CRYSTAL STRUCTURE OF PARACELSIAN

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After we had established the structure of hurlbutite [1-3] we found on comparing the structure with those of danburite and the feldspars that one form of celsian, δ $BaAl_2Si_2O_8$ or paracelsian [4], is very similar not only to danburite $CaB_2Si_2O_8$, as has been pointed out [4-6], but also to hurlbutite $CaBe_2P_2O_8$.

	a, A	b, A	c, A	β	$a:b:c$	Space group
Danburite	8.01	8.75	7.71	$\beta = 90°$;	0.915 : 1 : 0.881;	$D_{2h}^{16} = Pnam$
Hurlbutite	8.29	8.80	7.81	$\beta \approx 90°$;	0.942 : 1 : 0.887;	$C_{2h}^{5} = P2_1/a$
Paracelsian	9.08	9.58	8.58	$\beta \approx 90°$;	0.947 : 1 : 0.895;	$C_{2h}^{5} = P2_1/a$

The hurlbutite-paracelsian pair has

$$a'' : a' \approx b'' : b' \approx c'' : c' \approx 1.1.$$

A more detailed examination gave rise to the following conclusions.

Spencer [4] first described paracelsian in detail in 1942 for material from the Benallt Mine, Wales. Goniometric and optical studies showed that the crystals are strictly orthorhombic in form, but the optical measurements indicate a lower symmetry. Smith [5, 6] examined monocrystals from this same source in 1952-53; the powder, Weissenberg, and oscillation photographs showed that the mineral is monoclinic, but with a strictly pseudoorthorhombic unit cell: a = 9.08, b = 9.58, c = 8.58 A; $\beta = 90° \pm 10'$, Z = 4 $BaAl_2Si_2O_8$ ($\sigma = 3.31$). The absences imply space group $P2_1/a$, but some accidental absences cause the group to appear to be $Pna2_1$ or Pnam (unless the photographs are much overexposed). Smith found the structure by trial and error on the basis of the structure of danburite*; no distinction was made between Si and Al atoms, and it was assumed that they were randomly distributed over the sites for Si and B in danburite. The danburite-type orthorhombic form for the structure was refined by means of Fourier synthesis to give $R_{hk0} = 13\%$ and $R_{h0l} = 14\%$. No projections on the yz plane were calculated and 10 of the 13 atoms overlap in pairs in the xy projection, so no precise values could be given for the y coordinates of atoms associated with the mirror pseudoplane. The $\underline{x}$ and $\underline{z}$ of two pairs of (Si, Al) atoms and of the $\overline{O}$ of $(Si, Al)_2O_7$ remain of poor accuracy, because these overlap in the xy projection. Of the 39 parameters, 18 remain approximate. In some cases the $\underline{x}$ derived from the two projections do not agree very well. Smith thus gives a list of averaged values (for the danburite structure) together with the exact coordinates actually found; the analysis is performed with reference to that model, although the actual structure clearly deviates from it. He gives as probable reasons for the deviation that the specimens were twinned (at very small angles), that the atoms are slightly displaced for reasons of energy, and finally that a certain degree of order occurs in the array of Si and Al atoms, although he considers that perfect ordering could occur within the orthorhombic structure. His analysis implies that the two crystallographically distinct kinds of tetrahedron in the ideal model have Si:Al = 1:1, i.e. that a tetrahedron contains $Si_{\frac{1}{2}}Al_{\frac{1}{2}}$ [the mean (Si, Al)-O distances are 1.68 and 1.71 A to a low accuracy, since the usual difference in the Si-O and Al-O distances is about 0.1 A].

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*Spencer [4] stated that the cell parameters are similar to those of topaz, but Smith rejected the idea that there is any structural resemblance.

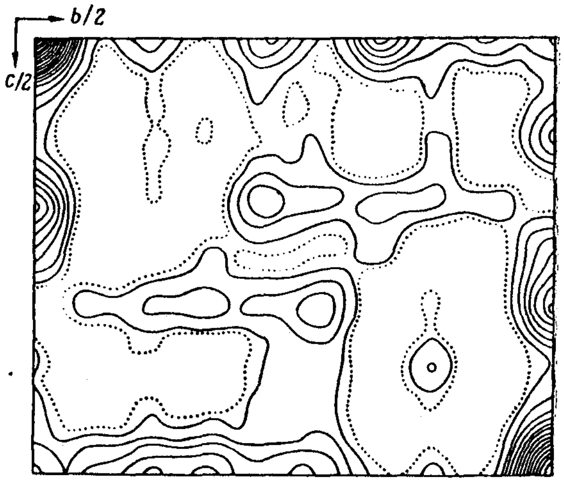

Fig. 1. Patterson projection on yz (one quadrant) for hurlbutite (paracelsian).

Smith would have that $Si_{\frac{1}{2}}Al_{\frac{1}{2}}$ expresses the crystallographic analysis; on this basis he compares the results with those for other aluminosilicates and proposes that the bond length is linearly related to the Si:Al ratio, with the consequence that he introduces new "standard" (and, in his view, exact) values for Si-O (1.60_5 A) and Al-O (1.78 A) for aluminosilicates; then the distances observed for paracelsian correspond exactly to $Si_{\frac{1}{2}}Al_{\frac{1}{2}}$.

A detailed study of Smith's work has shown us that the analysis has not been carried through properly. In any case, it is impossible to consider the $Si_{\frac{1}{2}}Al_{\frac{1}{2}}$ formula seriously when so many of the parameters are approximate, so we assumed that the distributions of the Si and Al remain unknown. Although Smith showed that paracelsian has no danburite Si_2O_7 and Al_2O_7 groups, he did not examine other possible ordered arrays for the Si and Al atoms. As soon as we had finished analyzing the structure of hurlbutite [3], we found that it was very probable that the cations in this mineral have the same distribution as those in paracelsian. The first indication of this is that the x-ray patterns of the two minerals have much in common. For example, paracelsian gives reflections of $0kl$ type with $k + l = 2n + 1$, which inevitably imply a plane of symmetry parallel to (100); these actually appear on overexposed films, whereas those of $00l$ type with $l = 2n + 1$ remain absent, although this feature is not an essential consequence of the space group. We have found the same effect [1], rather better developed, for hurlbutite, whose $0kl$ reflections with $k + l = 2n$ are rather stronger than the others of that type, whereas the $00l$ reflections with $l = 2n + 1$ do not appear at all. The reason for the weakened reflections is mainly that P and Be differ greatly in atomic number; this large difference enabled us to distinguish the atoms in terms of the "extra" reflections and to check the analysis on the electron-density patterns *. The effect has the same cause in the case of paracelsian, but is not nearly so strongly developed because there is only the minimum difference between Si and Al. We anticipated that we would be able to differentiate the Si and Al in terms of the volumes of their tetrahedra and that we would thereby be able to test for the hurlbutite pattern, so we analyzed Smith's results [6] with great care.

A great variety is seen in the complete set of (Si, Al)-O and O-O distances for the four kinds of tetrahedra. Some of this arises from the poor accuracy of 50% of the coordinates, so in our subsequent analysis we used only the most reliable ones (Smith's exact coordinates). We entirely neglected any bond that includes one of the four atoms that overlap in pairs on the xz projection; of the others we took account only of those whose lengths depend very little on the y coordinates, which remain undefined for most of the atoms. The four monoclinic tetrahedra can be split into two hurlbutite pairs, which differ on average by 0.12 A for the O-O distances and by 0.07 A for the (Si, Al)-O ones. The most reliable distances (in Smith's symbols) are 1.64 and 1.71 for $(Si, Al)_2$-O_5, 1.66 and 1.73 for $(Si, Al)_2$-O_2, 2.62 and 2.75 for O_2-O_5, etc. These results show that the Si actually is segregated from the Al in paracelsian; the two form an ordered array exactly as do P and Be in hurlbutite. We have calculated R for the ordered structure and for the structure with Si and Al disordered; the first gives a value better by 0.5% (by 3% of R itself). The Si and Al differ very little in scattering power, and Ba is very heavy, so this improvement is quite considerable.

The errors in the coordinates tended to obscure this ordered array of Si and Al atoms, so we have sought to revise the coordinates by means of the analogy with hurlbutite. The corrected coordinates, while not of very special precision, correspond better to the real structure than do ones averaged for overlapping atoms, the more so since many of the corrections do not exceed the error of experiment.

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*The Patterson diagram represents the intensities most fully. Figure 1 shows the yz pattern for hurlbutite, which, if it were exactly analogous to danburite, would give a centered yz projection (in accordance with the n in Pnam), in which case the peak in the right lower corner of the quadrant would be exactly the one at the top left corner; in fact, it is some 30% weaker. The same is true for other peaks related by the pseudocenter at the middle of the quadrant; the effect is very marked for most such pairs, but not for all, the controlling factor being the relative contribution from P + Be to each such peak.

Coordinates of the Basal Atoms in Paracelsian (and Hurlbutite) ***

	x	y	z	x	y	z	
Ba	0.397 —	0.088 —	0.751 —	0.386	0.085	0.753	Ca
Si_I $(Si, Al)_I$	0.067 (0.065*)	0.196 —	0.435 (0.440**)	0.059	0.196	0.435	Be_I
Si_{II} $(Si, Al)_{II}$	0.270 —	0.417 —	0.938 —	0.265	0.421	0.933	Be_{II}
Al_I $(Si, Al)_{II}$	0.274 —	0.419 (0.417*)	0.571 —	0.264	0.418	0.560	P_I
Al_{II} $(Si, Al)_I$	0.064 (0.065*)	0.196 —	0.067 (0.069**)	0.059	0.197	0.060	P_{II}
O_I (O_I)	0.194 (0.195*)	0.088 —	0.501 —	0.188	0.083	0.508	O_I
O_{II}	0.195 —	0.083 (0.088*)	0.003 —	0.189	0.085	0.993	O_{II}
O_{III} (O_{II})	0.130 —	0.360 (0.362*)	0.454 —	0.121	0.367	0.438	O_{III}
O_{IV}	0.128 —	0.365 (0.362*)	0.046 —	0.126	0.364	0.055	O_{IV}
O_V (O_{III})	0.428 (0.425*)	0.313 —	0.555 (0.560**)	0.412	0.308	0.565	O_V
O_{VI}	0.417 (0.425*)	0.316 (0.313*)	0.940 (0.931**)	0.415	0.309	0.931	O_{VI}
O_{VII} (O_{IV})	0.007 —	0.173 —	0.255 —	0.006	0.150	0.247	O_{VII}
O_{VIII} (O_V)	0.209 —	0.412 —	0.758 —	0.184	0.421	0.745	O_{VIII}

*Mean from the xy projection for two atoms related by pseudosymmetry

** Mean for two atoms overlapping in the xz projection.

*** The values in brackets are those from [6].

The Table gives the original coordinates and the revised ones, as well as the parameters for hurlbutite. Figures 2 and 3 show the main structural features of danburite and paracelsian.

The corrected coordinates give us revised distances as follows: Si-O and O-O in the SiO_4 tetrahedra, 1.65 and 2.70 A (average), respectively; Al-O and O-O in the AlO_4 tetrahedra, 1.72_5 and 2.82 A; Ba-O, seven values ranging from 2.73 to 2.83 A.

Thus paracelsian and hurlbutite have the same type of structure (Ba, Si, and Al replace Ca, Be, and P); the silicate has the same structure as the phosphate even though the cations are different.

The ordered array for the Si and Al agrees better than a random array with the experimental results; it is also in full agreement with current ideas on the distributions of the Si and Al in feldspars. For instance, in a recent [7] paper on celsian $BaAl_2Si_2O_8$ (the usual monoclinic form) it has been shown that the Si and Al alternate; each oxygen atom has one silicon atom and one aluminum atom as its neighbors. Reference is made there to the similar behavior of Si and Al in anorthite [8], and it is supposed (following Lowenstein [9]) that this alternation of Si and Al is electrostatically the most favorable if Al:Si = 1:1.

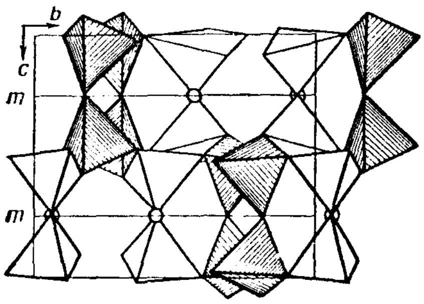

Fig. 2

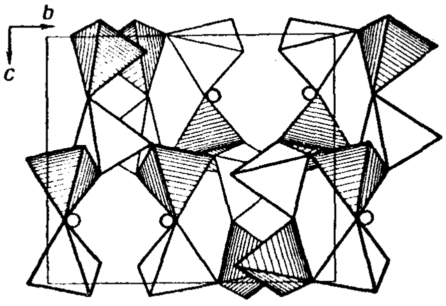

Fig. 3

The interatomic distances found for celsian (on average 1.64 and 2.67 A for Si-O and O-O in the Si tetrahedra, and 1.71_5 and 2.80 A for Al-O and O-O in the Al tetrahedra) agree well with the values we find for paracelsian; they do not agree with Smith's 'standard' values of 1.60_5 and 1.78 ± 0.02 A for Si-O and Al-O, respectively. However, in an attempt to avoid conflict with Smith's values, the explanation is offered for celsian that the Si and Al are not completely ordered, although no obvious causes for any effect on the degree of order are apparent. We consider that Smith's values for "pure" Si-O and Al-O bonds, which he discusses very one-sidedly in a later paper [10] on these distances, are unsound and must be revised.

Note. After this paper was written we saw the results of Smith et al. for spurrite [11]; the Si-O distances he gives there (1.626-1.637 A) agree completely with our figure (1.64 A). In that paper [11] doubt is cast on the earlier assumption that the Si-O distance is constant at 1.605 A unless special causes are operative (we must remember here that this dogmatic statement of Smith's was made in 1953, when he was only 22 years old).

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