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Crystal structure of rustumite

RUSTUMITE was first described by Agrell[1] as $Ca_4Si_2O_7(OH)_2$, space group Cc or C2/c, $a = 7.62(5)$, $b = 18.55(5)$, $c = 15.51(5)$Å, $\beta = 104°20'(10')$, with $Z = 10$. The crystal structure we describe here, in space group C2/c ($R = 11.3\%$ for all data) gives, instead, an ideal formula $Ca_{10}(Si_2O_7)_2SiO_4Cl_2(OH)_2$, with $Z = 4$. The important features of the completed structure are the presence of chlorine and of orthosilicate groups in addition to Si_2O_7 groups.

The experimental intensity data, from a naturally occurring single crystal, comprised 2,100 independent reflections for layers 0–9, k,l ($\sin^2\theta < 0.2$) obtained with a Hilger and Watts Y-190 linear diffractometer and Mo-Kα radiation, using the cell dimensions given by Agrell[1]. Of this data, 282 reflections were classed as 'unobserved', and were excluded from all further calculations.

Solution of the Patterson map was hindered by the large number of atoms in the unit cell ($\sim$ 150), permitting the detection of only four (or more)-multiple peaks, and the presence of subtranslations of $\sim a/4$, $\sim b/6$ and $\sim c/6$ among the Patterson peaks. Nevertheless, an initial structure was established in the space group C1 by double superposition using two multiple peaks as shift vectors[2] and consideration of the vector subsystem[3].

In the course of refinement by the usual Fourier methods, as the remaining atoms of the structure appeared, the presence of first the twofold axis and finally the c-glide became obvious. The final solution in the space group C2/c, refined by block diagonal least squares using all of the observed reflections except 171 which showed especially poor agreement between F_o and F_c, gave the parameters of Table 1. At this stage R was 7.4% for the data included in least squares (11.3% over all observed data).

In the asymmetric unit it is easy to pick out, apart from the five Ca atoms, an $(Si_2O_7)^{6-}$ group (involving Si1 and Si2) and an $(SiO_4)^{4-}$ group involving Si3 on a twofold axis (Fig. 1), leaving only O10 and O11. The atom O10 yields a peak in the electron density maps comparable in size with Si3, gives an occupancy factor (refined as oxygen) of $\sim$ 2.0 in least squares refinement and has no nearest-neighbour Ca atom closer than 2.75Å, all consistent with this atom being Cl. Bogomolov and Organova (personal communication) have given analytical data for chloride in rustumite.

Whereas all other O atoms, including O10, are four-coordinate, O11 has only three Ca nearest neighbours (Ca – O, 2.33 – 2.37Å) all to one side of it, clearly allowing completion of its tetrahedral coordination by a hydrogen atom. Therefore, although there is no clear evidence for the H atom in the electron density or difference maps, O11 can reasonably be regarded as a hydroxyl group to give the formula $Ca_5(Si_2O_7)(SiO_4)_{0.5}Cl(OH)$ for the formula of the assymetric unit (eight per cell) of rustumite. The cell contents are then $Ca_{40}Si_{20}O_{72}Cl_8(OH)_8$ compared with $Ca_{40}Si_{20}O_{70}(OH)_{20}$ from Agrell's formula.

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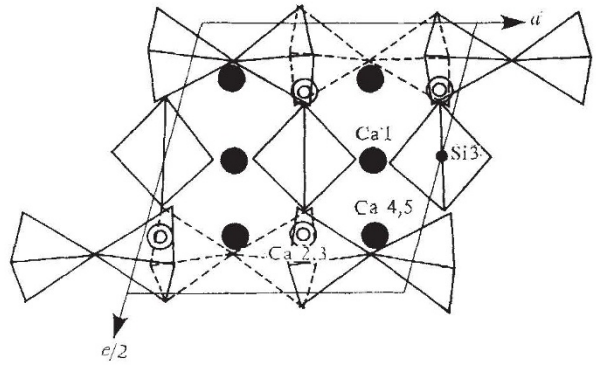

Fig. 1 Rustumite—(O10) projection of one half of the unit-cell. The Si_2O_7 and SiO_4 groups are indicated as polyhedra. The Ca atoms overlap in pairs: ●, (Ca1, Ca1′), (Ca4, Ca5); ○, (Ca2, Ca3).

Table 1 Rustumite—atomic parameters

Atom	Fractional coordinates (10^4) x/a	y/b	z/c	B_{iso} Å^2(10^2)	Occupancy (10^2)
Ca(1)	2,582(4)	3,520(1)	2,498(2)	95(4)	98(1)
Ca(2)	4,399(4)	3,024(1)	6,192(2)	96(4)	97(1)
Ca(3)	5,760(4)	2,068(1)	4,039(2)	95(4)	96(1)
Ca(4)	3,298(4)	232(2)	4,017(2)	102(4)	98(1)
Ca(5)	3,106(4)	5,148(1)	3,964(2)	93(4)	97(1)
Si(1)	4,420(5)	6,319(2)	5,614(2)	76(5)	98(1)
Si(2)	3,692(5)	1,340(2)	5,643(2)	83(5)	99(1)
O(1)	3,349(12)	3,786(5)	4,161(6)	99(16)	93(2)
O(2)	4,782(12)	1,759(5)	6,518(6)	96(15)	98(2)
O(3)	4,318(12)	523(5)	5,559(6)	118(15)	98(2)
O(4)	4,629(12)	5,760(5)	1,594(6)	95(15)	97(2)
O(5)	3,503(13)	1,770(5)	4,725(6)	110(17)	89(2)
O(6)	3,767(13)	6,870(5)	4,777(6)	105(16)	93(2)
O(7)	4,236(13)	3,277(5)	1,516(6)	136(16)	98(2)
O(8)	3,168(13)	4,778(5)	2,481(6)	107(15)	97(2)
O(9)	3,695(13)	4,476(5)	429(6)	119(16)	94(2)
O(10)	2,384(6)	2,961(2)	7,458(3)	54(6)	204(2)
O(11)	560(14)	5,881(5)	3,535(6)	123(17)	91(2)
Si(3)*	1/2	5,276(3)	1/4	82(8)	97(2)

Estimated standard deviations applicable to the least significant digits are given in parentheses.
*Si(3) is in the special position 4e of C2/c, while all other atoms occupy general (8f) positions.

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