Si_3O_{10} Groups in the Crystal Structure of Ardennite*

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Dedicated to Professor B. E. Warren for his 65th birthday

The rare mineral ardennite has the structural formula

$$Mn_2^{2+}(Mn^{2+},Ca)_2 (AlOH)_4[(Mg,Al,Fe^{3+})OH]_2(As,V)O_4Si_3O_{10}(SiO_4)_2.$$

Refined cell dimensions at 21 °C (λCu K$\alpha_1 = 1.54051$ Å) are 8.7126 ± 0.0008, 5.8108 ± 0.0008, 18.5214 ± 0.0011 Å; $Z=2$, $Pnmm$, $D_{calc} = 3.74$ g.cm^{-3}, $D_{obs} = 3.69$–3.74 g.cm^{-3}. A total of 900 reflections were obtained on a Weissenberg-type automated Supper-Pace diffractometer supplemented by Weissenberg and precession film data. The structure was refined by least-squares method to a residual R of 7.0% including 110 unobserved reflections which were given a value of $F(minimum)/\sqrt{3}$. The crystal structure can be derived from that of epidote by Ito-type twinning; it leads to the Si_3O_{10} groups, which strengthen the bond chains along c. As in epidote, chains of octahedra sharing edges extend along b. They are here connected by the SiO_4 and Si_3O_{10} groups. The cleavage is given as (001) in the literature for both epidote and ardennite; we determined it to be (100) for the two minerals. $(As,V)O_4$ tetrahedra do not share corners with SiO_4 tetrahedra. The polyhedra around Mn and especially (Mn,Ca) are irregular, suggesting abnormal magnetic behavior for ardennite. Bond lengths and temperature factors are normal. The average metal–oxygen distances are: for Mn 2.198 (5 nearest), for (Mn,Ca) 2.239 (5 nearest), for Al 1.911, for (Mg,Al,Fe) 2.011, for (As,V) 1.698, for Si 1.631 Å. The angle Si–O–Si is 126°.

Introduction

Ardennite is a rare arsenic-vanadium silicate, which has been found so far in the Ardennes, Belgium, in Piemont, Italy, and in the Jhabua district, India. The possibility that As and V might substitute for Si aroused our interest in the crystal structure. Professor J. D. H. Donnay collected a specimen at the type locality, Salm-Château, Ardennes, Belgium, which had been reopened on the occasion of the Liège meeting of the French Mineralogical Society in 1964. Other mineralogists did likewise, and as a result, Dr M. Semet and Professor J. Moreau (Semet & Moreau, 1965), of the University of Louvain, published a detailed account of ardennite mineralogy, with two new chemical analyses (Table 1) and a summary of previous work. They generously discontinued their own structure work when they heard of our efforts. A chemical analysis of a bulk sample (4·3 g) of our specimen was performed by C. O. Ingamells (Table 1).

Experimental procedure

The crystal chosen for data collection on the Weissenberg automated diffractometer has cell dimensions

$a = 8.7126 \pm 0.0008$, $b = 5.8108 \pm 0.0008$, $c = 18.5214 \pm 0.0011$ Å, at 21 °C. These were determined from back-reflection Weissenberg photographs about the a and b

Table 1. *Recent analyses of ardennite from Salm-Château, Belgium**

	1	2	3
SiO_2	28·20	27·85	28·14
Al_2O_3	23·80	23·55	23·22
MnO	26·75	25·70	25·33
Mn_2O_3	–	–	0·00
As_2O_5	11·25	13·25	9·85
V_2O_5	1·86	0·89	0·82
Fe_2O_3	1·22	0·86	1·50
FeO	0·00	0·00	0·00
MgO	2·30	2·30	3·83
CaO	1·17	1·17	1·50
CuO	0·57	0·26	0·46
Cr_2O_3	–	–	0·12
Misc.†	–	–	0·11
F_2	–	–	0·14
H_2O^+	5·10	5·10	5·04
H_2O^-	0·02	0·02	0·00
Total	101·26	100·95	100·06
Less O = F			0·06
			100·00

axes, with Cu $K\alpha$ radiation ($\lambda\alpha_1 = 1\cdot54051$, $\lambda\alpha_2 = 1\cdot54434$ Å), the measurements of which were treated by the Burnham LCLSQ least-squares refinement program. The crystal size is $0\cdot05 \times 0\cdot08 \times 0\cdot10$ mm. The density, calculated for 2 formula units per cell with the help of Inga-mells's analysis (Table 1) to obtain the formula weight, is $3\cdot74$ g.cm^{-3}. Densities measured on the Berman balance range from $3\cdot69$ to $3\cdot74$ g.cm^{-3} for the crystals used in the electron-probe analysis. Semet & Moreau (1965, p.559) concluded that $3\cdot747$ g.cm^{-3} should be considered the best experimental density for their ardennite sample. Systematic X-ray extinctions gave the aspect $Pn**$. Statistical analyses of F and E values indicate the presence of a center of symmetry leading to the space group $Pnmm$ (D_{2h}^{13}); for example $\langle|E|\rangle$ equals $0\cdot788$ and $\langle|E^2-1|\rangle$ equals $1\cdot061$ as compared with the theoretical values $0\cdot798$ and $0\cdot968$, respectively, for centrosymmetric space groups (Karle & Karle, 1963) and $0\cdot89$ and $0\cdot74$, respectively, for noncentrosymmetric space groups (Karle & Karle, 1966a).

Our choice of axes is different from that of Semet & Moreau (1965); it is meant to stress the structural relation between epidote and ardennite, first pointed out by Strunz (1935), which will be discussed below. In our setting, the unique, easy, and perfect cleavage is (100), which is to be expected from the structure as will be shown below. Since this finding disagrees with the data in the literature, where the cleavage is reported to be perpendicular to the $18\cdot52$ Å translation, we checked it repeatedly. Cleavage fragments were mounted with the cleavage face in polar position on the two-circle goniometer. Precession photographs always showed the $E-W$ line to correspond to the $8\cdot71$ Å translation.

The intensities were measured on the diffractometer, in Cu $K\alpha$ radiation, from five b-axis levels containing 898 independent reflections, 275 of which were too weak to be observed. Weissenberg photographs, taken with Cu $K\alpha$ radiation and 12-hour exposures, permitted visual estimation of an additional 165 weak reflections, leaving only 110 unobserved ones. Two more reflections, 020 and 040, were obtained by visual estimation from a (001)$_0^*$ precession film taken with Mo $K\alpha$ radiation, thus bringing the total number of reflections to 900 (Table 5). The intensities were corrected for Lorentz and polarization factors; Burnham's GNABS program was used to eliminate absorption errors. An estimate of the accuracy of the observed F values, based on the scatter of 13 sets of symmetry-related strong and medium-strong test reflections, indicates a standard deviation for a single intensity measurement ranging from $3\cdot4$ to $25\cdot0$%, with an average value of $9\cdot4$%, so that an R value of $4\cdot7$% is the best we should hope for. A striking intensity feature is the relative faintness of all reflections with $h+k=2n+1$, indicating a pseudo C-centering of the structure. Reflections $10l$; $14l$; $0,2n+1,2n+1$ are especially weak. This pseudo C-centering is also evident on a three-dimensional Patterson synthesis, where the peak at $\frac{1}{2}\frac{1}{2}0$ reaches half the height of the origin peak.

Structure determination

A comparison of the ardennite and epidote cell dimensions is indicative of an Ito-type twin relation between the two structures: a is equal to $8\cdot71$ Å for ardennite and $8\cdot88$ for epidote; b equals $5\cdot81$ and $5\cdot63$, respectively; c equals $18\cdot52$ for ardennite, is nearly equal to the ($2c\sin\beta$) value of $18\cdot32$ for epidote (calculated from $c=10\cdot22$ and $\beta=116°20'$, values we obtained for epidote from the Strathcona Mine, Sudbury area, Ontario, Canada).

One of us (Donnay, 1965, 1966) tried long and unsuccessfully to obtain a reasonable trial structure, beginning with the known epidote structure determined by Belov & Rumanova (1953) and Ito, Morimoto & Sadanaga (1954). The Patterson synthesis was calculated for us by Dr W. Fischer at the University Computing Center in Marburg, Germany. When analyzed in a manner analogous to the one used by Ito *et al.* (1954), this Patterson synthesis showed all the cations except (Mg, Al) but did not bring out the oxygen framework of tetrahedra and octahedra.*

We then decided to try the Karle-Karle symbolic addition procedure (Karle & Karle, 1963, 1966b), which had not yet been used on any inorganic compound containing heavy atoms. We obtained advice and generous computing aid from Dr I. Karle, who used the programs written in her laboratory to obtain a calculation of the E values and a listing of all possible combinations $E_\mathbf{h}, E_\mathbf{k}, E_\mathbf{h+k}$ with $E>1\cdot5$. A great number of strong relations between $E_{h2l}, E_{\bar{h}2\bar{l}}, E_{040}$, and $E_{hk6}, E_{\bar{h}\bar{k}6}, E_{0012}$ proved the signs of 040 and 0012 to be positive. Three more signs were chosen to fix the origin and five more unknown signs were included in the unit factors a to e (Table 2). After two cycles of hand calculations with the Σ_2 equation, 30 signs were known; c was found to be negative and e positive. The third cycle gave 15 more signs, confirmed a to be

Table 2. *Starting set of reflections used for statistical method*

h	k	l	$|E|$	Sign	
4	2	5	3·93	+	} from choice of
7	2	5	2·66	+	} origin
1	1	5	2·54	+	
0	4	0	3·98	+	} from strong
0	0	12	2·84	+	} relations
8	0	2	2·63 a	a becomes $+1$	
4	2	6	3·80 b	b doubtful	
4	2	7	3·54 c	c becomes -1	
2	2	5	2·94 d	d becomes $+1$	
5	3	10	2·82 e	e becomes $+1$	

* After the structure was solved, the coordinates of the cations as found in the Patterson synthesis were used for structure-factor calculations. In this calculation, 335 signs out of 369 for the reflections with $F_o > 36\cdot0$ were found to be correct. At the time when we had only the data from the Patterson synthesis, however, we did not trust our results because we could not place the expected anion polyhedra around the observed cation sites.

Table 3. *Fractional atomic coordinates in ardennite structure*

Values obtained from Patterson function, P; from E map, followed by ϱ_E maximum; final refined coordinates with standard deviation and isotropic temperature factor B from last isotropic refinement.

Atom and position occupied	From P	From E	ϱ_E Max.	Final	B (Å²)
(Mn,Ca) 4(f)	0·950 $\frac{1}{4}$ 0·154	0·950 $\frac{1}{4}$ 0·155	396	0·9441 ± 2 $\frac{1}{4}$ 0·1554 ± 1	0·95 ± 5
Mn 4(f)	0·400 $\frac{3}{4}$ 0·152	0·400 $\frac{3}{4}$ 0·160	392	0·3956 ± 3 $\frac{3}{4}$ 0·1600 ± 1	0·95 ± 5
Al(1) 4(c)	0 0 0	0 0 0	214	0 0 0	0·62 ± 7
Al(2) 4(d)	$\frac{1}{2}$ 0 0	$\frac{1}{2}$ 0 0	252	$\frac{1}{2}$ 0 0	0·76 ± 7
(Mg,Al,Fe) 4(e)		0·675 −0·002 $\frac{1}{4}$	213	0·6787 ± 4 −0·0016 ± 8 $\frac{1}{4}$	0·96 ± 7
Si(1) 4(f)	0·750 $\frac{3}{4}$ 0·096	0·767 $\frac{3}{4}$ 0·100	340	0·7641 ± 4 $\frac{3}{4}$ 0·0970 ± 2	0·37 ± 6
Si(2) 4(f)	0·267 $\frac{1}{4}$ 0·091	0·270 $\frac{1}{4}$ 0·097	264	0·2766 ± 4 $\frac{1}{4}$ 0·0951 ± 2	0·59 ± 7
Si(3) 2(a)	0·579 $\frac{1}{4}$ $\frac{1}{4}$	0·333 $\frac{1}{4}$ $\frac{1}{4}$	205	0·3412 ± 5 $\frac{1}{4}$ $\frac{1}{4}$	0·66 ± 9
(As,V) 2(b)	0·046 $\frac{3}{4}$ $\frac{1}{4}$	0·042 $\frac{3}{4}$ $\frac{1}{4}$	633	0·0426 ± 2 $\frac{3}{4}$ $\frac{1}{4}$	0·45 ± 5
O(1) 8(g)		0·117 0·025 −0·078	104	0·1284 ± 6 0·0265 ± 13 −0·0828 ± 3	0·82 ± 11
O(2) 8(g)		0·622 −0·008 −0·083	130	0·6241 ± 6 −0·0207 ± 13 −0·0833 ± 3	0·81 ± 11
O(3) 4(f)		0·133 $\frac{1}{4}$ 0·042	84	0·1127 ± 9 $\frac{1}{4}$ 0·0526 ± 4	0·86 ± 16
O(4) 4(f)		0·617 $\frac{3}{4}$ 0·040	123	0·6169 ± 10 $\frac{3}{4}$ 0·0415 ± 4	0·91 ± 16
O(5) 4(e)		0·950 −0·050 $\frac{1}{4}$	114	0·9299 ± 10 −0·0068 ± 21 $\frac{1}{4}$	1·02 ± 15
O(6) 4(e)		0·438 0·042 $\frac{1}{4}$	88	0·4431 ± 9 0·0146 ± 20 $\frac{1}{4}$	1·06 ± 16
O(7) 4(f)		0·675 $\frac{3}{4}$ 0·175	105	0·6817 ± 10 $\frac{3}{4}$ 0·1776 ± 5	1·19 ± 16
O(8) 4(f)		0·225 $\frac{1}{4}$ 0·182	81	0·2232 ± 9 $\frac{1}{4}$ 0·1805 ± 4	0·78 ± 16
O(9) 4(f)		0·200 $\frac{3}{4}$ 0·182	58	0·1540 ± 11 $\frac{3}{4}$ 0·1763 ± 5	1·36 ± 17

Table 3 *(cont.)*

Atom and position occupied	From P	From E	ϱ_E Max.	Final	B (Å²)
OH(1)		0·120		0·1128 ± 10	
4(f)		¾	101	¾	0·95 ± 16
		0·028		0·0323 ± 5	
OH(2)		0·622		0·6149 ± 9	
4(f)		¼	162	¼	0·35 ± 14
		0·038		0·0356 ± 4	
OH(3)		0·700		0·6973 ± 10	
4(f)		¼	132	¼	0·91 ± 17
		0·188		0·1817 ± 4	

Table 4. *Anisotropic temperature factors for ardennite*

The β_{ij} of the expression

$$\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{23}2kl + \beta_{31}2lh + \beta_{12}2hk)\right]$$

are converted into B_{ij} in Å², which are directly comparable with the B values of Table 3.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
(Mn,Ca)	1·18 ± 8	0·89 ± 15	0·82 ± 7	0	0·16 ± 6	0
Mn	1·03 ± 7	1·23 ± 15	0·79 ± 7	0	−0·15 ± 6	0
Al(1)	0·64 ± 11	0·78 ± 20	0·52 ± 11	−0·10 ± 14	0·04 ± 9	−0·05 ± 13
Al(2)	0·82 ± 12	0·91 ± 21	0·61 ± 11	0·06 ± 15	−0·02 ± 10	−0·01 ± 13
(Mg,Al,Fe)	1·29 ± 13	0·95 ± 22	0·76 ± 12	−0·08 ± 15	0	0
Si(1)	0·38 ± 11	0·56 ± 23	0·33 ± 11	0	−0·02 ± 9	0
Si(2)	0·56 ± 12	0·94 ± 24	0·47 ± 12	0	−0·03 ± 9	0
Si(3)	0·75 ± 16	0·80 ± 33	0·50 ± 16	0	0	0
(As,V)	0·63 ± 7	0·27 ± 14*	0·45 ± 6	0	0	0
O(1)	1·30 ± 21	0·88 ± 42	0·48 ± 21	−0·24 ± 23	−0·17 ± 17	−0·07 ± 21
O(2)	0·67 ± 20	1·03 ± 40	0·75 ± 21	0·20 ± 23	0·05 ± 17	0·28 ± 21
O(3)	0·72 ± 31	1·92 ± 57	0·48 ± 31	0	−0·14 ± 25	0
O(4)	0·96 ± 31	1·69 ± 57	0·50 ± 30	0	−0·01 ± 25	0
O(5)	1·39 ± 31	1·00 ± 50	0·88 ± 30	−0·13 ± 36	0	0
O(6)	0·91 ± 30	1·43 ± 53	1·22 ± 30	−0·03 ± 35	0	0
O(7)	1·01 ± 32	1·71 ± 63	0·74 ± 32	0	0·5 ± 27	0
O(8)	0·91 ± 30	0·33 ± 57	1·01 ± 32	0	−0·26 ± 25	0
O(9)	1·79 ± 36	1·26 ± 62	1·00 ± 33	0	0·35 ± 30	0
OH(1)	0·90 ± 32	1·08 ± 56	0·91 ± 33	0	0·24 ± 26	0
OH(2)	0·67 ± 26	0·27 ± 53*	0·27 ± 29*	0	−0·13 ± 22	0
OH(3)	0·74 ± 31	0·91 ± 60	1·06 ± 34	0	0·42 ± 25	0

* Values were kept constant, because they tended to become negative.

positive, and indicated d to be very probably positive. There was no hint as yet of the correct sign of b. After the fifth cycle 95 out of 118 signs with $E > 1·5$ were known, still leaving b undetermined. Then, for both possible signs of b, three more Σ_2 cycles for all 168 E values $> 1·3$ were calculated by computer, immediately followed by a three-dimensional E map. In the case of $b = +1$, 159 signs could be determined, and ϱ_{min} in the E map was -178; whereas for $b = -1$, 150 signs could be determined, and ϱ_{min} was -185. The latter E map made no sense at all, but the one calculated with $b = +1$ showed all the atoms, the cations being nearly in the same places as in the Patterson synthesis. The peak heights gave a good indication of the chemical nature of the atoms (Table 3). By checking against the final calculated signs, only one out of these 159 signs was found to be wrong (that of 702).

Refinement of coordinates was carried out with the modified Busing–Martin–Levy least-squares program at The Johns Hopkins University Computing Center. For atomic scattering factors we used As³⁺ from *International Tables for X-ray Crystallography*, Vol. III, p. 206; Mn⁺, Ca⁺, Fe⁺, Al⁺, Mg²⁺, V³⁺, Si³⁺, and O⁻ calculated by Hanson, Herman, Lea & Skillman (1966). With isotropic temperature factors and F(unobserved) set equal to $(1/\sqrt{3})F$(minimum), the residual $R = \Sigma \|F_o| - |F_c\|/\Sigma |F_o|$ dropped from 18·0 to 8·4%; continuing with anisotropic temperature factors the residual dropped to 7·9%. We experimented with refinement of the multiplier for various scattering factors but obtained no significant improvement.

Next we introduced anomalous dispersion corrections for all atoms, using the values of Dauben & Templeton (1955) and the SFLS5 least-squares pro-

gram of Prewitt. The consequent deviations from 0 (+) and 500 (−) for the phase angle, expressed in millicycles, run as high as 200 for several reflections (Table 5). Unobserved reflections are given the value $|F_{min}/|3|$. The R value with isotropic temperature factors (Table 3) for all 900 reflections dropped to 7·5% and, continuing with anisotropic temperature factors (Table 4) came to 7·0%. For the 240 strongest reflections with $F_o \geq 50$ an R value of 4·7% is obtained, in good agreement with the accuracy of our intensity measurements.

A comparison of atomic coordinates given by the Patterson map, the E map, and the final refinement (Table 3) shows the close agreement between the initial coordinates obtained from the E map and the final, refined ones. The bond lengths and their Pauling bond strengths (Table 6), as well as oxygen–oxygen approaches (Table 7), all fall within normal limits. Pauling bond strengths have been related roughly to bond lengths for all the cations except aluminum and silicon.

Discussion

The new and unexpected feature of the ardennite structure consists in the Si_3O_{10} groups of three tetrahedra, all pointing the same way and not alternating as in infinite chains, possessing symmetry $2mm$, and Si–O–Si bond angles of 126°. The usual value for this angle is close to 135° in infinite chains. This tritetrahedral group occurs jointly with individual SiO_4 groups in the ratio 1:2. Liebau (1962) surveyed the known silicate structures and stated the following rule: *tetrahedral groups that differ by more than one in the number of shared corners should not occur jointly in a silicate structure.* Professor F. Liebau (personal communication)

pointed out that ardennite is the third known exception to this rule; the other two are prehnite and zunyite.

The structural relationship with epidote is close indeed (Fig. 1): a mirror (001), passing through the origin of the cell, reflects the projected epidote structure in such a way that only very minor rearrangements in the immediate neighborhood of the mirror are needed to give ardennite (Fig. 2). In all the trial structures that we considered, we overlooked the possibility of placing one of the tetrahedra of the Si_2O_7 group on the 'Ito mirror', which thus reflects the second tetrahedron of the Si_2O_7 group on the other side, producing the Si_3O_{10} group. The formulae for the cell content of epidote and half the cell content of ardennite can be written so as to show their structural relation:

Epidote: Ca_2 Ca_2 $(Al, Fe^{3+})_2$ $(AlOH)_2$
Ardennite: Mn_2^{2+} $\square_2$ $(Mn^{2-}, Ca)_2$ $(AlOH)_2$

$\square_2$ $(AlO)_2$ $(Si_2O_7)_2$ $(SiO_4)_2$
$(AlOH)_2$ $[(Mg, Al, Fe^{3+})OH]_2$ $AsO_4 . Si_3O_{10}$ $(SiO_4)_2$
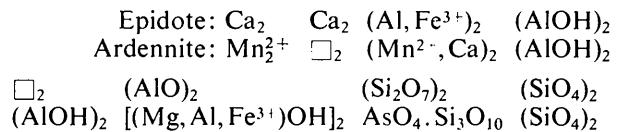
where $\square$ is a vacant site.

The epidote structure is composed of five-membered 'mixed rings' of the 'chair form' consisting of an aluminum octahedron, a silicon tetrahedron, another aluminum octahedron, and two linked silicon tetrahedra. In ardennite, two of these mixed rings, in addition to sharing their octahedra, share the central tetrahedron of the Si_3O_{10} group, forming a large bow-tie of two five-membered rings. Inversion through the centers of symmetry at the Al sites in both structures reproduces the individual rings or bow-ties and extends the chains along c. Combined with the chains of octahedra along b, the structures can be considered to consist of thick sheets parallel to (100). Neither mineral species can be

●Si ○Al ⊖Al,Fe ⊗Ca ○Oxygen ◎Oxygen and (OH)
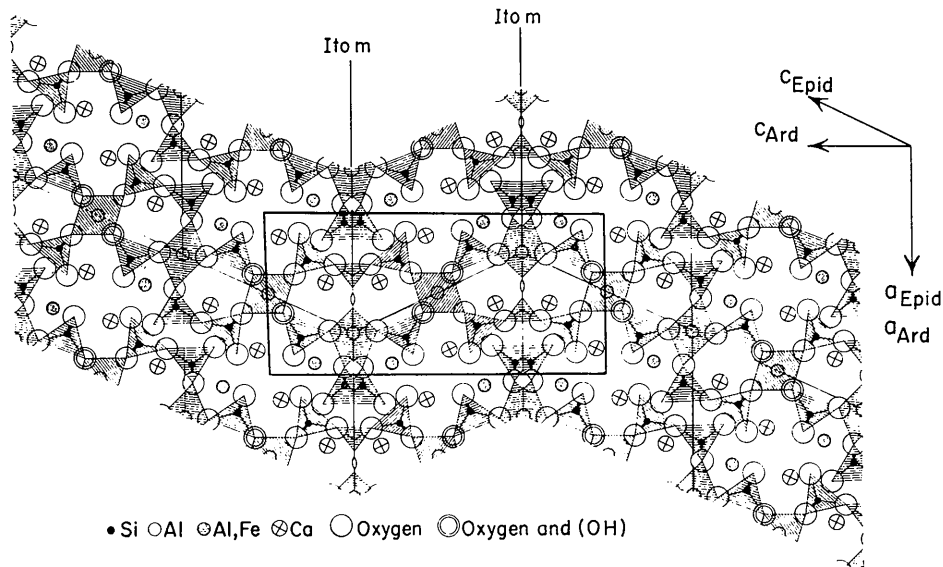
Fig. 1. The epidote structure (ten cells in all, after *Ito et al.*, 1954), projected on (010). The Ito mirrors, through the cell origin, are a distance d(001) apart. The outline of the orthorhombic cell related to that of ardennite, also projected on (010), is shown with heavy lines.

Table 5. *Observed and calculated structure factors**

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     0,0,L                   21   216   214   81          8   177   150   530        18   190   2C8   519         6   253   292   521
 2   396   408   545                                      9   670   703   510        19   264   284   521         7   405   427   41
 4   654   680   978              5,0,L                                              20   245   254   38          8   163   152   14
 6   275   232   394         0   64*   71   288              0,1,L                   21   163   161   955
 8   561   585   12          1   137   78   153          1   365   317   13                                          0,2,L
10   988  1062   531         2   137  136   972          3   327   362   512             5,1,L               0  2299  2344   517
12  3221  3383   13          3   656  642   14           5   212   212   10          0   317   359   40         2  1206  11C8   15
14  1145  1116   503         4   416  442   524          7   171   124   494          1   803   829   23         4  1965  1753   16
16   177   172   658         5  1042 1036   522          9   272   292   1           2   704   726   514         6  1679  1581   519
18   396   376   481         6   652  653   26          11   179   176   523          3   336   330   13         8  1393  1313   5
20  1430  1443   2C          7   579  566   25          13   565   549   18          4   565   528   995        1C  1495  1437   22
22   194   157   732         8   177  189   528         15   216   242   526          5   397   395   544        12   114   177   857
                            9   112  134   467         17   66*   23   593          6   115   1CC   97         14  1546  1526   2
     1,0,L                  10   158  166   554         19   66*   68   85           7   163   138   433        16  1477  1438   24
 0   275   258   11         11   112  112   611         21   66*   37   4            8   452   482   17         18   162   164   585
 1   137   61   551         12   112   59   259                                      9   66*   54   149        20   332   352   546
 2   227   208   507        13   251  224   505              1,1,L                  10  1249  1245   516        22   377   376   62
 3   137   144   512        14   187  181   1C           0   282   268   452         11   599   590   533
 4   112   35   978         15   610  6C8   29           1   366   412   552         12   350   331   30            1,2,L
 5   323   320   2C         16   437  463   53C          2   624   571   515         13   298   341   28         C   508   62d   510
 6   177   136   507        17   603  6C0   53G          3   799   752   512         14   141   150   32         1   804   852   12
 7   239   243   526        18   273  256   41           4   272   217   954         15   163   167   64         2   636   557   9
 8   292   264   18         19   177  168   10           5  2018  1878   18          16   370   421   990        3   725   654   5C8
 9   137   128   1C         20   64*   66   497          6  1785  1612   13          17   427   479   535        4   441   372   5C7
10   346   333   515                                     7  1464  1312   518         18   212   2C5   508        5   433   471   2
11   230   218   2C              6,0,L                   8   66*   17   904          19   231   222   504        6   568   465   9
12   158   137   998        0   266  271   561           9   115   75   669          20   289   3C6   39         7   535   463   5C2
13   64*   35   585         1   425  443   509          10  1073  1048   517                                     8   561   545   515
14   158   140   33         2   158  151   36           11   669   651   39               6,1,L               9   486   5CC   11
15   112   124   523         3   706  679   12          12   141   101   392         0   923   983   29         10   581   556   15
16   137   152   C          4  1289 13C0   16           13   491   508   995         1   66*   93   545        11   804   772   514
17   158   1C8   61         5   64*   64   577          14   313   377   13          2   438   447   529        12   384   381   5C8
18   137   151   541         6   302  331   955          15   755   768   531         3   66*   40   13         13   539   532   17
19   177   177   532         7   359  364   8           16   115   67   761          4   295   264   553        14   114   1C6   986
20   224   243   33         8   602  559   11           17   921   934   29          5   141   147   489        15   303   33C   510
21   64*   60   521         9   291  313   3            18   231   101   45          6   115   127   176        16   294   257   5C9
22   177   170   911        10   475  481   29          19   325   362   510         7   303   312   996        17   293   316   C
                           11   689  671   9            20   340   347   493         8   304   325   6          18   286   3C3   29
     2,0,L                  12   320  312   974          21   276   305   562         9   212   184   505        19   174   177   5C2
 0   645   720   24         13   334  353   521          22   586   605   527        10   820   8C4   530        20   350   376   528
 1   812   841   25         14   281  296   989                                     11   66*   75   57          21   303   338   19
 2   370   392   987        15   208  195   40               2,1,L                  12   678   695   31          22   242   267   16
 3   992   951   11         16  1191 1233   20           0   384   423   993         13   225   211   527
 4  1636  1492   997        17   766  8C3   510          1   365   342   992         14   66*   42   72             2,2,L
 5  1270  1206   526        18   158  116   935          2   386   378   499         15   66*   25   504        0   932   953   5c6
 6  1203  1161   18         19   177  186   523          3   748   688   509         16   329   330   557        1   322   226   853
 7  1303  1179   487                                     4   562   523   12          17   66*   73   66         2   895  1C3C   14
 8  1519  1384   4               7,0,L                   5   803   767   16          18   115   69   129        3   759   837   559
 9   767   692   492        0   327  319   532           6   509   438   522         19   141   128   962        4   184   222   33
10  1128  1034   518        1   502  514   41            7   417   418   517                                     5  1980  1757   16
11  1164  1139   522        2   257  277   19            8   510   534   13               7,1,L               6   272   2C3   947
12   602   588   22         3   236  2C4   21            9   141   103   978         C   469   471   998        7   373   259   556
13   311   335   22         4   64*  116   463          10   186   179   494         1   206   184   51         8   140   74   976
14  1017  1039   11         5   898  926   528          11   141   12C   469         2   66*   30   570        9   711   672   521
15  1433  1473   18         6   64*   68   605          12   231   213   980         3   303   3C8   499        10  2232  2C52   13
16   546   568   986        7   809  8C7   23           13   396   403   10          4   115   58   433        11   587   571   46
17   374   361   567        8   263  269   511          14   432   363   500         5   390   461   530        12   449   482   520
18   437   442   18         9   64*   59   303          15   600   546   520         6   706   716   517        13   66*   55   781
19   64*   78   472        10   486  486   23           16   243   245   28          7   554   586   17         14   114   51   565
20   487   498   23         11   504  522   545          17   501   519   18          8   179   141   36         15   501   467   535
21   372   357   46         12   158  155   539          18   457   466   525         9   447   4C6   23         16   276   3C4   37
22   452   473   532        13   64*   46   203          19   182   191   500        10   141   173   20         17   583   565   38
                           14   64*   45   941          20   185   189   25          11   437   411   531        18   398   426   2
     3,0,L                  15   355  378   42           21   66*   32   677         12   226   227   990        19   114   1C2   5C5
 0  1648  1737   14         16   64*   36   265          22   66*   48   415         13   163   175   507        2C   182   2CC   96C
 1   614   613   51C        17   335  351   552                                     14   177   192   506        21   929   9C2   526
 2  1126  1144   512                                         3,1,L                  15   141   111   90
 3   358   403   11              8,0,L                   0  2311  2409   16          16   141   124   49             3,2,L
 4   412   404   992        0   577  567   995           1   141   163   503         17   115   76   911        0   915   915   518
 5   410   362   506        1   539  527   523           2   66C   667   521                                     1   330   371   12
 6   177   213   467        2  1648 16C2   9             3   516   492   509              8,1,L               2   339   379   17
 7   367   335   1          3   64*   66   501           4   990   971   522         0   968   941   24         3   270   259   510
 8   683   664   9          4   112  122   498           5   200   212   15          1   293   364   45         4   220   246   42
 9   177   172   505        5   64*   54   55            6   596   631   39          2   678   691   518        5   225   196   3
10  1093  1039   515        6   112  155   0             7   66*   56   999          3   393   337   19         6   26C   332   541
11   428   425   15         7   563  564   2             8   299   316   3           4   115   81   902        7   246   176   493
12   974   982   19         8   237  231   525           9   226   241   3           5   592   588   537        8   114   55   48C
13   526   490   52C        9   112   91   966          10   405   439   557         6   242   283   51         9   114   98   955
14   572   614   507        10  1097 10C5   15          11   221   219   506.        7   289   277   46         10   478   444   28
15   381   379   17         11   279  274   38          12  1187  1199   23          8   66*   62   1          11   295   29C   515
16   137   134   948        12   64*   57   955          13   231   223   494         9   66*   64   132        12   434   4CC   525
17   158   149   492        13   592  577   519          14   502   484   497        10   632   639   529        13   295   337   23
18   363   370   50C        14   495  5C5   3            15   371   343   517        11   270   2C2   583        14   162   147   566
19   64*   27   706         15   137  113   523          16   974  1005   528        12   596   590   30         15   299   3C6   517
20   542   553   23                                     17   146   162   14          13   141   132   35         16   265   26C   5C
21   275   289   511             9,0,L                  18   66*   65   304          14   342   336   507        17   66*   85   973
22   457   487   534        0   551  547   548          19   182   179   19          15   446   419   38         18   66*   58   858
                           1   344  323   502          20   568   592   30                                      19   66*   79   7C
     4,0,L                  2   112   99   1C0          21   146   93   997               9,1,L               2C   211   225   53C
 0   759   720   514        3   589  564   12           22   335   349   565         0   206   191   527        21   2C5   238   8
 1  1333  1383   1o         4   493  510   37                                        1   115   11C   522
 2   64*   41   230         5   269  315   528               4,1,L                  2   218   155   504            4,2,L
 3   700   701   499        6   512  473   551           0   452   453   21          3   685   692   12         0   239   273   36
 4   514   5C4   17         7   158  146   43            1   485   534   526         4   322   334   21         1   140   162   523
 5  1349  1275   52C        8   112   69   35            2   387   393   513         5   231   198   514        2   659   665   559
 6   404   371   972        9   294  277   511           3   200   247   517         6   66*   35   672        3   6C3   722   515
 7   977   975   17         10   362  347   61           4   141   120   976         7   150   139   517        4  1258  12C8   959
 8  1304  1271   7          11   317  295   1            5  1094  1101   19          8   115   105   18         5  23C8  2283   15
 9   409   390   34         12   318  328   557          6   66*   79   45           9   360   376   507        6  2181  2132   11
10  1519  1513   11         13   227  211   5C7          7  1087  1052   515         10   198   184   494        7  1982  1957   513
11   970   966   526                                     8   315   309   16          11   428   448   13         8   339   355   956
12   381   414   987            1C,0,L                   9   141   145   973         12   66*   38   563        9   675   672   994
13   230   223   23         0   137  131   9            10   431   439   524                                    1C   661   643   515
14   289   269   4          1   188  197   12           11   285   249   61              10,1,L              11   114   1C1   3C6
15   112   115   153        2   690  671   8            12   182   178   27          0   199   2C1   537        12   338   338   484
16   615   6C0   2C         3   499  511   7            13   163   164   538         1   175   155   116        13   622   585   6
17   112   144   619        4   220  199   1            14   66*   22   270          2   126   1C6   26         14   372   373   12
18   476   461   991        5   137   95   494          15   412   364   531         3   66*   47   105        15   812   759   529
19   237   27*   1          6   749  789   13           16   64*   55   929          4   182   163   39         16   4C8   435   568
20   674   716   7          7   504  472   5C9          17   419   432   39          5   540   553   546
```

Table 5 (cont.)

4,2,L

L	|F|obs	|F|calc	phase
16	408	439	988
17	685	711	33
18	902	897	17
19	786	782	51C
20	162	142	1C

5,2,L

L	|F|obs	|F|calc	phase
0	422	482	534
1	393	475	531
2	499	488	2C
3	185	202	522
4	140	190	477
5	443	531	33
6	140	142	576
7	162	142	566
8	254	310	502
9	199	199	543
10	663	638	23
11	358	393	39
12	324	352	541
13	114	87	534
14	215	207	18
15	353	348	539
16	66*	83	104
17	351	336	4C
18	66*	44	724
19	66*	35	58

6,2,L

L	|F|obs	|F|calc	phase
0	1495	1453	18
1	66*	20	4
2	775	755	995
3	1596	1569	5C7
4	114	91	621
5	236	284	496
6	459	499	31
7	66*	3	315
8	487	499	8
9	493	467	4
10	353	337	965
11	331	319	508
12	710	659	26
13	66*	64	62
14	298	348	13
15	738	742	514
16	367	381	54C
17	488	5C8	9
18	379	391	22

7,2,L

L	|F|obs	|F|calc	phase
0	261	3C9	33
1	114	99	669
2	229	215	523
3	455	449	521
4	66*	91	953
5	1217	12C4	26
6	66*	80	86
7	1105	1108	522
8	192	234	12
9	250	247	986
10	366	4C7	526
11	215	192	94
12	140	154	39
13	267	285	995
14	66*	19	323
15	563	548	537
16	66*	40	676

8,2,L

L	|F|obs	|F|calc	phase
0	301	289	18
1	379	334	27
2	285	274	5
3	280	289	1C
4	66*	26	839
5	199	227	532
6	641	634	14
7	353	398	498
8	125	120	20
9	267	267	499
10	462	457	997
11	114	134	559
12	595	602	8
13	436	425	19
14	824	798	15

9,2,L

L	|F|obs	|F|calc	phase
0	800	747	4C
1	66*	34	889
2	405	399	535
3	182	249	511
4	140	131	607
5	66*	37	135
6	241	256	78
7	114	110	980
8	267	243	10
9	66*	8	876
10	654	6C4	541
11	66*	65	447

10,2,L

L	|F|obs	|F|calc	phase
0	438	4C4	10
1	162	154	21
2	114	45	993
3	162	164	523
4	405	388	14
5	429	413	12
6	114	59	575

0,3,L

L	|F|obs	|F|calc	phase
1	241	235	516
3	357	353	12
5	188	187	512
7	145	159	998
9	252	270	501
11	145	132	27
13	503	444	521
15	270	248	26
17	68*	29	63
19	68*	46	621
21	68*	67	5C4

1,3,L

L	|F|obs	|F|calc	phase
0	176	142	598
1	394	486	42
2	300	331	24
3	759	763	12
4	118	1C3	426
5	1190	1266	525
6	938	951	519
7	807	853	25
8	68*	50	19
9	145	163	444
10	708	811	21
11	685	620	558
12	145	126	587
13	299	295	491
14	380	366	514
15	790	775	30
16	68*	70	186
17	786	710	536
18	68*	43	694
19	249	251	12
20	361	332	994

2,3,L

L	|F|obs	|F|calc	phase
0	338	333	492
1	321	314	492
2	252	250	999
3	584	578	11
4	313	170	515
5	606	659	518
6	344	416	22
7	336	351	18
8	368	393	516
9	176	127	485
10	168	148	994
11	155	152	978
12	242	2C5	482
13	418	366	511
14	259	255	999
15	518	492	22
16	249	2C6	530
17	468	472	519·
18	464	410	26
19	230	185	1
20	163	146	530

3,3,L

L	|F|obs	|F|calc	phase
0	2193	2218	517
1	68*	45	8
2	467	438	30
3	172	131	23
4	773	827	25
5	206	225	515
6	168	167	647
7	68*	28	18
8	206	21C	5C4
9	68*	14	33
10	291	316	75
11	220	226	7
12	1286	1189	523
13	118	130	989
14	370	358	997
15	145	144	31
16	965	897	30
17	168	180	514
18	168	171	952
19	168	111	525
20	543	5C6	533

4,3,L

L	|F|obs	|F|calc	phase
0	324	352	526
1	344	338	38
2	393	329	16
3	199	186	21
4	118	96	472
5	831	899	522
6	68*	97	542
7	812	851	18
8	234	245	519
9	118	109	466
10	396	382	27
11	206	178	58C
12	145	150	532
13	118	1C8	53
14	68*	22	959
15	341	317	35
16	68*	57	438
17	415	390	541
18	191	172	22
19	262	261	22

5,3,L

L	|F|obs	|F|calc	phase
0	145	164	582
1	728	803	523
2	746	785	13
3	418	422	511
4	647	613	497
5	239	216	74
6	199	193	548
7	252	250	970
8	462	525	512
9	116	119	55C
10	1303	1190	17
11	596	575	33
12	258	198	546
13	374	391	524
14	68*	43	596
15	217	238	544
16	449	457	475
17	394	349	43
18	172	121	9

6,3,L

L	|F|obs	|F|calc	phase
0	738	781	534
1	145	121	33
2	350	369	33
3	68*	28	518
4	213	220	60
5	145	161	991
6	145	131	652
7	279	284	497
8	279	277	507
9	168	142	6
10	752	671	34
11	68*	75	553
12	586	562	534
13	232	210	29
14	68*	27	607
15	68*	21	998
16	315	307	58

7,3,L

L	|F|obs	|F|calc	phase
0	248	295	497
1	145	114	577
2	145	156	0
3	378	428	2
4	68*	43	602
5	473	414	33
6	490	515	21
7	495	540	518
8	208	209	526
9	554	489	520
10	68*	62	538
11	306	335	35
12	145	127	481
13	204	191	8
14	237	246	8

8,3,L

L	|F|obs	|F|calc	phase
0	883	814	526
1	347	301	551
2	589	581	20
3	295	292	521
4	68*	67	387
5	578	525	39
6	284	217	562
7	279	241	550
8	68*	54	503
9	68*	53	658
10	599	542	32
11	168	167	96
12	564	527	532

9,3,L

L	|F|obs	|F|calc	phase
0	68*	56	45
1	145	119	20
2	118	87	2
3	524	489	514
4	184	228	526
5	205	197	15
6	118	106	51
7	118	88	20
8	68*	36	535

0,4,L

L	|F|obs	|F|calc	phase
0	4502	4714	12
2	402	362	546
4	499	435	971
6	67*	137	314
8	768	680	10
10	648	624	547
12	2396	2239	17
14	780	772	504
16	67*	129	705
18	219	251	476

1,4,L

L	|F|obs	|F|calc	phase
0	232	194	18
1	67*	56	546
2	201	19C	510
3	67*	49	527
4	64*	69	590
5	164	169	37
6	116	85	507
7	142	153	535
8	250	221	21
9	67*	81	15
10	304	252	921
11	201	158	24
12	67*	130	4
13	67*	37	576
14	116	64	62
15	67*	74	532
16	116	123	999
17	67*	51	112
18	116	122	545
19	142	135	537

2,4,L

L	|F|obs	|F|calc	phase
0	412	416	37
1	395	425	43
2	183	186	974
3	534	520	17
4	992	922	996
5	918	827	534
6	1098	928	20
7	481	420	468
8	821	844	6
9	450	346	485
10	738	670	525
11	728	663	533
12	399	419	28
13	218	172	34
14	812	748	13
15	1049	969	23
16	435	453	985
17	313	311	570
18	360	327	22

3,4,L

L	|F|obs	|F|calc	phase
0	1179	1129	19
1	410	380	514
2	758	742	517
3	296	272	15
4	328	323	992
5	340	273	510
6	231	239	475
7	281	281	3
8	450	493	11
9	127	126	505
10	800	740	524
11	233	285	18
12	778	720	23
13	378	362	524
14	452	443	509
15	290	275	22
16	116	117	55C
17	116	127	456
18	335	296	5C1

4,4,L

L	|F|obs	|F|calc	phase
0	67*	54	652
1	632	675	29
2	201	23C	25
3	279	34C	456
4	260	243	26
5	732	851	528
6	67*	12C	519
7	734	7C4	22
8	775	798	1C
9	284	252	46
10	1198	1C62	13
11	634	614	535
12	358	392	55C
13	116	81	51
14	164	194	4
15	67*	119	128
16	448	4C8	25
17	155	136	611

5,4,L

L	|F|obs	|F|calc	phase
0	67*	63	158
1	67*	64	169
2	67*	89	564
3	510	461	18
4	271	280	533
5	668	7C4	529
6	461	442	32
7	367	382	33
8	142	146	532
9	67*	12C	47C
10	116	116	567
11	67*	82	641
12	67*	51	242
13	142	157	5C6
14	116	124	12
15	524	474	34
16	328	33C	536

6,4,L

L	|F|obs	|F|calc	phase
0	164	160	59C
1	246	282	512
2	116	117	41
3	587	6C1	14
4	1002	975	19
5	116	1C2	548
6	183	236	944
7	204	228	13
8	477	458	13
9	67*	95	3
10	351	314	29
11	531	45C	11
12	264	232	970
13	307	238	528
14	298	235	589
15	229	224	35

7,4,L

L	|F|obs	|F|calc	phase
0	246	268	536
1	307	321	56
2	183	22C	22
3	142	147	26
4	67*	87	456
5	636	678	534
6	67*	42	665
7	602	596	28
8	223	196	514
9	67*	55	332
10	396	371	27
11	429	379	555
12	116	14C	541

8,4,L

L	|F|obs	|F|calc	phase
0	352	372	552
1	385	392	527
2	1132	1136	11
3	67*	67	458
4	67*	66	492
5	67*	43	97
6	201	154	1
7	460	445	4
8	183	147	535

9,4,L

L	|F|obs	|F|calc	phase
0	533	430	555
1	296	247	5C3

* Column 1, running index L; column 2, $|F|_{obs}$, an asterisk following the value indicates an unobserved reflection; column 3, $|F|_{calc}$; column 4, calculated phase angle in millicycles.

Table 6. *Bond lengths* (Å), *each with its standard deviation and estimated Pauling bond strength*

Anions	(Mn,Ca)	Mn	Al(1)	Al(2)	(Mg,Al,Fe)	Si(1)	Si(2)	Si(3)	(As,V)	ΣII‡
					Cations					
O(1)	2·189±7 0·5*		1·904±7 0·5*			1·623±8 1·0*				2·0
O(2)		2·127±7 0·5*		1·888±7 0·5*			1·604±8 1·0*			2·0
O(3)	(2·403±8) 0·0		2·006±8 0·5†				1·631±9 1·0			2·0
O(4)				1·934±9 0·5†		1·644±9 1·0				2·0
O(5)	2·305±10 0·3†				2·189±10 0·3				1·721±10 1·1*	2·0
O(6)		2·305±10 0·25†			2·055±10 0·4			1·631±10 1·0*		1·9
O(7)		(2·514±9) 0·0			1·970±10 0·45†	1·657±10 1·0				1·9
O(8)	(2·473±8) 0·0						1·649±9 1·0	1·647±9 1·0*		2·0
O(9)		2·127±9 0·5							1·675±9 1·4*	1·9
OH(1)			1·853±9 0·5†							1·0
OH(2)				1·883±8 0·5†						1·0
OH(3)	2·207±8 0·4				1·940±9 0·45†					1·3
ΣI‡	2·0	2·0	3·0	3·0	2·5	4·0	4·0	4·0	5·0	
Cation coordination number	5 (7)	5 (6)	6	6	6	4	4	4	4	
Average bond length	2·239 (2·296)	2·198 (2·250)	1·921	1·902	2·011	1·637	1·622	1·639	1·698	

* Two bonds for cation, one for anion.
† Two bonds for cation, two for anion.
‡ ΣI = sum of Pauling bonds emanating from cation. ΣII = sum of Pauling bonds reaching anion.

Table 7. *Oxygen approaches less than* 3 Å *in ardennite*

Standard deviations = 0·01 Å.

As in Fig. 2, the primes represent atoms in sites that are transformed as follows: $xyz' = \bar{x}, \bar{y}, \bar{z}$; $xyz'' = 1-x, \bar{y}, \bar{z}$; $xyz''' = x, y, \frac{1}{2}-z$; $xyz^{iv} = 1-x, 1-y, \bar{z}$; $xyz^{v} = 1-x, \frac{1}{2}+y, \bar{z}$; $xyz^{vi} = 1-x, \frac{1}{2}+y, \bar{z}$; $xyz^{vii} = x, \frac{1}{2}-y, z$; $xyz^{viii} = x-1, 1+y, z$; $xyz^{ix} = x-1, \frac{1}{2}-y, z$.

Around Al(1)			Around Al(2)			Around (Mg,Al,Fe)			Empty octahedron around ($\frac{1}{4}0\frac{1}{2}$)		
Two	O(1)–O(3)	2·83	Two	O(2)–O(4)	2·67	Two O(5) —O(7)	2·91		3 sides as in oct. Al(1)		
Two	O(1)–O(3')	2·70	Two	O(2)–O(4'')	2·73	Two O(5) —OH(3)	2·82		3 sides as in oct. Al(2)		
Two	O(1)–OH(1)	2·67	Two	O(2)–OH(2)	2·71	Two O(6) —O(7)	2·91		1 side as in tet. Si(1)		
Two	O(1)–OH(1')	2·64	Two	O(2)–OH(2'')	2·63	Two O(6) —OH(3)	2·89		1 side as in tet. Si(2)		
Two	O(3)–OH(1)	2·93	Two	O(4)–OH(2)	2·91	Two O(7)—OH(3)	2·91		O(1) —OH(2'')	2·89	
Two*	O(3)–OH(1')	2·52	Two*	O(4)–OH(2'')	2·47	* O(7) —O(7''')	2·68		O(2'')–OH(1)	2·94	
						* OH(3)–OH(3''')	2·53		O(3) —O(4'')	2·93	
Average of 10		2·75	Average of 10		2·73				OH(1)–OH(2'')	2·69	
Average of 12		2·71	Average of 12		2·69	Average of 10	2·89				
						Average of 12	2·84		Average of 4	2·86	

Around Si(1)			Around Si(2)			Around Si(3)		Around (As,V)	
	O(1^{iv})–O(1^{v})	2·60		O(2'')–O(2^{vi})	2·66	O(6)–O(6^{vii})	2·74	O(5^{viii})–O(5^{ix})	2·83
Two	O(1^{iv})–O(4)	2·68	Two	O(2'')–O(3)	2·71	Four O(6)–O(8)	2·68	Four O(5^{viii})–O(9)	2·77
Two	O(1^{iv})–O(7)	2·74	Two	O(2'')–O(8)	2·61	O(8)–O(8''')	2·57	O(9) —O(9)	2·73
	O(4)—O(7)	2·58		O(3)–O(8)	2·56				
						Average of 6	2·67	Average of 6	2·77
Average of 6		2·67	Average of 6		2·64				

Other distances: O(1)–OH(3'') 2·87   O(9) —OH(1) 2·69
O(8)–O(9) 2·97   OH(2)–OH(3) 2·80

* Shared edge.

expected to show a (001) cleavage that would cut through the strong bonds of the sheets. A perfect (001) cleavage is, however, reported for epidote throughout the literature and was discussed at length in the papers describing the epidote-structure determination. We tested the cleavage of epidote crystals from many localities and not once did we observe a (001) cleavage plane. If it exists at all, and is not just a misprint in the literature, it must be extremely difficult to produce. The (100) cleavage parallel to the chains, imperfect in epidote, is perfect in ardennite.

All the coordination polyhedra are normal except those about Mn^{2+} and (Mn^{2+}, Ca) for which a regular octahedral environment is expected. One of the six Mn–O bonds is 0·3 Å longer than the average bond length of the other five (Table 6), leading to a distorted octahedron around Mn. The five nearest bonds emanating from (Mn, Ca) have a configuration similar to that of the shortest five Mn–O bonds. There are, however, two next-nearest oxygen atoms only 0·2 Å farther away than the average (Mn, Ca)–(O, OH) bond length. Including them would give sevenfold coordination (six O and one OH). We may therefore expect ardennite to show unusual magnetic properties, and a study of its magnetic susceptibility down to liquid-helium temperature is under way.*

The original question, whether all the As and V ions that are present in ardennite substitute for Si, received

* *Note added in proof.*: – Dr F. Senftle and coworkers have observed antiferromagnetism below liquid nitrogen temperatures.

a negative answer. An $(As, V)O_4$ tetrahedron, sharing two of its corners with (Mg, Al, Fe) and (Mn, Ca) polyhedra and the other two with Mn polyhedra, exists in the structure. It is readily identified by its peak height in the E map (Table 3) and by the metal–oxygen bond lengths (Table 6). In addition, the assumption that all As and V are in the 2(*b*) space-group position, and the consequent choice of scattering factors, led to normal values for the temperature factors (Table 3). The slightly low B value of Si(1) suggests that this isolated Si(1) tetrahedron is the most likely one to incorporate any excess of As and V.

We therefore looked at the chemical data in the literature and transformed the analyses considered most reliable by Senet & Moreau (1965, p. 560) to structural formulae for $(O + OH) = 56$ (Table 8). As and V form a complete series of solid solutions. The amount of Ca substituting for Mn also varies within wide limits. Both (Mn, Ca) and (Mg, Al, *etc.*) positions show surprisingly large and unexplained variations from the expected values of 4 each, and their sum, instead of being 8, ranges from 6·90 to 8·65. In conclusion, it is fair to state that starting with the available chemical analyses one could hardly have arrived at the correct structural formula given above.

The temperature factors of the anions are normal (Table 3), except that of OH(2), which is much too low. Only complete substitution of F for OH(2) could possibly account for it, but the chemical analysis of our specimen (Tables 1 and 8) indicates that not more than 4 at.% of F is available for replacement of OH(2).
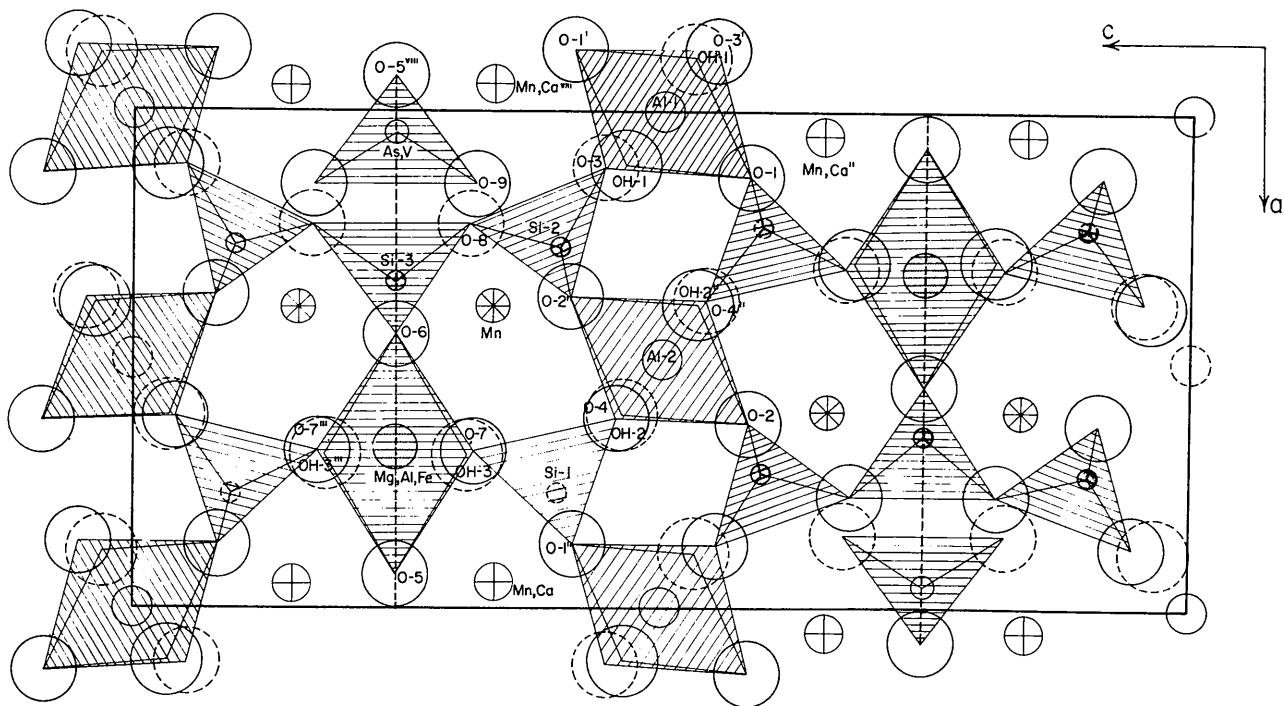
Fig. 2. Projection of refined ardennite structure on (010). Note that the coordinates given in Table 3 refer to an origin at the midpoint of the *c* repeat in this figure. Unprimed atoms refer to coordinates given in Table 3; primed atoms are defined in legend of Table 7.

Table 8. *Chemical analyses of ardennite written as structural formulae, so that* (O+OH) = 56

All samples are from Salm-Château, Belgium, except No. 5, which comes from Ceres, Val d'Ala, Piemont, Italy. Only full analyses were used. Two decimal places are given throughout; they are not to be considered a reflection on the quality of the individual analysis. Each analysis contains 4 Mn, 8 Al, and 6 Si in addition to the amounts shown below.

	4(Mn, Ca)	4(Mg, Al, Fe³⁺)	2(As, V)	4(Si, As)	12(OH)	O 44	Analyst	Reference
1	Mn 3·53 Ca 0·49 —— 4·02	Mg 2·00 Al 0·60 Fe 0·40 Cu 0·12 —— 3·12	As 1·81 V 0·19 —— 2·00	Si 3·87	OH 11·79 F 0·16 —— 11·95	O 44·05	C. O. Ingamells	Present paper
2	Mn 3·90 Ca 0·44 —— 4·34	Mg 1·19 Al 1·77 Fe 0·32 Cu 0·15 —— 3·43	As 1·80 V 0·20 —— 2·00	Si 3·83 As 0·25 —— 4·08	OH 11·83	O 44·17	O. Vandenberg	Semet & Moreau (1965)
3	Mn 3·50 Ca 0·43 —— 3·93	Mg 1·18 Al 1·56 Fe 0·16 Cu 0·07 —— 2·97	As 1·99 V 0·20 —— 2·19	Si 3·60 As 0·40 —— 4·00	OH 11·70	O 44·30	O. Vandenberg	Semet & Moreau (1965)
4	Mn 3·82 Ca 0·95 Fe⁺² 0·27 —— 5·04	Mg 1·04 Al 2·19 Fe⁺³ 0·03 —— 3·26	As 0·76 V 1·12 —— 1·88	Si 4·00	OH 11·80	O 44·20	B. Gossner & H. Strunz	Gossner & Strunz (1932)
5	Mn 1·51 Ca 2·08 —— 3·59	Mg 2·08 Al 1·15 Fe 0·81 Cu 0·20 —— 4·24	As 0·87 V 0·06 P⁺⁵ 0·04 Si 0·24 —— 1·21	Si 4·00	OH 12·51	O 43·49	F. Zambonini	Zambonini (1922)
6	Mn 2·66 Ca 0·53 Fe⁺² 0·19 —— 3·38	Mg 2·68 Al 1·92 Fe⁺³ 0·14 Cu 0·06 —— 4·80	As 1·79 V 0·19 —— 1·98	Si 3·62 Al 0·38 —— 4·00	OH 12·08	O 43·92	W. Prandtl	Prandtl (1905)
7	Mn 3·87 Ca 0·81 —— 4·68	Mg 1·56 Al 1·94 —— 3·50	As 0·19 V 2·12 —— 2·31	Si 3·69 As 0·31 —— 4·00	OH 11·61	O 44·39	A. Bettendorff	von Lasaulx (1876)
8	Mn 4·28 Ca 0·59 —— 4·87	Mg 0·74 Al 1·60 Fe 0·31 Cu 0·05 —— 2·70	As 1·75 V 0·13 —— 1·88	Si 3·85	OH 12·22	O 43·78	A. Bettendorff	von Lasaulx (1876)
9	Mn 3·43 Ca 1·09 —— 4·52	Mg 2·07 Al 1·66 Fe 0·34 Cu 0·06 —— 4·13	As 1·13 V 0·70 —— 1·83	Si 3·69 Al 0·31 —— 4·00	OH 11·81	O 44.19	F. Pisani	Pisani (1873)
10	Mn 3·67 Ca 0·68 —— 4·35	Mg 1·76 Al 1·68 Fe 0·44 —— 3·88	V 2·13	Si 4·35	OH 9·40	O 46·60	A. von Lasaulx & A. Bettendorff	von Lasaulx & Bettendorff (1873)
11	Mn 3·74 0·77 —— 4·51	Mg 1·79 Al 1·74 Fe 0·51 —— 4·04	V 2·12	Si 4·47	OH 9·46	O 46·54	A. von Lasaulx & A. Bettendorff	von Lasaulx & Bettendorff (1873)

The increased length of the b cell edge (5·81 Å) in ardennite over that found in other aluminum silicates with octahedral chains along b (5·45–5·63 in zoisite, 5·57 in kyanite, 5·61–5·64 in epidote, 5·66 in staurolite, 5·75 in allanite) is due to the substitution of the larger Mg and Fe ions for Al in about half of the octahedra that have centers on the mirror planes (001).

As can be seen on Fig.2, a nearly regular but empty octahedron around the point $\frac{1}{4}00$ shares a face with each of two Al octahedra and an edge with each of two Si tetrahedra. The average length of the remaining four edges is 2·86 Å (Table 7), very comparable to the edge length of the other filled octahedra. The reason that no cation, M, is found at the center is ascribed to the short Al(1)–Al(2) separation, which would lead to M–Al distances of only 2·18 Å.

We thank Professor J.D.H.Donnay for his continued interest in the work. The senior author wishes to thank Professor E.Hellner, Director of the Mineralogical Institute of the University of Marburg, for his hospitality during the summer of 1966 when she was working on this problem. We are indebted to Drs W. Fischer, H.Burzlaff, and A.Kutoglu of the same institution, who helped in many ways, especially with the computations. Dr A.J.Naldrett kindly provided the hand specimen (No. S-2183) from which we obtained our epidote crystal.

References

BELOV, N. V. & RUMANOVA, I. M. (1953). *C.r. Acad. Sci. URSS*, **89**, 853.

DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.

DONNAY, G. (1965). *Carnegie Inst. Wash. Year Book* **64**, 209.

DONNAY, G. (1966). *Carnegie Inst. Wash. Year Book* **65**, 294.

GOSSNER, B. & STRUNZ, H. (1932). *Z. Kristallogr.* **83**, 415.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1966). Personal communication; see also *Acta Cryst.* **21**, 435.

ITO, T., MORIMOTO, N. & SADANAGA, N. (1954). *Acta Cryst.* **7**, 53.

KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**, 969.

KARLE, I. L. & KARLE, J. (1966a). *Acta Cryst.* **21**, 860.

KARLE, J. & KARLE, I. L. (1966b). *Acta Cryst.* **21**, 849.

LASAULX, A. VON (1876). *Neues Jahrb. Mineral.* p. 363.

LASAULX, A. VON & BETTENDORFF, A. (1873). *Neues Jahrb. Mineral.* p. 124.

LIEBAU, F. (1962). *Naturwissenschaften*, **49**, 481.

PISANI, F. (1873). *C.r. Acad. Sci. Paris*, **77**, 329.

PRANDTL, W. (1905). *Z. Kristallogr.* **40**, 392.

SEMET, J. & MOREAU, J. (1965). *Ann. Soc. géol. Belgique*, **88**, 545.

STRUNZ, H. (1935). *Z. Kristallogr.* **92**, 402.

ZAMBONINI, F. (1922). *Att. Accad. Naz. Lincei, Rend.*, Ser. 5, **31**, 147.

The Configuration at C(13) in Labdanolic and Eperuic Acids by an X-ray Crystal Structure Analysis of the p-Bromophenacyl Ester of Labdanolic Acid

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The crystal structure of the p-bromophenacyl ester of labdanolic acid, determined by three-dimensional X-ray analysis, establishes the common configuration for labdanolic and eperuic acids at C(13) as (S) (Prelog's notation). The crystals are monoclinic, space group $P2_1$, with two molecules of $C_{28}H_{41}O_4Br$ in a unit cell of dimensions $a = 11·55$, $b = 6·05$, $c = 19·90$ Å; $\beta = 99·0°$. The structure has been refined by least-squares methods to a final R of 11·4% for 1672 reflexions.

Introduction

Labdanolic acid, $C_{20}H_{36}O_3$, was first isolated by Cocker, Halsall & Bowers, 1956) from Spanish gum labdanum obtained from *Cistus ladaniferus* (rockrose). The structure of this new bicyclic diterpene hydroxyacid was determined in a subsequent paper (Cocker & Halsall, 1956) as (I), but the configuration at C(13) remained undetermined.
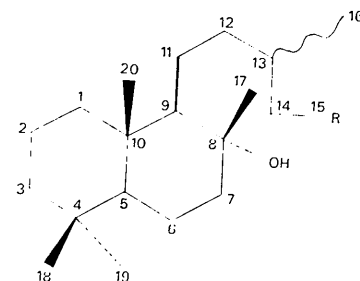
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(I)   R =CO₂H