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The crystal structure of davidite

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Abstract

Davidite from the Pandora Prospect, Pima County, Arizona, crystallizes in the space group $R\bar{3}$ with lattice parameters $a = 9.190(3)$A, $\alpha = 68.73(1)°$. Its formula, determined from microprobe analysis, is $REE_{0.91}U_{0.33}Ca_{0.20}Y_{0.25}(Sr,Th,Pb)_{0.09}Ti_{12.53}Fe_{5.97}Mg_{0.24}Cr_{0.21}Al_{0.14}(Mn,V,Zr,Nb,Sc)_{0.23}O_{38}$. In its natural state the mineral is metamict. The crystal structure was reconstituted by heating in air at 920°C for two hours. Davidite is isostructural with the crichtonite-group minerals, having a structure based on a close-packed anion lattice with a mixed stacking sequence (hhc ···), and with rare-earth elements (REE), M(0), occupying a site in the anion framework. The uranium atom does not substitute for REE in M(0), but occupies an octahedral site M(1) along with yttrium and small REE. The remaining small metal atoms, mainly titanium and iron, occupy a tetrahedral site, M(2), and three other octahedral sites, M(3), M(4), and M(5). A comparison is made of the site occupancies and average metal–oxygen bond lengths for five crichtonite-group minerals—senaite, crichtonite, davidite, loveringite, and landauite. A linear correlation is observed between the unit-cell edge, a_{rh}, and the M(1)–O bond length.

Introduction

The mineral davidite, an iron titanate containing a considerable amount of rare earths and uranium, was first described and named by Mawson (1906). The type material, found at Radium Hill, South Australia, occurs in an intimate intergrowth with ilmenite and rutile. Early studies were hampered by the metamict nature of the mineral, and the fact that samples reconstituted by heat treatments gave powder diffraction patterns that proved difficult to index. In a study on davidites from various localities, Pabst (1961) reconstituted samples from Norway and Arizona to single crystals and determined the space group and unit-cell parameters, rhombohedral $R\bar{3}$ or $R3$ with $a = 9.178$A, $\alpha = 68°48'$. Using these parameters, Pabst was able to completely index powder patterns of davidites from various localities and validate the mineral as a distinct species. Specific gravity data and chemical analyses were consistent with a cell content of 36 O, and Pabst proposed a general formula $Y_6Z_{15}O_{36}$, where Y = large cations: Ca, Fe^{2+}, REE, U, Pb, *etc.*, and Z = small cations: Ti, V, Cr, Fe^{3+}.

Rouse and Peacor (1968) pointed out the close structural relationship between davidite, crichtonite, and senaite as shown by their similar unit-cell parameters, powder patterns, and compositions. From preliminary single-crystal X-ray studies, they determined that the structures were based on a close-packed anion framework, with a nine-layer stacking

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sequence and with one large cation (Pb in senaite) occupying an anion site. Rouse and Peacor's suggested formula for senaite was $Pb(Ti,Fe,Mn,Mg)_{24}O_{38}$ with $Z = 1$ in the primitive cell. By analogy with senaite, they suggested that davidite should also have 39 anion sites per primitive cell or else have anion vacancies, to be consistent with Pabst's (1961) formula.

We have recently carried out a structure determination on senaite (Grey and Lloyd, 1976) which confirmed the close-packed (O + Pb) anion framework model of Rouse and Peacor (1968) but showed that the primitive cell contained only 21 small cations rather than 24, giving a formula $AM_{21}O_{38}$, A = Pb and M = Fe,Ti,Mn predominantly. These studies have recently been extended to the structurally related minerals crichtonite (Grey *et al.*, 1976), loveringite (Gatehouse *et al.*, 1978), and landauite (Grey and Gatehouse, 1978), which conform to the same general formula and for which the dominant A cation is Sr, Ca, and Na respectively. As an extension of this work, we report here the determination of the structure of davidite from Arizona, and compare the crystallochemical properties of the crichtonite-group minerals.

Experimental

Davidite from the Pandora Prospect, Quijotoa Mts., Pima County, Arizona (NMNH #R12472) was kindly provided by John S. White, Jr. The material was lightly crushed to separate the black, vitreous davidite from associated albite. A number of fragments of the metamict davidite were heated in air at 920°C for 2 hours to reconstitute the mineral. Examination of the treated fragments by Weissenberg and precession X-ray diffraction techniques showed that they reconstituted generally to single crystals, giving patterns identical to those for other members of the crichtonite group (Grey *et al.*, 1976), *i.e.* rhombohedral symmetry $R\bar{3}$ or $R3$, with $a \simeq 9.19$A, $\alpha \simeq 69°$. A triangular prism-shaped fragment measuring 0.09mm along the triangular edge by 0.075mm long was transferred to a Philips PW1100 4-circle automatic diffractometer for intensity data collection. Sixteen carefully centered medium- and high-angle reflections ($2\theta > 20°$) provided the 2θ values used to calculate the lattice parameters reported in Table 1. Intensities were collected with graphite-monochromated Mo$K\alpha$ radiation. A θ–2θ scan, 3–32°, was used with a variable scan width given by $\Delta\theta = (1.20 + 0.3 \tan\theta)$ and a speed of 0.03° sec^{-1}. Two background measurements, each for half the scan time, were made for each scan, one at the lower and one at the upper limit. The intensities were processed using a program written for the PW1100 diffractometer by Hornstra and Stubbe (1972). An absorption correction was not applied ($\mu R = 0.51$). However, a partial compensation was achieved by averaging the intensities of equivalent reflections, ***h k l***, ***l h k***, ***k l h***, in the standard rhombohedral cell. (Interscale *R* factor for equivalent reflections = 0.047.) Thus the 4373 reflections measured were reduced to a unique set of 1464, of which 1200 had $I > 2\sigma[I]$ and were used in the structure refinement.

Table 1. Crystal data for Arizona davidite, trigonal, $R\bar{3}$

$a_{rh} = 9.190(3)$ Å $a_{hex} = 10.376(4)$ Å

$\alpha_{rh} = 68.73(1)^{o}$ $c_{hex} = 20.910(9)$ Å

$Z_{rh} = 1$ $Z_{hex} = 3$

$d_{calc} = 4.72$

$d_{meas} = 4.42$ (Pabst, 1961)

$\mu = 127.3$ cm^{-1}

$\mu R = 0.51$ (effective μR for spherical crystal with same volume as crystal used)

Scattering factor curves for Ca, Ce, Pb, U, Y, Zr, Mg, Fe, Ti, Cr and O neutral atoms are those of Cromer and Mann (1968). Anomalous dispersion corrections for all atoms are from Cromer and Liberman (1970). All computing was performed on the Monash University CDC3200 and Burroughs 6700 and the CSIRO CDC7600 computers.

Two small fragments of reconstituted davidite taken from the same original uncrushed sample were mounted and polished for a microprobe analysis, the results of which are given in Table 2. Because the reconstitution was effected in air, all iron is expressed in the ferric form. Some of the minor elements such as uranium and cerium may be in higher valence states than those shown in the table. A bulk chemical analysis of Arizona davidite from Pabst (1961) is in good agreement with the microprobe analyses (particularly in regard to the major elements, Ti, Fe, and REE), indicating that the davidite from the Pima County locality is quite homogeneous. Pabst's analysis shows that over a quarter of the iron in the unreconstituted mineral is ferrous.

The calculated unit cell composition for grain 1, normalized to 38 oxygens, is $REE_{0.91}U_{0.33}Ca_{0.20}Y_{0.25}(Sr,Th,Pb)_{0.09}Ti_{12.53}Fe_{5.97}Mg_{0.24}Cr_{0.21}Al_{0.14}(Mn,V,Zr,Nb,Sc)_{0.23}O_{38}$.

Table 2. Microprobe analyses of Arizona davidite

	Davidite, Arizona		Davidite, Arizona	Davidite, Norway	Davidite, S. Aust.
	Microprobe analyses		Bulk chemical analysis	Microprobe analyses	
	Grain 1*	Grain 2	(Pabst, 1961)	U.S.N.M. R11905	U.S.N.M. C1696-1
TiO_2	54.88	54.02	55.20	51.33	50.13
Fe_2O_3	26.16**	26.28	27.30 (19.80	28.46	27.90
FeO	-	-	(7.50	-	-
Al_2O_3	0.41	0.38	0.39	0.96	0.26
SiO_2	-	-	0.34	-	-
MgO	0.54	0.55	0.77	0.03	0.03
MnO	0.10	0.17	0.22	0.83	0.10
ZnO	0.04	0.00	-	0.09	0.03
Cr_2O_3	0.88	0.93	0.91	0.02	1.59
V_2O_5	0.42	0.39	0.33	0.02	3.12
Sc_2O_3	0.18	0.15	-	0.85	0.12
Nb_2O_5	0.19	0.24	-	0.71	0.12
Ta_2O_5	0.04	0.17	-	0.41	0.07
ZrO_2	0.37	0.64	0.55	0.31	0.09
Na_2O	-	0.07	0.03	0.06	0.01
K_2O	0.03	0.07	0.08	0.01	0.03
CaO	0.63	0.51	-	0.10	0.22
SrO	0.16	0.15	0.27	0.03	0.10
PbO	0.14	0.18	-	0.50	1.54
ThO_2	0.73	1.18	0.45	0.19	0.10
UO_2	4.94	5.62	3.74	1.22	6.00
Ce_2O_3	2.85)	2.77)		4.69****	2.76
La_2O_3	4.66)	4.58)		2.85	3.36
Nd_2O_3	0.23) 9.67	0.18) 9.31	9.41	0.61	0.26
R.E.E.***	0.36)	0.36)		0.93	0.80
Y_2O_3	1.57)	1.42)		3.03	2.05
Total	100.51	101.01	100.00	98.24	100.79

*Analysis for grain 1 used as basis for structure refinement. Unit cell composition for this grain is $R.E.E._{0.91}U_{0.33}Ca_{0.20}Y_{0.25}(Sr,Th,Pb)_{0.09}Ti_{12.53}Fe_{5.97}Mg_{0.24}Cr_{0.21}Al_{0.14}(Mn,V,Zr,Nb,Sc)_{0.23}O_{38}$.

**All iron assumed to be ferric in the reconstituted grains.

***Sum of remaining R.E.E., estimated from chondrite curves.

****Believed to be present largely as Ce^{4+} in this compositional variant of the mineral

Refinement of the structure

The atomic coordinates obtained for loveringite (Gatehouse *et al.*, 1978) in centrosymmetric space group $R\bar{3}$ were used as starting parameters, and a similar ordering of metals into sites M(0) to M(5) on the basis of decreasing size was considered. As a first approximation, the scattering curves used were Ce for sites M(0) and M(1), Fe for sites M(2) and M(3), and Ti for sites M(4) and M(5). An initial *R* factor of 0.16 was obtained. Subsequent least-squares refinement of coordinates and isotropic temperature factors proceeded smoothly to an *R* value of 0.06. At this stage the temperature factor of M(1) was not positive definite, suggesting that U may occupy this site. A new set of composite scattering curves for each of the sites was prepared, giving careful consideration to grouping of cations of similar radii and known natural associations. The final scattering curves, which are consistent with the unit-cell composition, are given in Table 3 (contributions of very minor elements have been absorbed into scattering curves of similar, more dominant elements, *e.g.* Zr represented by Y curve, Cr,V,Mn by Fe). The deficiency in the number of small cations, $\Sigma M = 20.27$

Table 3. Arizona davidite: final atomic coordinates and isotropic temperature factors

Atom site	Occupancy	x	y	z	B(Å^2)
M(0)	0.20 Ca + 0.54 R.E.E. + 0.09 (Sr,Th,Pb)	0.0000	0.0000	0.0000	1.17(2)
M(1)	0.33 U + 0.30 Y* + 0.37 R.E.E.	0.5000	0.5000	0.5000	0.53(2)
M(2)	0.24 Mg + 1.58 Fe	0.3090(1)	0.3090(1)	0.3090(1)	0.47(2)
M(3)	0.67 Ti + 4.57 Fe + 0.21 Cr	0.3474(1)	0.1269(1)	0.0184(1)	0.51(2)
M(4)	6.00 Ti	0.3086(1)	0.7218(1)	0.1448(1)	0.34(2)
M(5)	6.00 Ti	0.4749(1)	0.0775(1)	0.6444(1)	0.30(2)
O(1)	6.00 O	0.2999(5)	0.6300(5)	0.3765(5)	0.54(5)
O(2)	6.00 O	0.1486(5)	0.2347(5)	0.9391(5)	0.49(6)
O(3)	6.00 O	0.9192(5)	0.4574(5)	0.3025(5)	0.43(5)
O(4)	6.00 O	0.1446(5)	0.5137(5)	0.9897(5)	0.55(5)
O(5)	6.00 O	0.3891(5)	0.4869(5)	0.1345(5)	0.52(5)
O(6)	6.00 O	0.7131(5)	0.2404(5)	0.0688(5)	0.48(5)
O(7)	2.00 O	0.2134(4)	0.2134(4)	0.2134(4)	0.59(9)

*Minor elements (Sc,Zr), Al and (Cr,V,Mn) accounted for by scattering curves for Y, Ti and Fe respectively.

relative to the number of sites, 21, was met by incorporating vacancies in those sites containing Fe, M(2) and M(3), which would have been most affected by valence changes during reconstitution, *cf.* loveringite (Gatehouse *et al.*, 1978). Furthermore, to attain a reasonable temperature factor at site M(1), a considerable amount of REE (most likely the smallest trivalent ones, together with Ce^{4+}, see discussion below) had to be incorporated with the U^{4+} in this site, leaving an incompletely filled M(0) site, as for crichtonite (Grey *et al.*, 1976).

Using the new composite scattering curves for sites M(0) to M(5), further least-squares refinement of all positional and isotropic temperature factors was carried out. The refinement converged at a final *R* value of 0.045 for the 1200 observed data. The final atomic coordinates and temperature factors are given in Table 3. Note that even with only 0.83 occupancy, the temperature factor for metal atom site M(0) in the anion framework is much higher (by a factor of 2–3) than those of the other metals. This feature is common to the crichtonite-group minerals. The very reasonable temperature factors obtained for the other elements indirectly lend support to the site occupancies chosen. However, factors such as the distribution of vacancies and ordering of similar-sized elements have been obtained by crystallochemical reasoning only, and the site occupancies given in Table 3 must certainly be treated with caution. Calculated bond lengths and angles are given in Table 4, and observed and calculated structure factors are listed in Table 5.[1]

Discussion of structure and composition

Davidite is isostructural with crichtonite, having a structure based on a close-packed anion framework with one large cation per formula unit, predominantly REE, occupying an anion site. The close-packed anion layers have a stacking sequence along the trigonal axis, $\overline{\text{ABCBCACABA}}$, *i.e.* having a nine anion-layer repeat and rhombohedral symmetry. A full description of the structure of the crichtonite-group minerals, including diagrams, is given in earlier papers (Grey and Lloyd, 1976; Grey *et al.*, 1976). We include here a polyhedral representation of the structure viewed down the trigonal axis (Fig. 1), which shows the five different types of small-cation sites, *i.e.* tetrahedral site M(2) and octahedral sites M(1), M(3), M(4), M(5). In this diagram the large cations, M(0), in the anion framework are represented by the filled circles, and the hexagonal unit cell is outlined.

Polyhedral bond lengths and angles for davidite are given in Table 4. The average M–O bond lengths agree closely with those calculated on the basis of the site occupancies given in Table 3, using Shannon and Prewitt's (1969) ionic radii[2], and thus lend support to the ordering scheme chosen. For example, $\overline{\text{M}}$(4)–O and $\overline{\text{M}}$(5)–O values of 1.975(4) and 1.972(4)A compare with Ti^{4+}–O, 1.975A. Similarly, the calculated value for $\overline{\text{M}}$(3)–O, 2.01A agrees with the observed 2.010(4)A. For site M(2), the observed $\overline{\text{M}}$(2)–O is 1.981(4)A. A calculated value of 1.98A is obtained if all the iron in this site is assumed to be ferrous. This

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[1] To obtain a copy of this table, order Document AM-79-097 from the Business Office, Mineralogical Society of America, 2000 Florida Ave., N.W., Washington, D. C. 20009. Please remit $1.00 in advance for the microfiche.

[2] In davidite, oxygens O(1), O(3), and O(4) are three-coordinated and O(2), O(5), O(6), and O(7) are four-coordinated to metal atoms. An oxygen radius of 1.37A, which is intermediate between the values listed for three- and four-coordinated oxygen by Shannon and Prewitt (1969), has thus been used to calculate M–O bond lengths.

Table 4. Arizona davidite: interatomic distances (A) and angles (degrees)

		Distance	O-M-O angle			Distance	O-M-O angle			Distance	O-M-O angle
M(1) octahedron				M(2) tetrahedron				M(0) site			
M(1) - O(1)	[6]	2.243*		M(2) - O(5)	[3]	1.975		M(0) - O(2)	[6]	2.745	
				- O(7)		2.000		- O(6)	[6]	2.794	
O(1) - O(1)'	[6]	3.10	87.55*	O(5) - O(5)'	[3]	3.27	111.70	O(2) - O(6)	[6]	2.73	59.00
- O(1)''	[6]	3.24	92.45	- O(7)	[3]	3.20	107.14	O(2) - O(2)	[6]	2.73	59.67
								O(6) - O(6)	[6]	2.81	60.31
								O(2) - O(6)'	[6]	2.84	61.67
M(3) octahedron				M(4) octahedron				M(5) octahedron			
M(3) - O(4)		1.951		M(4) - O(2)		1.871		M(5) - O(1)		1.887	
- O(3)		1.976		- O(1)		1.968		- O(4)		1.839	
- O(2)		1.995		- O(3)		1.962		- O(3)		1.923	
- O(4)'		2.024		- O(6)		1.937		- O(5)		1.968	
- O(7)		2.020		- O(5)		2.038		- O(6)		2.037	
- O(2)'		2.093		- O(6)'		2.075		- O(5)'		2.180	
O(4) - O(4)'		2.69	85.25	O(1) - O(6)		2.59	79.67	O(5) - O(5)'		2.57	76.27
- O(2)		2.75	83.88	O(5) - O(3)		2.60	81.07	- O(3)		2.60	78.39
O(7) - O(2)		2.72	82.74	- O(6)		2.61	82.09	O(6) - O(1)		2.59	82.56
- O(2)'		2.72	85.26	- O(1)		2.71	85.26	- O(5)		2.61	81.36
O(2) - O(2)'		2.73	83.82	O(2) - O(6)		2.73	87.32	O(1) - O(5)		2.82	87.35
O(4) - O(7)		2.79	87.36	O(1) - O(3)		2.85	92.99	O(4) - O(6)		2.80	92.49
- O(3)		2.86	91.41	O(6) - O(6)'		2.81	88.73	O(3) - O(5)'		2.82	92.80
- O(2)'		2.89	91.00	O(2) - O(1)		2.86	96.23	- O(4)		2.82	97.16
O(4) - O(3)		2.85	93.17	- O(3)		2.91	98.94	O(1) - O(4)		2.82	98.39
O(3) - O(7)		2.89	92.50	- O(6)		2.84	96.44	- O(3)		2.92	100.21
- O(2)		3.05	100.35	O(6)' - O(3)		2.92	97.09	O(5)' - O(4)		2.90	99.16
O(4)' - O(2)'		3.04	100.84	- O(5)		2.98	92.84	-O(6)		3.03	91.62
				Metal-Metal distances**							
M(1) - M(5)	c	3.685		M(2) - M(5)	c	3.337		M(0) - M(4)	c	3.370	
- M(4)	c	3.826		- M(3)	c	3.491					
				- M(4)	c	3.537					
M(3) - M(3)'	e	2.925		M(4) - M(5)	e	3.012		M(5) - M(5)	e	3.266	
- M(3)''	e	3.012		- M(5)'	e	3.017					
- M(5)	e	3.349		M(4) - M(4)	c	3.979					
- M(4)	c	3.436									
- M(5)'	c	3.462									
- M(4)'	c	3.523									
- M(5)''	c	3.608									
- M(4)''	c	3.586									

*Standard deviations for M-M, M-O and O-O are 0.002, 0.004 and 0.006 Å respectively and for angle O-M-O 0.2 degrees.

**c and e refer to corner- and edge-shared linkages.

would require that the iron in this site is not oxidized during the reconstitution process, an unlikely situation. For octahedral site M(1), using the observed $\overline{\mathrm{M}}$(1)–O of 2.243(4)A and Shannon and Prewitt's ionic radius of oxygen, the calculated average radius of the metal atoms in site M(1) is 0.875A. Subtracting the contributions from Y^{3+} and REE gives a calculated radius for the U of 0.88A. Ionic radii for U^{3+} and U^{5+} in octahedral coordination are 1.06 and 0.76A respectively (Shannon and Prewitt, 1969), suggesting that U in site M(1) is tetravalent (for which, unfortunately, no value is given in Shannon and Prewitt's listing). Finally, the average M(0)–O bond length is 2.769(4)A, whereas the calculated value is 2.71A. For comparison, the average anion-anion separation is approximated by $a_{hex}/\sqrt{13}$ = 2.88A, *i.e.* M(0) is slightly smaller than the average anion site diameter and "rattling" may partly account for the high temperature factor for this atom. However, the high B may also be associated with the partial occupation of this site (P. B. Moore, private communication).

Information on the unit-cell composition of davidite, obtained from this structure refinement, is in disagreement with the previous literature in some details. First of all, the number of oxygens per unit cell derived from the structure refinement is 38 (see Table 3). There was no evidence in the temperature factors or the difference Fourier maps for vacancies in any of these sites. However, published values of ΣO in the unit cell are in the range 32.2 to 34.2 (Hayton, 1960) and 34.7 to 36.0 (Pabst, 1961) for two of the more detailed studies, using measured unit-cell dimensions and specific gravities together with chemical analyses. Both these ranges for ΣO are considerably lower than the value of 38 from the structure determination. The discrepancy is unlikely to result from the different chemical analyses (compare

Pabst's analysis of Arizona davidite with our microprobe analysis in Table 2) or unit-cell volumes. A possible explanation is that the measured densities are lower than the true densities, *i.e.* during metamictization, there is a general expansion of the davidite lattice with consequent "opening-up" of the mineral by formation of networks of micro-cracks and pores. If these are on a fine enough scale, then the liquid used in the density determination is unable to penetrate completely and an artificially low reading results. The observed differences in ΣO would require the measured density to be about 90 percent of the true density.

A second conclusion in the literature that needs clarifying is exemplified by the statement "there can hardly be any doubt that uranium substitutes for the rare earths in the davidite structure" (Neumann and Sverdrup, 1960). In fact, U and the dominant REE (La^{3+},Ce^{3+}) occupy different sites in the davidite structure, M(1) and M(0) respectively. However, the structure determination confirms that *small* REE such as Er and Yb, together with Y, substitute for U in the octahedral site M(1). The occupation of two distinct crystallographic sites in davidite by the REE explains the unusual distribution curves reported by different authors (Neumann and Sverdrup, 1960; Dixon and Wylie, 1951), which show pronounced enrichment of both light and heavy REE, while the content of intermediate REE's is exceptionally low. We have previously reported similar observations in the isostructural mineral loveringite (Gatehouse *et al.*, 1978). In general, the heavy REE enrichment peak is no more than 10 percent of the light REE peak, and so the elements Er, Yb, *etc.* only partly account for the REE contribution to site M(1) in Arizona davidite (which has 40 percent of the total REE, Table 3). The remainder is most likely accounted for by tetravalent REE, predominantly cerium. Ce^{4+} has an ionic radius of 0.80 (Shannon and Prewitt, 1969). Indirect evidence for Ce^{4+} occupation at site M(1) is indicated by the analysis of Norwegian davidite, (Table 2). This sample has a very low uranium content, with concomitant high cerium and yttrium contents. Similar results for REE analyses on Norwegian davidite are given by Neumann and Sverdrup (1960), where the cerium levels are more than twice those expected for typical light REE distribution curves for davidites [compare data given by Hayton (1960) and for South Australian davidite in Table 2]. We believe that the extra cerium is in the tetravalent form, substituting for U^{4+} in site M(1).

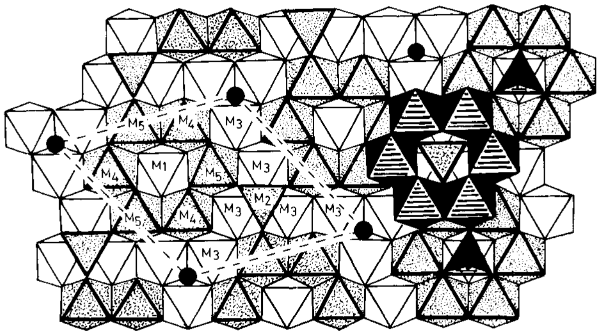

Fig. 1. Representation of three consecutive $(001)_{hex}$ layers of polyhedra in davidite, viewed along $[001]_{hex}$. Only part of the third layer (heavy shading) is shown for clarity. The hexagonal unit-cell edges, *a* and *b*, are shown by the dashed lines. The small filled circles represent rare-earth atoms. The atom labels M(1) to M(5) correspond to those given in Table 3.

Comparison of crichtonite-group minerals

The structures of five members of the crichtonite-group have now been completed. The minerals are characterized by the dominant large cation which for crichtonite, senaite, loveringite, landauite and davidite is Sr, Pb, Ca, Na, and REE respectively. Their unit-cell compositions are $A_{0.90}M_{21.00}O_{38}$, $A_{1.00}M_{21.00}O_{38}$, $A_{1.00}M_{20.34}O_{38}$, $A_{1.08}M_{20.84}O_{38}$, and $A_{0.83}M_{20.27}O_{38}$ respectively, where $A = \Sigma$ large cations and $M = \Sigma$ small cations (the Fe^{2+}/Fe^{3+} ratio in senaite and crichtonite was calculated to give 21 M cations), *i.e.* they all conform quite closely to the general formula $AM_{21}O_{38}$, particularly when allowance is made for some Fe^{2+} in the davidite and loveringite samples. The site occupancies and average metal–oxygen bond lengths for the five minerals are given in Table 6. Although the minerals have widely different combinations of metal atoms of both A and M type, certain compositional and structural features are common to the minerals. In particular, the average M(4)–O and M(5)–O bond lengths are identical, within the associated errors, for all five minerals, and correspond to ordering of Ti^{4+} in these sites, *i.e.* the six-membered hexagonal rings of octahedra (see Fig. 1) contain only titanium. The $M(3)O_6$ octahedra in each case contain Ti^{4+} and M^{3+}. For senaite, crichtonite, davidite, and landauite, M = Fe and the $\overline{M}(3)$–O values are equal within the associated error. Loveringite differs in having an appreciable amount of Cr^{3+} substituting for Fe^{3+} in this site and the associated $\overline{M}(3)$–O is shorter, although the difference is hardly outside the probable error.

The greatest bond-length variations are associated with the cations which lie on the trigonal axes, *i.e.* M(0), M(1), and M(2). Wide variations occur in the valence state and type of dominant cations in each of these sites, and this is reflected in the significant variations in the average metal–oxygen bond lengths (Table 6). Site M(0) in the anion framework seems able to cope with large local charge variations, incorporating dominant monovalent cations in landauite, divalent cations in senaite, crichtonite, and loveringite, and trivalent cations in davidite. Additionally the dominant M(1) cation is tetravalent in loveringite (Zr^{4+}) and davidite (U^{4+},Ce^{4+}), but divalent in the other minerals (Mn^{2+},Fe^{2+}).

Also listed in Table 6 is the rhombohedral cell parameter for each of the minerals. It shows a significant decrease from davidite through senaite, landauite, and crichtonite to loveringite. Note that the A cation, whose presence controls the structure type,[3] has no obvious influence on the overall size of the unit cell. In fact, davidite, with the smallest A cations, has the largest cell dimension. However, from Table 6, there is a very strong correlation of the rhombohedral cell edge with the M(1)–O bond length. A graph of M(1)–O *vs.* a_{rh} is linear, with remarkably small deviations for all five minerals. The marked effect of the size of M(1) is due to the generally large ions in this octahedral site. The ideal oxygen radius for a close-packed oxygen lattice with the same volume (V) as the davidite cell is given by $39 \times 5.66r^3 = V = 650.8$, *i.e.* $r = 1.43$A, and the smallest radius of an octahedrally-coordinated ion tolerated in this close-packed framework is $0.414 \times r$(oxygen) = 0.59A (this corresponds to the case of all oxygens just touching). For comparison, the radius of the smallest M(1) ion in the crichtonite group, Z^{4+}, is 0.72A, and there will thus be a considerable expansion of the oxygen lattice, even about this ion. For Y^{3+} in davidite the radius is 0.89A (Shannon and Prewitt, 1969). The smooth dependence of a_{rh} on the size of M(1) is presumably at least partly due to the fact that the $M(1)O_6$ octahedron is relatively isolated and thus not subject to the influence of neighboring cations, as is the case where considerable articulation of polyhedra occurs. The $M(1)O_6$ octahedron does not articulate to any other polyhedra within the basal plane, and shares only corners with $M(4)O_6$ and $M(5)O_6$ octahedra in adjacent layers.

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[3] For example, in the absence of the few percent of A cations (Na, K, and Pb), and considering all iron as ferrous in landauite (Grey and Gatehouse, 1978), its resulting formula approximates closely to $(Fe,Mn,Zn)Ti_2O_5$, which would have the pseudobrookite structure type.

Table 6. Site occupancies** and mean bond lengths for crichtonite-group minerals

	DAVIDITE*		SENAITE*		LANDAUITE*		CRICHTONITE*		LOVERINGITE*	
	Site occupancy	$\overline{M\text{-}O}$ (Å)	Site occupancy	$\overline{M\text{-}O}$ (Å)	Site occupancy	$\overline{M\text{-}O}$ (Å)	Site occupancy	$\overline{M\text{-}O}$ (Å)	Site occupancy	$\overline{M\text{-}O}$ (Å)
M(0)	0.20 Ca +0.54 R.E.E. +0.09 (Sr,Th,Pb) +0.17 □	2.769(4)	0.83 Pb +0.17 □	2.817(17)	0.70 Na +0.15 K +0.15 Pb	2.822(9)	0.70 Sr +0.20 Pb +0.10 □	2.792(7)	0.72 Ca 0.23 R.E.E. +0.05 (Th,Pb)	2.790(11)
M(1)	0.33 U +0.30 Y +0.37 R.E.E.	2.243(4)	Mn	2.227(17)	Mn	2.211(9)	0.70 Mn +0.30 Fe	2.205(7)	0.58 Zr +0.10 R.E.E. +0.32 Mg	2.166(11)
M(2)	0.12 Mg +0.79 Fe +0.09 □	1.981(4)	Fe	1.996(18)	0.98 Zn +0.02 □	1.964(9)	Fe	1.972(7)	0.30 Mg +0.61 Fe +0.09 □	1.994(11)
M(3)	0.11 Ti +0.80 Fe,Cr +0.09 □	2.010(4)	0.28 Ti +0.72 Fe	1.998(18)	0.62 Ti +0.36 Fe,Zn +0.02 □	1.997(9)	0.27 Ti 0.73 Fe	2.006(7)	0.41 Cr,V +0.36 Fe +0.14 Ti,+0.09 □	1.983(11)
M(4)	Ti	1.975(4)	Ti	1.976(18)	Ti	1.973(9)	Ti	1.969(7)	Ti	1.971(11)
M(5)	Ti	1.972(4)	Ti	1.964(18)	Ti	1.969(9)	Ti	1.967(7)	Ti	1.970(11)
a_{rh}(Å)	9.190(3)		9.172(1)		9.152(5)		9.148(2)		9.117(4)	
α_{rh}(°)	68.73(1)		69.02(1)		68.99(1)		69.08(1)		69.07(1)	

*References: davidite, this work; landauite (Grey and Gatehouse, 1978); senaite (Grey and Lloyd (1976); crichtonite (Grey et al., 1976); loveringite (Gatehouse et al., 1978).

**Site occupancies normalized to 1 by dividing by site multiplicity. □ = vacancy.

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