALITE

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A re-examination of the x -ray powder patterns of two recently synthesised, but unidentified, strontium zeolites (Barrer and Marshall, 1964) has revealed similarities between these species and two rare natural zeolites. The zeolite Sr-D is very closely related to the natural mineral ferrierite reported by Graham (1918) and Staples (1955), whilst Sr-Q has some similarity to yugawaralite (Sakurai and Hayashi, 1952).

Sr-D. This zeolite was formed under hydrothermal conditions from silica-rich gels at temperatures between 340° and 440° C. (Barrer and Marshall, 1964). Several crystal habits were observed, one of which was similar to that described by Graham (1918) for ferrierite. The synthetic and natural species both lost zeolitic water in a similar fashion. The total loss on ignition was 11.2% for Sr-D, compared with 13.05% for ferrierite, and a theoretical value of 11.8% for a pure strontium form. The formula of the natural mineral is given as $(\text{Na}, \text{K})_4\text{Mg}_2(\text{Si}_{30}\text{Al}_6)\text{O}_{72}(\text{OH})_2 \cdot 18\text{H}_2\text{O}$. In a comparison of the natural and synthetic minerals it should be noted that there was no magnesium in the synthetic zeolite, and that the only cation present was strontium. The formation of Sr-D from aqueous gels of composition $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7-9\text{SiO}_2$ suggests that the silica:alumina ratio may be lower than the value 10:1 observed for ferrierite.

The refractive indices of the synthetic zeolite were $\alpha = 1.473$, $\gamma = 1.488$. It was not found possible to determine β on account of the small size and unusual crystal habit of the crystals. The values given for natural ferrierite are $\alpha = 1.478$, $\beta = 1.479$, $\gamma = 1.482$.

Staples (1955) obtained an orthorhombic unit cell for ferrierite from Weissenburg and precession photographs using single crystals, and with this result was able to index the x -ray powder pattern. The same indices were used for the almost identical powder pattern of the synthetic species Sr-D, and a unit cell was calculated by the least squares method of Cohen (1935) using a program written by Dr. R. D. Diamand of this department for the Mercury computer. Weighted values of the first 31 lines were used and the unit cell thus obtained is given in Table 1, where it is compared with that found by Staples (1955) for natural ferrierite.

The observed and calculated d -spacings for Sr-D, are given in Table 2. Those for natural ferrierite, which are also given, are in very good agreement. Sr-D is therefore a synthetic strontium ferrierite. A synthetic sodium form has been briefly described by Senderov (1963) and a mixed

TABLE 1

Cell edge	Sr-D powder	Ferrierite single crystal
a	19.01 ₃	19.12
b	14.13 ₄	14.14
c	7.47 ₃	7.48

Ca-Na form was also produced by Coombs *et al.* (1959) but not identified as such.

Sr-Q. In an attempt to identify others of the synthetic zeolites prepared in these laboratories it was noted that the *x*-ray spacings given by Sakurai and Hayashi (1952) for a number of well-known zeolites were not in agreement with other published data. This casts doubt on the spacings recorded by them for yugawaralite, which was reported as a new zeolite with the composition $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 4\text{H}_2\text{O}$.

A small crystal of yugawaralite from Heinabergsjökull, southeastern Iceland, was kindly supplied by Dr. G. P. L. Walker of the geology department of this college. The optical and morphological measurements of this specimen were very close to those of the original Japanese specimen (Walker, 1964).

The Icelandic yugawaralite gave an *x*-ray powder pattern which appeared to have certain similarities to that of the synthetic zeolite *Sr-Q* (Barrer and Marshall, 1964). This species was formed under hydrothermal conditions from aqueous gels of composition $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 5-9\text{SiO}_2$ at temperatures between 270° and 350° C. The unit cell of the natural yugawaralite was determined by Mr. D. J. Williams of this department by means of Weissenberg and precession photographs from a single crystal. Systematic absences showed that the space group could be either *P2/c* or *Pc*. The intensities of the *Ok*l reflections were obtained from precession photographs, and were treated by the statistical method of Howells *et al.* (1950). A plot of $N(I/\langle I \rangle)$ against $(I/\langle I \rangle)$ showed unequivocally that the structure was non-centrosymmetric, and confirmed the space group as *Pc*. A two-dimensional Patterson projection viewed down the *a* axis was calculated, but did not provide sufficient evidence to decide between several possible structures. Further work to determine the structures is in progress.

Yugawaralite was found to be monoclinic, with the following parameters:

$$\begin{aligned} a &= 6.73 \text{ \AA} \\ b &= 13.95 \text{ \AA} \\ c &= 10.03 \text{ \AA} \end{aligned}$$

TABLE 2

Ferrierite			Strontium-D			
d(Å)		int.	hkl	d(Å)		int.
calc.	obs.			calc.	obs.	
11.38	11.33	2	110	11.34	—	—
9.56	9.61	10	200	9.51	9.49	75
7.07	7.00	3	020	7.07	7.07	20
6.97			101	6.96	6.96	15
6.61	6.61	2	011	6.61	6.61	55
5.81	5.84	5	310	5.78	5.77	15
5.44	—	—	211	5.43	5.43	5
4.96	4.96	<1	121	4.96	4.96	15
4.78	4.80	<1	400	4.75	4.76	15
4.57	4.58	<1	130	4.57	—	—
3.99	3.99	9	031	3.99	3.99	45
3.96	—	—	420	3.94	3.94	35
3.87	3.88	1	411	3.86	3.86	25
3.79	3.79	2	330	3.78	3.78	50
3.74	—	—	002	3.74	3.74	10
3.69	3.69	5	510	3.67	3.67	30
3.68			231	3.68		
3.55	3.54	8	112	3.552	3.555	10
3.53			040	3.534	3.536	90
3.48	3.49	8	202	3.480	3.483	100
3.41	3.42	2	501	3.390	3.389	15
3.32	3.31	2	240	3.313	3.313	20
3.19	3.20	1	600	3.185	—	—
3.15	3.15	3	141	3.151	3.142	55
3.07	3.07	3	521	3.057	3.058	45
2.97	2.97	3	530	2.959	2.960	25
2.95	—	—	402	2.939	2.938	25
2.905	2.90	2	620	2.892	2.897	35
2.719	2.72	2	422	2.714	2.715	30
2.645	2.64	2	051	2.644	2.646	15
2.585	2.58	3	350	2.582	2.583	10
2.489	2.49	2	631	2.481	2.480	15
2.425	2.43	2	602	2.418	2.416	20
2.364	2.37	4	730	2.353	2.353	20
—	2.32	<1	—	—	2.312	5
—	2.26	<1	—	—	2.264	5
—	2.11	2	—	—	2.110	5
—	2.04	2	—	—	2.031	5
—	2.00	3	—	—	2.000	10
—	1.94	3b	—	—	1.928	15
—	1.87	3	—	—	1.871	25
—	—	—	—	—	1.836	10
—	—	—	—	—	1.810	10
—	1.78	4	—	—	1.779	25
—	1.72	<1	—	—	1.770	25
—	1.65	2	—	—	1.656	5
—	1.63	2b	—	—	1.619	10
—	1.60	2	—	—	1.610	15
—	1.55	<1	—	—	1.582	15
—	1.50	2	—	—	1.484	25
—	1.47	2	—	—	1.461	10
—	1.43	3	—	—	1.424	30
—	1.41	<1	—	—	1.412	5
—	1.37	2	—	—	1.363	10
—	1.34	1	—	—	1.307	15
—	1.27	1	—	—	1.271	20
—	1.25	2	—	—	1.235	20
—	—	—	—	—	1.218	5
—	—	—	—	—	1.206	5

TABLE 3

Sr-Q				Yugawaralite			
hkl	d _{calc}	d _{obs}	int.	hkl	d _{calc}	d _{obs}	int.
011	7.81	7.80	5	011	7.79	7.79	20
020	6.96	6.91	25	020	6.99	6.99	60
200	6.29	6.28	15	100	6.29	6.26	25
111	5.87	5.85	95	11 $\bar{1}$	5.83	5.82	90
11 $\bar{2}$	4.76	4.74	80	021	5.60	5.62	5
220	4.66	4.65	40	002	4.68	4.68	85
211	4.29	4.30	45	10 $\bar{2}$	4.66	4.65	85
031	4.16			012	4.44	4.45	10
13 $\bar{1}$	4.15	4.16	25	11 $\bar{2}$	4.42	4.41	30
30 $\bar{2}$	3.93	3.93	10	111	4.29	4.30	65
131	3.77	3.76	30	031	4.17	4.18	30
040	3.47	3.48	5	022	3.89	3.89	15
032	3.30	3.30	20	12 $\bar{2}$	3.87	3.87	5
041	3.26	3.26	70	121	3.79	3.78	20
231	3.230	3.231	5	13 $\bar{1}$	3.77		
400	3.138	3.137	10	130	3.74	3.75	5
330	3.104	3.105	35	032	3.30	3.30	5
42 $\bar{1}$	3.035	3.030	100	041	3.27	3.27	5
222	2.930	2.928	60	131	3.238	3.235	55
113	2.750			20 $\bar{2}$	3.205	3.198	10
050	2.777	2.76	20	200	3.139	3.135	20
41 $\bar{3}$	2.737	2.735	20	140	3.052	3.056	100
232	2.649	2.650	25	12 $\bar{3}$	2.997	2.997	10
25 $\bar{1}$	2.549	2.550	5	122	2.930	2.937	30
51 $\bar{3}$	2.412	2.413	25	22 $\bar{2}$	2.913	2.907	60
22 $\bar{4}$	2.375	2.374	5	220	2.863	2.864	10
41 $\bar{4}$	2.308	2.310	5	141	2.760	2.763	30
61 $\bar{1}$	2.194	2.194	10	21 $\bar{3}$	2.724	2.720	35
45 $\bar{1}$	2.143	2.146	15	13 $\bar{3}$	2.702	2.706	5
				051	2.677	2.680	25
25 $\bar{3}$	2.134			132	2.652	2.650	20
62 $\bar{2}$	2.134	2.132	10	23 $\bar{2}$	2.640	2.638	15
51 $\bar{4}$	2.132			230	2.603	2.603	5
034	2.094	2.096	15	22 $\bar{3}$	2.581	2.578	15
26 $\bar{2}$	2.073	2.076	10	15 $\bar{1}$	2.561	2.562	5
540	2.033	2.033	10	10 $\bar{4}$	2.512		
63 $\bar{1}$	2.003	2.005	20	221	2.512	2.513	15
070	1.982	1.980	5	11 $\bar{4}$	2.472	2.474	15
53 $\bar{4}$	1.955			24 $\bar{1}$	2.425	2.428	15
214	1.953	1.954	5	14 $\bar{3}$	2.405	2.407	10
352	1.924	1.922	5	142	2.370	2.368	20
224	1.897	1.897	25	24 $\bar{2}$	2.361	2.360	10
063	1.860	1.863	5	004	2.338	2.338	10
54 $\bar{4}$	1.832	1.833	5	31 $\bar{1}$	2.195	2.197	5
53 $\bar{5}$	1.735			25 $\bar{1}$	2.150	2.153	5
65 $\bar{1}$	1.734	1.734	10	15 $\bar{3}$	2.136	2.138	5
62 $\bar{5}$	1.703	1.703	10	25 $\bar{2}$	2.105	2.106	10
612	1.679	1.677	5	300	2.092	2.092	25
045	1.651	1.651	15	33 $\bar{2}$	2.018	2.018	10
254	1.607	1.608	10	33 $\bar{1}$	2.005	2.005	15
72 $\bar{5}$	1.588			11 $\bar{5}$	1.984	1.977	10
57 $\bar{2}$	1.588			25 $\bar{3}$	1.969		
		1.569	10	30 $\bar{4}$	1.954	1.958	15
		1.552	5	24 $\bar{4}$	1.936		
		1.528	5	31 $\bar{4}$	1.935	1.934	20
		1.498	5	330	1.908	1.909	10
		1.455	5	170	1.901	1.900	25
		1.426	5	26 $\bar{2}$	1.883	1.883	5

TABLE 3 (continued)

Sr-Q				Yugawaralite			
hkl	d _{calc}	d _{obs}	int.	hkl	d _{calc}	d _{obs}	int.
		1.394	10	22 $\bar{5}$	1.878		
		1.371	5	34 $\bar{1}$	1.874	1.876	5
		1.348	5	334	1.802	1.801	5
		1.334	5	254	1.787	1.788	5
		1.322	5	261	1.761	1.759	5
		1.307	10	252	1.753	1.753	5
		1.251	5	315	1.734	1.735	20
				172	1.696		
				353	1.696	1.696	10
				073	1.680		
				180	1.681	1.681	5
				064	1.649		
				116	1.649	1.649	5
				36 $\bar{2}$	1.613		
				22 $\bar{6}$	1.613	1.613	5
				136	1.564	1.564	5
						1.538	15
						1.528	10
						1.510	15
						1.497	5
						1.486	5
						1.468	15
						1.453	10
						1.429	15
						1.394	15
						1.373	5
						1.356	10
						1.342	10
						1.337	10
						1.314	10
						1.301	5
						1.285	5
						1.279	10
						1.248	10
						1.229	5
						1.222	5
						1.202	5

$$\beta = 111^{\circ}30'$$

space group Pc or C_s^2

density 2.2 g/cm³

cell volume 882 Å³

Z = 2

M = 582.

Using this cell the powder pattern of yugawaralite was indexed (Table 3) and compared visually with that of Sr-Q. 17 lines which corresponded in position and intensity were given the same indices and used in the least squares program to determine a unit cell. This cell was in turn used in an attempt to index the remainder of the powder pattern of Sr-Q. The least

squares program was then repeated using 42 lines, but the agreement between the observed and calculated values was not considered satisfactory. A unit cell with the a dimension double that of yugawaralite was then taken and the procedure repeated. The final values obtained are given in Table 3 and show satisfactory agreement between the observed and calculated values. A possible unit cell for Sr-Q is therefore

$$a = 13.48 \text{ \AA}$$

$$b = 13.86 \text{ \AA}$$

$$c = 10.10 \text{ \AA}$$

$$\beta = 111^{\circ}41'$$

The similarities between this cell and that found for natural yugawaralite suggest that these two species have related structures and that Sr-Q may be a strontium near-yugawaralite.

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