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The Crystal Structure of Paracelsian, $BaAl_2Si_2O_8$

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Paracelsian, $BaAl_2Si_2O_8$, is isostructural with danburite, $CaB_2Si_2O_8$, whose structure is similar to that of the felspars. It is monoclinic but very nearly orthorhombic. The structure has been determined by two-dimensional Fourier methods. Fairly accurate dimensions of the barium polyhedra were obtained. The value for the mean distance $Si_{\frac{1}{2}}Al_{\frac{1}{2}}$–O is of interest. Correlation with recent values for Si–O, $Si_{\frac{3}{4}}Al_{\frac{1}{4}}$–O suggests values of $1{\cdot}60_5$ Å for Si–O and $1{\cdot}78 \pm 0{\cdot}02$ Å for Al–O. The latter value agrees well with the sum of the Goldschmidt radii but is larger than the sum of the Pauling radii.

Introduction

A preliminary investigation of paracelsian is described in a short note by Smith (1952) which may be summarized as follows: Spencer (1942) first gave a full optical and morphological description of paracelsian, $BaAl_2Si_2O_8$; Davis & Tuttle (1952) of this Laboratory suggested that paracelsian might be similar to the synthetic orthorhombic form of $CaAl_2Si_2O_8$, but measurements of the lattice parameters and space group of $CaAl_2Si_2O_8$ by Davis & Tuttle and of paracelsian by Smith disproved this hypothesis; comparison of the lattice properties of paracelsian and danburite $CaB_2Si_2O_8$ (Dunbar & Machatschki, 1930), suggested that they were isostructural.

This paper describes the determination of the structure of paracelsian.

Morphological and optical data

Spencer writes, 'The crystals of paracelsian have the form of simple orthorhombic crystals from which they cannot be distinguished by goniometric measurements. But when examined optically in thin sections they show complex twinning of more than one kind'. (This indicates lower symmetry.) Three crystals from the same locality as those of Spencer (Benallt Mine, near Rhiw, Carnarvonshire) have been examined in the present work, and the orthorhombic morphology was confirmed by goniometric and X-ray methods. A crystal examined on a universal stage microscope by W. S. MacKenzie of this Laboratory showed, however, no evidence of twinning. The isogyres were not doubled as shown in Fig. 2(*a*) of Spencer's paper and no peculiar effects occurred upon rotation of the crystal in convergent polarized light. MacKenzie found: $a = X$, $b = Z$, $c = Y$, $2V = 52{\cdot}7 \pm 0{\cdot}5°$ (sodium light), negative. These values agree with Spencer's results: $\alpha = 1{\cdot}5702$, $\beta = 1{\cdot}5824$, $\gamma = 1{\cdot}5869$, negative, $2V = 50° \, 35'$, $a = X$, $b = Z$, $c = Y$.

X-ray measurements

X-ray measurements were made on three single crystals, using precession and Weissenberg methods. From the precession and Weissenberg photographs it was found by comparison of intensities that the crystals were monoclinic but strongly pseudo-orthorhombic with $\beta = 90 \pm 0{\cdot}5°$, $a \sin\beta = 9{\cdot}02 \pm 0{\cdot}09$ Å, $b = 9{\cdot}50 \pm 0{\cdot}09$ Å, $c \sin\beta = 8{\cdot}47 \pm 0{\cdot}09$ Å (Mo $K\alpha$ radiation). A powder record obtained on a Philips Geiger-counter spectrometer was indexed on the basis of an orthorhombic crystal with

$$a' = 9{\cdot}076 \pm 0{\cdot}005,\ b = 9{\cdot}583 \pm 0{\cdot}005,$$
$$c' = 8{\cdot}578 \pm 0{\cdot}005 \text{ Å}$$

(Cu $K\alpha$ radiation, $\lambda_{\alpha1} = 1{\cdot}54050$, $\lambda_{\alpha2} = 1{\cdot}54434$ Å) (see Table 1). Reflexions $(h0l)$ and $(h0\bar{l})$ are not resolved, showing that paracelsian must be very closely orthorhombic. The maximum separation of $(h0l)$ and $(h0\bar{l})$ reflexions cannot be more than $0{\cdot}05°$, which corresponds to $\beta = 90° \pm 10'$. The resulting axial ratios, $a':b:c' = 0{\cdot}9471:1:0{\cdot}8952$, agree very closely with Spencer's goniometric axial ratios, $a:b:c = 0{\cdot}9470:1:0{\cdot}8956$. Using Spencer's density, $3{\cdot}31_5$ g.cm.$^{-3}$, there are four (calc. $3{\cdot}95$) units of $BaAl_2Si_2O_8$ in the unit cell.

Comparison of intensities on single-crystal photographs showed that there are pseudo-planes of symmetry parallel to (100) and (001) and that the mismatch of intensities over these planes is very small. Systematic absences were found only for reflexions with h odd in $(h00)$, k odd in $(0k0)$, l odd in $(00l)$, h odd in $(h0l)$. In addition, absences for reflexions with $(k+l)$ odd in $(0kl)$ were at first found; however, long-exposure photographs revealed a few very weak reflexions with $(k+l)$ odd in $(0kl)$. The space group is therefore $P2_1/a$, assuming that reflexions with k odd in $(0k0)$ are truly absent; if not, the space group is $P2/a$ or Pa. The crystals have a pseudo space-group $Pna2_1$ or $Pnam$.

Table 1. *Powder record of paracelsian*

Cu $K\alpha$ radiation; calibrated with silicon standard

$2\theta_{obs.}$	$2\theta_{calc.}$	Intensity	Index	$d_{obs.}$
13·44	13·44	20	110	6·582
13·88	13·87	20	011	6·379
16·98	16·98	7	111	5·217
22·18	22·17	100	201	4·004
23·41	23·43	70	121	3·797
24·06	24·06	4	211	3·696
24·76	24·79	45	112	3·593
27·08	27·08	35	220	3·290
27·91	27·93	15	022	3·194
28·63	28·63	7	202	3·115
29·05	29·02	7	221	3·074
29·65	29·65 29·64	35	130 122	3·010
29·86	29·85	50	031	2·990
30·16	30·14	30	212	2·961
31·03	30·97	5	310	2·880
32·76	32·73	50	311	2·731
34·18	34·19	20	113	2·621
34·35	34·32 34·33	35	222 230	2·609
35·09	35·06	50	320	2·555
37·55	37·55 37·56	20	040 312	2·3932
37·93	37·97	45	123	2·3701
39·75	39·69	3	400	2·2810
40·43	40·43	20	232	2·2291
41·11	41·08 41·07	45	330 322	2·1938
41·8	41·83	5	223	2·1591
42·11	42·15	15	004	2·1440
44·04	44·02	7	241	2·0544
44·5 to 44·6	44·43 44·45 44·61	7	114 142 313	2·034 2·030
48·55	48·55	20	150	1·8736
49·25	49·23 49·23	10	430 422	1·8486
49·77	49·77	5	151	1·8305
50·45	50·44	5	431	1·8073
50·72	50·73	7	143	1·7984
51·21	51·18	7	510	1·7823
52·42	52·37 52·53	7	134 333	1·7440
53·28	53·23 53·32	13	342 152	1·7178
55·14	55·12	13	521	1·6642
57·95	57·96	20	351	1·5900
59·56	59·52	15	531	1·5508
etc.	etc.	etc.	etc.	etc.

Note: The recorded ($h0l$) and (hkl) lines are doublets; see text.

Complete sets of intensities were recorded for the ($hk0$) and ($h0l$) zones from Weissenberg photographs and of the ($0kl$) zone from precession photographs. Absorption errors were reduced by using Mo $K\alpha$ radiation and reasonably equi-dimensional crystals. The intensities were eye-estimated and the correction factors were applied in the usual way.

Determination of the structure

Spencer pointed out the agreement between the axial ratios of topaz, danburite and paracelsian. Comparison of the idealized space group, *Pnam*, and composition $BaAl_2Si_2O_8$ of paracelsian showed that it could not be isostructural with topaz but it could be isostructural with danburite, $CaB_2Si_2O_8$, whose space group is *Pnam* also. Preliminary structure-factor calculations for the pinacoid reflexions of paracelsian, using the coordinates of the danburite structure and replacing Ca by Ba and B by Al, gave values which did not agree with the observed structure amplitudes. Closer examination of the atomic coordinates of danburite showed that in order to get the expected interatomic distances in paracelsian the framework of tetrahedra should be rotated, the Al should be moved into the centre of the tetrahedron and the Ba should be moved. New calculations gave good agreement and after trial-and-error adjustment of the atomic coordinates of Ba, Si and Al, the structure was refined by successive Fourier series. No distinction between Al and Si was made.

The y-axis projection was first studied because this projection shows directly the deviation from orthorhombic symmetry. An F_o synthesis was computed, using signs obtained for the ideal orthorhombic structure (R-factor = 0·22). In order to show clearly the deviation from orthorhombic symmetry it was computed in two parts, one part containing the terms $(F_{h0l}+F_{h0\bar{l}})$ and the other part containing the terms $(F_{h0l}-F_{h0\bar{l}})$. The first one, Fig. 1(a), gives the averaged 'orthorhombic' structure, and the other one, Fig. 1(b), gives the deviation from the 'orthorhombic' structure. On Fig. 1(b) there are adjacent positive and negative peaks which lie on either side of the atomic positions of Fig. 1(a). This shows that the deviation from orthorhombic symmetry is partly caused by small shifts of atomic coordinates from the ideal orthorhombic structure. It is possible that ordering of Al and Si atoms is also involved, but this is difficult to

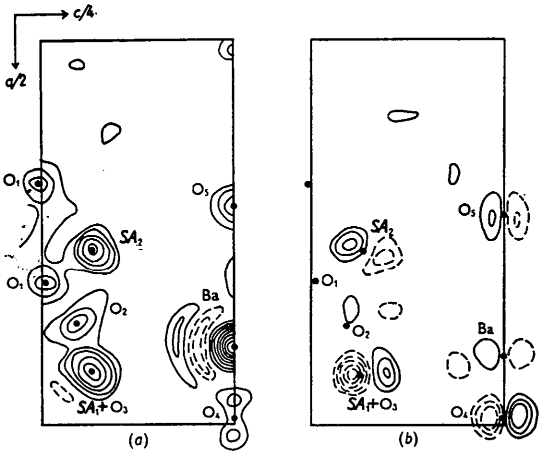

Fig. 1. (a) The y-axis projection of the $(F_{h0l}+F_{h0\bar{l}})$ synthesis. Contour levels are at arbitrary levels of 50 for O atoms, background and diffraction ripples of Ba atom, 100 for (Si, Al) and 200 for the Ba atom. Note the effect of the diffraction ripples on O_4. (b) The y-axis projection of the $(F_{h0l}-F_{h0\bar{l}})$ synthesis. Contour levels at arbitrary units of 20. (SA = Si, Al.)

detect because of the small difference in scattering of Al and Si atoms. The pairs of positive and negative peaks in Fig. 1(*b*) do not lie quite symmetrically about the positions of the Al and Si atoms in Fig. 1(*a*), suggesting that ordering does occur. The deviation of these peaks, however, is hardly significant and no deductions were made. Structure factors for the monoclinic structure were calculated and an R factor of 0·14 was obtained. An (F_o-F_c) synthesis (Cochran, 1951) was then calculated in order to check the accuracy of the atomic coordinates from the F_o synthesis (Fig. 2). The peaks in this synthesis are small and only small corrections were made to the atomic coordinates (maximum movement, 0·05 Å for an oxygen atom). It was not possible to separate the Al and Si atoms from this synthesis. No appreciable improvement in the R factor was obtained from these coordinates, and the refinement was judged to be complete. The agreement between F_o and F_c is good except for a few large intensities. These discrepancies are probably caused by absorption and extinction.

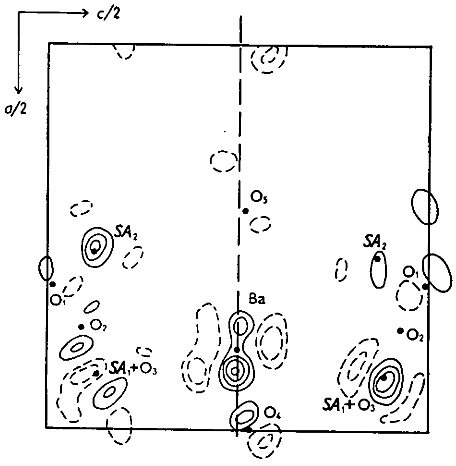

Fig. 2. The y-axis projection of the (F_o-F_c) synthesis. Contour levels at arbitrary units of 12·5 (on same scale as Figs. 1(*a*) and 1(*b*)).

The z-axis projection was then refined. Each peak in the F_o synthesis (except for the atoms in 'special'

Table 2(*a*). *Atomic peak positions*

	From y-axis projection		From z-axis projection‡	
Atom	z	x	x	y
Ba	0·2492	0·8972	0·8975	0·4123
SA_1*	0·560$_0$† 0·930$_8$†	0·070$_0$ 0·067$_8$	0·065$_0$	0·196$_1$
SA_2*	0·938$_3$ 0·570$_8$	0·230 0·226	0·228$_8$	0·917$_3$
O_1	0·997 0·499	0·190 0·194	0·195	0·088
O_2	0·954 0·546	0·128 0·130	0·128	0·362
O_3	0·440† 0·069†	0·930 0·932	0·925	0·187$_5$
O_4	0·745	0·010	0·003$_5$	0·173
O_5	0·758	0·286	0·296$_5$	0·912

* SA denotes (Si, Al).

† SA_1 and O_3 not resolved in y-axis projection; identical values (except for sign reversal) given.

‡ The value of x and y found for the z-axis projection are mean values for two atoms except for Ba, O_4 and O_5. See text for full information.

Table 2(*b*). *Mean atomic coordinates*‡

	x	y	z
Ba	0·8973	0·4123	0·2500†
SA_1*	0·065$_0$	0·196$_1$	0·935$_4$
SA_2*	0·228$_3$	0·917$_3$	0·933$_7$
O_1	0·193	0·088$_3$	0·998
O_2	0·128$_7$	0·362	0·954
O_3	0·925	0·187$_5$	0·064$_8$
O_4	0·006$_7$	0·173	0·750†
O_5	0·291	0·912	0·750†

* SA denotes (Si, Al).

† Atoms moved on to mirror plane at z = 0·25 or 0·75.

‡ See text for meaning of 'mean atomic coordinates'.

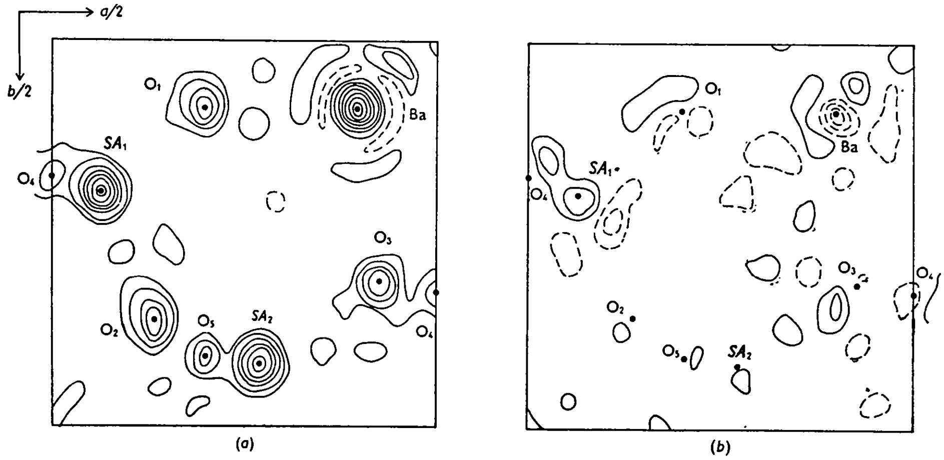

Fig. 3. (*a*) The z-axis projection of the F_o synthesis. Contour levels in arbitrary units of 50 for O atoms and the background, 100 for (Si, Al) and 200 for the Ba atom. (*b*) The z-axis projection of the (F_o-F_c) synthesis. Contour levels at units of 20 (on same scale as (*a*)).

Table 3(*a*). *Calculated and observed structure amplitudes*

(*hk*0) zone

k	*h*	F_c	F_o
0	0	696	—
	2	+18	22
	4	−110	115
	6	−188	180
	8	+14	*x*
	10	+103	86
	12	+13	*x*
	14	−33	20
	16	−20	16
1	1	−85	82
	2	−27	22
	3	+61	55
	4	−42	29
	5	+189	189
	6	+62	77
	7	−61	68
	8	+88	91
	9	−71	78
	10	−43	45
	11	−80	71
	12	−60	56
	13	+78	68
	14	−66	62
	15	+61	48
	16	+50	61
	17	+26	17
2	0	+34	58
	1	+22	22
	2	−115	117
	3	+192	189
	4	−20	14
	5	−12	*x*
	6	−13	18
	7	−55	47
	8	+64	77
	9	−96	92
	10	+69	71
	11	+59	47
	12	−13	12
	13	+79	74
	14	−62	57
	15	−38	38
	16	−50	52
	17	−58	35
3	1	−71	95
	2	−146	124
	3	−77	83
	4	−132	−122
	5	−6	23
	6	+62	65
	7	+70	88
	8	+144	150
	9	+51	62
	10	−47	42
	11	−7	11
	12	−36	21
	13	−41	38
	14	−71	74
	15	−37	22
	16	+94	81
	17	−17	*x*
4	0	−202	202
	1	+38	49
	2	+50	42
	3	+144	138
	4	+69	78
	5	−94	112
	6	+52	66
	7	−90	95
	8	−50	72
	9	−52	62
	10	−74	70
	11	+91	89
	12	+10	17
	13	+91	88
	14	+44	42
	15	−22	22
	16	+28	24
	17	−48	45
5	1	+210	205
	2	−81	81
	3	+6	12
	4	−23	38
	5	−212	214
	6	+42	42
	7	−38	56
	8	+49	58
	9	+26	26
	10	−42	52
	11	+88	82
	12	−7	*x*
	13	−31	28
	14	−20	21
	15	−24	*x*
	16	+32	24
6	0	−174	185
	1	+13	25
	2	+94	114
	3	+20	40
	4	+47	49
	5	+26	35
	6	+111	96
	7	+25	38
	8	−63	67
	9	+13	*x*
	10	−114	106
	11	−32	40
	12	−7	*x*
	13	−43	50
	14	+92	70
	15	−5	*x*
	16	+72	71
7	1	+13	18
	2	+87	90
	3	−4	14
	4	+76	78
	5	−88	90
	6	−34	24
	7	+42	58
	8	−74	58
	9	+58	52
	10	+19	18
	11	+85	83
	12	+25	20
	13	−61	61
	14	+30	32
	15	−66	69
	16	−41	45
8	0	−127	133
	1	−59	61
	2	−27	28
	3	−174	175
	4	−11	14
	5	+30	38
	6	+74	82
	7	+78	79
	8	+33	52
	9	+65	69
	10	−15	18
	11	−63	44
	12	−26	26
	13	−62	50
	14	−14	*x*
	15	+33	35
	16	+101	93
9	1	−42	46
	2	+101	93
	3	+5	14
	4	+24	23
	5	+32	24
	6	−94	86
	7	+6	*x*
	8	−109	102
	9	−33	36
	10	+73	75
	11	−23	14
	12	+60	58
	13	+2	*x*
	14	+68	70
	15	+19	26
10	0	+162	154
	1	−17	22
	2	+35	31
	3	−102	95
	4	−54	50
	5	+37	49
	6	−115	94
	7	+42	30
	8	−11	23
	9	+34	39
	10	+59	59
	11	−48	49
	12	+26	22
	13	−40	42
	14	−34	*x*
11	1	−32	33
	2	+32	40
	3	+17	17
	4	+27	42
	5	+114	79
	6	+18	18
	7	−26	19
	8	−30	40
	9	−62	58
	10	0	*x*
	11	−67	70
	12	−19	34
	13	+60	57
12	0	+123	104
	1	+41	40
	2	−31	41
	3	+50	51
	4	−32	26
	5	+7	*x*
	6	−61	56
	7	−29	29
	8	+52	48

Table 3(*a*) (*cont.*)

k	*h*	F_c	F_o
	9	−13	*x*
	10	+94	81
	11	+14	*x*
	12	+ 5	*x*
13	1	−75	69
	2	−89	83
	3	0	*x*
	4	−57	54
	5	+94	88
	6	+53	55
	7	+19	22
	8	+69	64
	9	− 2	*x*

k	*h*	F_c	F_o
	10	−23	*x*
	11	−44	51
14	0	+20	42
	1	+26	21
	2	−22	21
	3	+83	75
	4	+ 9	*x*
	5	−43	50
	6	− 8	*x*
	7	−71	67
	8	+16	*x*
	9	−39	26

k	*h*	F_c	F_o
15	1	+47	50
	2	−66	64
	3	− 4	*x*
	4	−40	41
	5	−44	34
	6	+34	24
	7	−39	51
16	0	−63	53
	1	+ 5	*x*
	2	+16	*x*
	3	+63	71
	4	+42	26
	5	+ 3	*x*

Table 3(*b*). *Calculated and observed structure amplitudes*

(*h*0*l*) zone

l	F_c	F_o	F_c	F_o
	h = +0			
2	− 2	*x*		
4	+254	250		
6	−255	238		
8	+33	42		
10	−173	222		
12	+112	156		
14	−40	44		
16	+128	172		
18	−41	36		

l	*h* = +2		*h* = −2	
0	+20	16	—	—
1	+255	179	−250	188
2	−85	98	−84	90
3	−22	26	+33	20
4	+23	21	+31	26
5	+196	224	−271	266
6	−50	58	−54	48
7	−69	73	+89	101
8	+20	24	+27	40
9	+93	129	−92	114
10	−38	45	−41	51
11	−113	146	+155	205
12	+ 6	*x*	+14	*x*
13	+55	58	−47	52
14	−23	20	−37	65
15	−78	94	+90	117
16	+11	*x*	+20	*x*
17	+63	43	−86	93
18	−11	*x*	−22	*x*

l	*h* = +4		*h* = --4	
0	−121	107	—	—
1	+139	105	−136	126
2	+110	107	+98	101
3	−44	50	+59	63
4	−124	130	−122	112
5	+123	132	−126	131
6	+75	66	+74	88
7	−54	70	+70	66
8	−121	147	−86	91
9	+33	48	−67	82
10	+102	104	+84	94
11	−88	105	+86	94
12	−63	54	−52	54
13	+11	26	−38	38
14	+96	129	+69	78
15	−48	46	+62	65
16	−46	34	−54	48
17	+40	35	−39	35

l	*h* = +6		*h* = −6	
0	−193	202	—	—
1	−95	72	+87	70
2	+36	22	+46	42
3	+177	157	−160	161
4	−65	82	−71	90
5	−56	42	+38	46
6	+165	162	+170	198
7	+100	106	−80	81
8	+15	17	− 6	*x*
9	−108	152	+99	115
10	+115	128	+118	135
11	+43	23	−20	15
12	−58	52	−70	79
13	−88	114	+72	70
14	+18	30	+39	30
15	+66	88	−56	46
16	−81	69	−83	91
17	−34	*x*	+14	*x*

l	*h* = +8		*h* = −8	
0	+18	17	—	—
1	−131	114	+160	144
2	−92	80	−103	95
3	+47	45	−32	16
4	+54	52	+48	34
5	−147	157	+129	169
6	−50	44	−42	28
7	+81	60	−77	80
8	+53	51	−66	62
9	−66	98	+46	30
10	−52	62	−38	29
11	+106	98	−115	128
12	+23	*x*	+17	*x*
13	−54	54	+35	30
14	−53	73	−31	51
15	+67	91	−59	49
16	+14	*x*	+ 0	*x*

l	*h* = +10		*h* = −10	
0	+104	109	—	—
1	+14	17	−32	27
2	−140	134	−133	146
3	−16	*x*	+ 3	*x*
4	+125	150	+127	134
5	+25	41	−12	*x*
6	−86	55	−91	81
7	+ 1	*x*	+23	*x*
8	+141	167	+117	123
9	+24	18	− 2	*x*
10	−67	81	−77	60
11	−15	20	+17	*x*
12	+87	77	+88	89
13	+11	*x*	+ 3	*x*
14	−88	117	−67	49
15	−22	*x*	+ 7	*x*

l	*h* = +12		*h* = −12	
0	+27	*x*	—	—
1	+78	74	−68	58
2	+ 4	*x*	− 7	*x*
3	−171	180	+178	194
4	+ 2	*x*	+11	*x*
5	+28	14	−36	22
6	−19	*x*	−21	23
7	−102	104	+106	107
8	−10	*x*	+ 5	*x*
9	+109	110	−121	114
10	− 6	*x*	−11	*x*
11	−26	*x*	+39	*x*
12	+12	*x*	+19	*x*
13	+104	109	−108	107
14	+17	*x*	− 4	*x*

l	*h* = +14		*h* = −14	
0	−29	22	—	—
1	+35	25	−44	64
2	+104	105	+105	105
3	−22	43	+21	*x*
4	−80	68	−83	91
5	−40	46	−40	46
6	+33	34	+23	*x*
7	−31	20	+44	66
8	−111	106	−118	122
9	+14	38	−15	*x*
10	+38	23	+29	34
11	−36	34	+49	49
12	−68	61	−59	35
13	+13	*x*	−22	*x*

Table 3(*b*) (*cont.*)

l	F_c	F_o	F_c	F_o
	$h = +16$		$h = -16$	
0	−26	28	—	—
1	−64	62	+66	57
2	+68	62	+76	84
3	+74	40	−68	57
4	−36	50	−35	29
5	−65	59	+46	43
6	+41	24	+56	62
7	+63	56	−66	44
8	−52	48	−49	48
9	−59	25	+52	35
10	+32	35	−25	35
11	+62	76	−40	36

positions, Ba, O_4, O_5) contains two atoms related by the pseudo-orthorhombic symmetry. It was impossible to distinguish the two atoms, and the resulting atomic coordinates are the mean values for the two atoms. Refinement was carried out by one F_o synthesis and one (F_o-F_c) synthesis giving a final R factor of 0·13. The F_o and (F_o-F_c) syntheses are shown in Figs. 3(*a*) and (*b*). The agreement between F_o and F_c is good for all the intensities, showing that the absorption and extinction errors are small. No attempt was made to refine the x-axis projection because this depends on the very weak $(k+l)$ reflexions in the $(0kl)$ zone. It would be difficult and not very profitable to attempt to find the signs of these very weak terms. The y coordinates of the related atoms, therefore, are unresolved by this structure analysis.

The determined peak positions are given in Table 2(*a*). In Table 2(*b*) the nearest mean 'orthorhombic' values are given. (Ba, O_4, O_5 lie at special positions on planes at $z = 0·25$, 0·75 in the ideal orthorhombic structure. The determined values of z have been idealized to these values.) Observed and calculated structure amplitudes are given in Table 3. The atomic structure factors for Ba, $\frac{1}{2}(Si+Al)$ and O have been used in the calculations. No correction for ionic displacement of electrons was made, since (*a*) the amount of ionic displacement is not known, and (*b*) the correction is small because of the presence of the heavily diffracting barium atom. Estimation of the random errors by Cruickshank's method (Cruickshank, 1949) gives standard errors in interatomic distances of about 0·02, 0·03 and 0·03 Å for Ba–O, Si–O and O–O, respectively. Deviations of less than twice these amounts in the interatomic distances listed in Table 4 are of doubtful significance.

Table 4. *Interatomic distances in paracelsian*

	Atoms	Distance (Å)
In $(SA_1.O_4)$ group	O_1–O_2	2·71
	O_1–O_3	2·67
	O_1–O_4	2·86
	O_2–O_3	2·67*
	O_2–O_4	2·75
	O_3–O_4	2·80
	Mean	2·74
In $(SA_2.O_4)$ group	O_1–O_2	2·74*
	O_1–O_3	2·90
	O_1–O_5	2·86
	O_2–O_3	2·89
	O_2–O_5	2·68*
	O_3–O_5	2·70
	Mean	2·795
	SA_1–O_1	1·65
	–O_2	1·70
	–O_3	1·69
	–O_4	1·69
	Mean	1·68
	SA_2–O_1	1·76
	–O_2	1·70
	–O_3	1·72
	–O_5	1·68
	Mean	1·71
	Ba–O_1	2·85
	–O_2	2·79
	–O_2	3·33
	–O_3	2·69
	–O_5	2·82

* Shared edges.

Discussion

From the X-ray measurements paracelsian appears to be monoclinic with β very nearly 90°, and its symmetry is very closely orthorhombic. This would explain the conflicting goniometric and optical measurements obtained by Spencer. The deviation from the ideal orthorhombic symmetry is produced by small movements of the atoms which destroy the mirror planes in the ideal space-group, *Pnam*. It is possible that twinning exists in the crystals used in this investigation; however, the twinning angles must be very small for no doubled reflexions were observed on the X-ray records and no optical effects were observed. The deviation from orthorhombic symmetry may be caused by ordering of the Al and Si atoms, even though complete segregation of Al and Si is possible in the ideal orthorhombic space group. The mean X–O distances in the two sets of tetrahedra of the idealized orthorhombic structure are 1·68±0·02 and 1·71±0·02 Å. The expected values for Si–O and Al–O differ by about 0·1 or $0·1_5$ Å. It appears therefore that the averaged ideal tetrahedra both contain about $Si_{\frac{1}{2}}Al_{\frac{1}{2}}$; the deviation from orthorhombic symmetry may therefore be caused by segregation of Si and Al in the pairs of tetrahedra related by the ideal orthorhombic symmetry. It is also possible that this segregation does not occur and that small movements of tetrahedra occur in order to produce an energetically more favorable structure. Taylor, Darbyshire & Strunz (1934) write, 'Celsian is probably structurally monoclinic, dimensionally only pseudo-monoclinic and actually triclinic'. This probable reduction in symmetry of celsian may be related to that of paracelsian.

The z-axis projection of the paracelsian structure is shown in Fig. 4. The idealized space group *Pnam* of

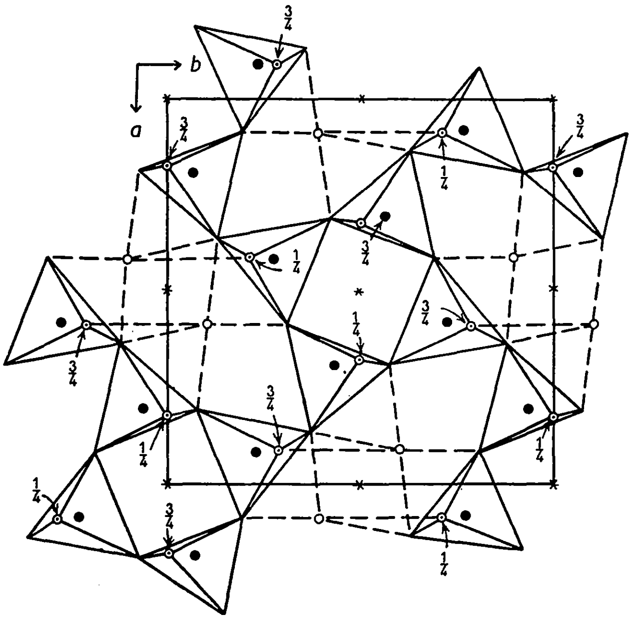

Fig. 4. The z-axis projection of the structure. Heavy dots are (Si, Al) atoms, open circles Ba atoms and the centred open circles are oxygen atoms lying on the mirror planes.

paracelsian has two mirror planes perpendicular to the z axis at heights $z = \frac{1}{4}$ and $\frac{3}{4}$. The oxygen atoms in paracelsian fall into two groups; those with z coordinates nearly 0 or $\frac{1}{2}$, and those with z coordinates $\frac{1}{4}$ or $\frac{3}{4}$. The latter lie on mirror planes and the former occur in pairs related by the mirror planes. Each tetrahedron has at its apices one oxygen atom on the mirror planes at $z = \frac{1}{4}$ or $\frac{3}{4}$ and three oxygen atoms all of which have the same z coordinate of either 0 or $\frac{1}{2}$. In Fig. 4 the oxygen atoms on the mirror planes are shown by centred circles and the z coordinate is also shown. The tetrahedra are shown in outline and, because of the horizontal mirror planes, each tetrahedron in the diagram represents two tetrahedra in the unit cell, one pointing up and one pointing down. It is now possible to study the linkage of the tetrahedra. In each unit cell there are two layers of tetrahedra, the layers being linked at the apices of the tetrahedra. Half of the tetrahedra in each layer point upwards and half downwards. The arrangement of one layer can be deduced from Fig. 4. The coordinates of the oxygen atoms which link the layers are shown (either $\frac{1}{4}$ or $\frac{3}{4}$). For the lowest layer in the unit cell, the tetrahedra with apices at $\frac{1}{4}$ are pointing upwards and those with apices at $\frac{3}{4}$ are pointing downwards. The reverse holds for the higher layer in the unit cell. An alternative way of looking at the structure is to consider the packing parallel to the z axis. In the centre of Fig. 4, four tetrahedra are shown. These represent eight tetrahedra, four in each layer. Of the four tetrahedra in any one layer, two point upwards and two downwards in such a way that those pointing the same way are *adjacent* and not *opposite*. These tetrahedra are part of an infinite zigzag lying parallel to the z axis.

This zigzag is identical (apart from slight rotations of the tetrahedra) with the zigzag in the felspars, as shown in Fig. 4 of Taylor's paper (1933). The difference between the paracelsian and felspar structures arises in the cross linkage of the zigzags. Fig. 5 shows projections parallel to the zigzags in paracelsian and a felspar. The figure shows directly the sheets of tetrahedra perpendicular to the zigzags, and in projection these are seen to be identical apart from slight rotations of the tetrahedra. U and D in the diagram show whether the tetrahedra are pointing upwards or downwards. The zigzags can be located by looking for rings of four tetrahedra with two adjacent tetrahedra pointing up and the other two pointing down. The zigzags occur in both diagrams, but it will be seen that alternate zigzags in paracelsian must be rotated by 90° in order to obtain the felspar structure. This is the essential difference between the felspar and paracelsian structures.

The demonstration of the similarity between the felspar and paracelsian structures parallels Prof. W. L. Bragg's demonstration (in Taylor's paper, pp. 439–441) of the similarity between the felspar and danburite structures, for paracelsian and danburite have the same structure. Fig. 5 of this paper is based on Figs. 4 and 7 of Taylor's paper. It is interesting to compare the corresponding dimensions of the three crystals:

Felspar (sanidine)	Paracelsian	Danburite
$a' = 13{\cdot}2$ Å	$[110] = 13{\cdot}2$ Å	$[110] = 11{\cdot}9$ Å
$b' = 12{\cdot}9$ Å	$[1\bar{1}0] = 13{\cdot}2$ Å	$[1\bar{1}0] = 11{\cdot}9$ Å
$c' = 8{\cdot}4$ Å	$c = 8{\cdot}6$ Å	$c = 7{\cdot}7$ Å
$\gamma' = 90°$	$[110] : [1\bar{1}0] = 87°$	$[110] : [1\bar{1}0] = 85°$

The cations occupy the same holes in the tetrahedral frameworks in all three crystals.

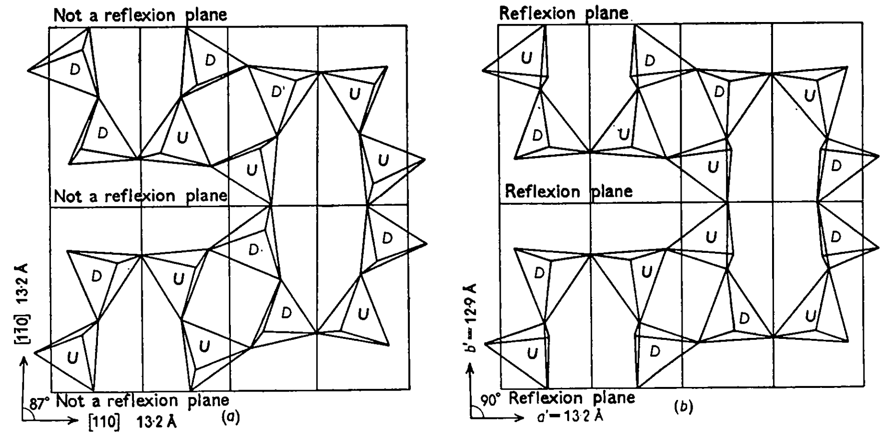

Fig. 5. (*a*) A projection of the paracelsian structure. *U* and *D* denote tetrahedra pointing upwards or downwards respectively. For convenience, (*a*) is drawn on a rectangular frame instead of an 87° frame. (*b*) A projection of the felspar structure. After Fig. 4 of Taylor (1933).

Two other compounds of the composition $BaAl_2Si_2O_8$ are known, celsian and hexagonal $BaAl_2Si_2O_8$. Celsian is a felspar (Taylor, *et al.*, 1934) and its structure is related to paracelsian in the way already described. Ito (1950) has shown that the structure of hexagonal $BaAl_2Si_2O_8$ is related to that of celsian. The structures of the analogous $CaAl_2Si_2O_8$ compounds, hexagonal $CaAl_2Si_2O_8$ (Donnay, 1951) and orthorhombic $CaAl_2Si_2O_8$ (Davis & Tuttle, 1952) are not identical with their barium counterparts although anorthite and celsian both have the same felspar structure.

In paracelsian, the mean $Si_{\frac{1}{2}}Al_{\frac{1}{2}}$–O distance is $1{\cdot}69_6 \pm 0{\cdot}01$ Å. This value is to be compared with the recently measured values of $1{\cdot}60 \pm 0{\cdot}01$ Å for Si–O in afwillite (Megaw, 1952), $1{\cdot}61 \pm 0{\cdot}02$ Å for Si–O in tilleyite (Smith, 1953), and 1·642 Å for $Si_{\frac{3}{4}}Al_{\frac{1}{4}}$–O in sanidine (Cole, Sörum & Kennard, 1949). The theoretical values corrected for 4-coordination are, 1·60 Å, 1·76 Å for Si–O, Al–O (sum of ionic radii; Goldschmidt) and 1·60 Å, 1·68 Å for Si–O, Al–O (sum of ionic radii, Pauling). The experimental values are in agreement with values of about $1{\cdot}60_5$ Å for Si–O and $1{\cdot}78 \pm 0{\cdot}02$ Å (extrapolated) for Al–O (assuming a linear relation between bond length and atomic composition). These values agree very well with the sums of Goldschmidt's ionic radii but do not agree very well with those of Pauling. Cole *et al.* (1949) deduced the values 1·62 and 1·70 Å respectively for Si–O and Al–O from old structure determinations. The new values are probably more accurate than these values and should be of interest in any work on the segregation of aluminium and silicon.

The deviations from the mean value of the Si, Al–O distances in paracelsian are probably not significant. The deviations of the O–O distances from their mean value are possibly significant, but there is some uncertainty in the position of O_3 and SA_1 because of the overlap in the y-axis projection. The three edges shared between the tetrahedra and the barium polyhedron are rather short, as would be expected (Pauling, 1929). Three of the remaining nine edges are also short, but this is not significant when account is taken of the possible errors.

The barium atom has 7 near oxygen atoms at about 2·8 Å and two more at 3·3 Å. The sum of the ionic radii is 2·75 Å (uncorrected). The Ba–O_3 distance, 2·69 Å, is rather low. This may be caused by an error in the position of the O_3 atom because of the overlapping of SA_1 and O_3 in the y-axis projection. The other values of 2·79, 2·82 and 2·85 Å compare well with the sum of the ionic radii and with the values found by Evans (1951) in $BaTiO_3$, 2·782, 2·826 and 2·896 Å.

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