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THE CRYSTAL STRUCTURE OF LANDAUITE, $Na[MnZn_2(Ti,Fe)_6Ti_{12}]O_{38}$

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ABSTRACT

Landauite from the Burpala alkaline complex, North Baikal region, USSR, crystallizes in the rhombohedral space group $R\bar{3}$ with lattice parameters a 9.152(5)Å, α 68.99(1)°. Its formula, determined from microprobe analysis, is $Na_{0.76}K_{0.16}Pb_{0.16}Ti_{15.70}Zn_{2.30}Fe_{1.76}Mn_{1.00}(Nb,Zr)_{0.08}O_{38}$. The structure was solved using 611 symmetry-independent reflections collected using Mo$K\alpha$ radiation and refined to an R value of 0.063. Landauite does *not* have the structure built of tetragonal pyramids and octahedra reported by Nikolayeva & Belov (1970). It is isostructural with senaite and crichtonite, having a structure based on close-packed anions with a mixed stacking sequence (*hhc*...) and with Na (and K,Pb) atoms ($M(0)$) ordered into one of the 38 anions sites per cell. Zn atoms occupy 2 tetrahedral sites and Ti, Fe, Mn atoms occupy 19 octahedral sites per cell. The octahedra articulate to give two basic structural units, a trigonal grouping of three-edge-shared octahedra containing $M(3)$ and a 6-member ring of edge-shared octahedra containing alternately $M(4)$ and $M(5)$. The trigonal triads link further by edge-sharing into 12-member rings. The tetrahedra, $M(2)$, and an octahedron, $M(1)$, link the 6-member and 12-member rings via corner-sharing. The metals show considerable ordering into the individual sites, with Mn in $M(1)$, Zn in $M(2)$, Ti + Fe in $M(3)$ and Ti in $M(4)$ and $M(5)$. The compositions of senaite, crichtonite, loveringite, davidite and landauite closely conform to the general formula $AM_{21}O_{38}$ where A = large cations (Ca, R.E., Pb, Sr, Na, K) and M = small cations (Ti, Fe, Mn, Zn). The individual minerals may be characterized by the dominant large cation in each case, *i.e.*, lead in senaite, strontium in crichtonite, calcium in loveringite, rare-earth elements in davidite and sodium in landauite.

SOMMAIRE

La landauite provenant du complexe alcalin Burpala, région du Baïkal nord, URSS, cristallise en $R\bar{3}$ avec paramètres a 9.152(5)Å, α 68.99(1)°. Une analyse à la microsonde donne la formule $Na_{0.76}K_{0.16}Pb_{0.16}Ti_{15.70}Zn_{2.30}Fe_{1.76}Mn_{1.00}(Nb,Zr)_{0.08}O_{38}$. La structure a été affinée sur 611 réflexions non-équivalentes jusqu'à un résidu R=0.063. La structure de la landauite ne se compose pas de pyramides tétragonales et d'octaèdres, ainsi que l'ont annoncé Nikolayeva & Belov (1970); comme celle des minéraux isostructuraux sénaite et crichtonite, elle est fondée sur un assemblage compact d'anions dont les couches successives présentent des modes d'empilement différents (*hhc*...). Na, K, Pb se trouvent en $M(0)$, un des 38 sites anioniques de la maille. Zn occupe deux sites tétraédriques, et Ti, Fe, Mn 19 sites octaédriques par maille. Les octaèdres s'assemblent en deux unités structurales fondamentales: (1) le groupe trigonal de trois octaèdres qui partagent chacun trois arêtes contenant $M(3)$; de tels groupes s'unissent par partage d'arête en anneaux de 12 membres; (2) l'anneau de six octaèdres, liés deux à deux par arête commune et contenant alternativement $M(4)$ et $M(5)$. Les tétraèdres, $M(2)$, et un octaèdre, $M(1)$, lient les anneaux de 6 et de 12 membres par partage de sommets. Les métaux sont largement ordonnés dans des sites spécifiques: Mn dans $M(1)$, Zn dans $M(2)$, Ti+Fe dans $M(3)$ et Ti dans $M(4)$ et $M(5)$. Sénaite, crichtonite, loveringite, davidite et landauite répondent à la formule générale $AM_{21}O_{38}$, dans laquelle A représente les gros cations (Ca, T.R., Pb, Sr, Na, K) et M, les petits cations (Ti, Fe, Mn, Zn). Ces minéraux se caractérisent chacun par la prédominance d'un gros cation: Pb dans la sénaite, Sr dans la crichtonite, Ca dans la loveringite, les terres rares dans la davidite et Na dans la landauite.

(Traduit par la Rédaction)

INTRODUCTION

Landauite, a titanate of zinc, iron and manganese, was discovered by A. M. Portnov in 1963 in the Burpala alkaline complex, North Baikal region of the USSR and described in detail by Portnov *et al.* (1966). From single-crystal X-ray diffraction studies, they obtained an *a*-centred monoclinic cell, a 5.22(5), b 8.95(5), c 9.53(5)Å, β 107°35′. The chemical analysis and unit-cell composition were given as $(Zn_{0.39}Mn_{0.15}Fe^{2+}_{0.09}Fe^{3+}_{0.29})_{\Sigma 0.91}(Ti_{2.87}Fe^{3+}_{0.13})_{\Sigma 3.00}O_7$, (Z=4), corresponding to the schematic formula $R^{2+}Ti_3O_7$.

Nikolayeva & Belov (1970) determined the crystal structure of landauite. However, their model did not refine below an *R* of 16%, and some discrepancies were apparent in the reported X-ray data. The *c* parameter reported by Nikolayeva & Belov (1970), 9.783(7)Å, differed by 0.25Å from the 9.53Å reported previously (Portnov *et al.* 1966). Moreover, neither set of cell parameters gave a satisfactory fit to the powder pattern of landauite, using the indices reported in the 1966 paper.

Landauite was brought to our attention via Kostov's (1968) treatise on mineralogy, in which he included this mineral with senaite in the ilmenite group. The powder pattern of landauite is almost identical to that of senaite (Rouse & Peacor 1968) if allowance is made for a constant correction to the former. We have recently determined the structure of senaite (Grey & Lloyd 1976); in view of the previous unsatisfactory structural analysis for landauite, and its possible structural relationship to senaite, we decided to redetermine the landauite structure. A sample of the type specimen was obtained from the Mineralogical Museum, Moscow, and subjected to microprobe analysis and single-crystal X-ray diffraction studies.

TABLE 1a. CHEMICAL ANALYSES OF LANDAUITE (WEIGHT PERCENT)

	Microprobe analyses*		Bulk chemical analysis
	Grain 1***	Grain 2	(Portnov et al. 1966)
TiO_2	72.59	71.77	73.46
Fe_2O_3**	6.77	7.65	10.75
FeO	1.26	1.42	2.00
MnO	4.12	4.33	3.45
Na_2O	1.36	1.39	
K_2O	0.45	0.41	
ZnO	10.85	10.49	9.97
ZrO_2	0.30	0.25	
PbO	2.10	1.85	
Nb_2O_5	0.29	0.33	
Total	100.09	99.89	99.63

*Si, Al, Mg, Ca, Cr, Ni, Cu, Sr, Y, Ce, La, Nd, Ta, Th, Sc, Hf, V also analyzed for - all less than 0.1%.

**Fe^{3+}/Fe^{2+} ratio assumed equal to that obtained by Portnov et al. (1966), column 3.

***Grain 1 also used for X-ray diffraction structure analysis. Unit cell composition for this grain, normalized to 38 oxygens is $(Na_{0.76}K_{0.16}Pb_{0.16})_{\Sigma 1.08}$ $(Ti_{15.70}Zn_{2.30}Fe^{3+}_{1.46}Fe^{2+}_{0.30}Mn_{1.00}(Nb,Zr)_{0.08})_{\Sigma 20.84}O_{38}$.

EXPERIMENTAL

The type specimen of landauite consists of a number of poorly faceted, rounded black grains very similar to altered ilmenite grains in beach sand deposits, as well as some black columnar crystals, ranging in size from 0.5 to 1 mm. Initially each of the grains was examined in a scanning electron microscope using an energy dispersive X-ray analyzer (EDAX). Two of the grains showed only a titanium peak in the EDAX pattern and were identified by X-ray diffraction as brookite; a third grain showed yttrium and titanium peaks only. The remaining grains contain titanium, zinc, iron and manganese as main elements by EDAX analysis, *i.e.*, they were qualitatively consistent with the reported chemical analysis for landauite (Portnov *et al.* 1966). One of the grains was selected for an X-ray diffraction study, using Weissenberg and precession methods. The photographs were identical to those obtained previously for twinned crichtonite (Grey *et al.* 1976), showing hexagonal symmetry with $a_{\text{hex}} \simeq 37.4$Å and $c_{\text{hex}} \simeq 20.7$Å. Following the procedure used for crichtonite, we progressively fragmented the grain of landauite, breaking it into smaller and smaller pieces, each time examining the fragments by X-ray diffraction, until an untwinned fragment $0.063 \times 0.058 \times 0.038$mm was found. All reflections could be indexed on a trigonal cell with $a_{\text{hex}} = 37.4/\sqrt{13} \simeq 10.4$Å, $c_{\text{hex}} = 20.7$Å. Because the crystal symmetry and unit-cell parameters obtained in this study differed from those previously reported (Portnov *et al.* 1966), a second fragment was taken from the same original twinned crystal and was mounted and polished for a microprobe analysis. The results of the analysis are given in Table 1a together with an analysis of an unfragmented grain, and the original analysis of Portnov *et al.* (1966). There is close agreement between our microprobe analyses and the "bulk" chemical analysis for titanium, zinc and manganese obtained by Portnov *et al.* (1966). The only element for which a large difference occurs, iron, is also the element that shows the maximum variation between individual grains. In addition to the elements reported above, we also found significant levels of sodium, lead and potassium in landauite (Table 1a).

For the intensity data collection, the untwinned crystal fragment was mounted on a Philips PW1100 4-circle automatic diffractometer. Fourteen high-angle ($2\theta > 20°$, Mo$K\alpha_1$ radiation) reflections provided the 2θ values used to calculate the lattice parameters reported in Table 1b. Intensities were collected with graphite-monochromated MoKα radiation with a tower angle of 12.18°. A θ-2θ scan, 3–25°, was used with a variable scan width given by $\Delta\theta = (1.0 + 0.3 \tan\theta)$ 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 PW 1100 diffractometer by Hornstra & Stubbe (1972). Because of the very small size of the crystal an absorption correction was not applied. However, a partial compensation was achieved by averaging the intensities of equivalent reflections, ±*(hkl, lhk, klh)* in the rhombohedral cell (interscale *R* factor for equivalent reflections = 0.059.) Thus the 2423 reflections were reduced to a unique set of 760, of which 611 had $I > 2\sigma[I]$; these were used in the structure refinement.

Scattering factor curves for Na, K, Pb, Ti, Fe, Zn and Mn neutral atoms are those of Cromer & Mann (1968). Anomalous dispersion corrections for all atoms are from Cromer & Liberman (1970). All computing was performed on the Monash University CDC 3200 and Burroughs 6700 and the CSIRO CDC 7600 computers.

REFINEMENT OF THE STRUCTURE

A satisfactory refinement for landauite in space group $R\bar{3}$ was obtained, based on the assumption that it was isostructural with senaite (Grey & Lloyd 1976); the atomic coordinates previously obtained for this mineral were used as starting parameters. A composite Na-K-Pb scattering curve was used for the origin atom, *M*(0), and the titanium, iron, manganese and zinc atoms were ordered into site *M*(1) to *M*(5) in order of decreasing size, consistent with the metal-atom ordering schemes found for senaite and crichtonite. A series of full-matrix least-squares refinements resulted in a satisfactory convergence of all positional and isotropic thermal parameters. A final *R* index of 0.063 was obtained for the 611 observed data. A difference Fourier synthesis showed features indicative of anisotropic thermal motion of some of the atoms along the direction of the three-fold axes. However, because of the large number of extra variables involved, and the relatively few observed data, an anisotropic-temperature-parameters refinement was not attempted. The final atomic coordinates, isotropic thermal parameters and site occupancies are given in Table 2. Calculated bond lengths and angles are given in Table 3 and observed and calculated structure factors are listed in Table 4, available at nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 1b. UNIT-CELL PARAMETERS FOR LANDAUITE, TRIGONAL $R\bar{3}$

a_{rh}	= 9.152(5) Å	a_{hex}	= 10.366(7)
α_{rh}	= 68.99(1)°	c_{hex}	= 20.77(1)
Z_{rh}	= 1	Z_{hex}	= 3
d_{calc}	= 4.46		
d_{meas}	= 4.42 (Nikolayeva & Belov 1970)		
$\overline{\mu R}$	= 0.24		

TABLE 2. LANDAUITE: FINAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

Atom	Site Multiplicity	Scattering Curve	X	Y	Z	B(Å^2)
M(0)	1	0.70Na + 0.15K + 0.15 Pb*	0.0000	0.0000	0.0000	2.3(1)
M(1)	1	Mn	0.5000	0.5000	0.5000	0.59(9)
M(2)	2	Zn	0.3103(1)	0.3103(1)**	0.3103(1)	0.79(5)
M(3)	6	0.64Ti + 0.36Fe*	0.3493(3)	0.1261(3)	0.0190(3)	0.51(4)
M(4)	6	Ti	0.3025(3)	0.7196(3)	0.1503(3)	0.48(4)
M(5)	6	Ti	0.4752(3)	0.0862(3)	0.6363(3)	0.43(4)
O(1)	6	O	0.3023(11)	0.6285(11)	0.3778(11)	0.53(14)
O(2)	6	O	0.1555(11)	0.2375(11)	0.9391(11)	0.40(14)
O(3)	6	O	0.9182(11)	0.4592(11)	0.3009(11)	0.43(14)
O(4)	6	O	0.1447(11)	0.5170(10)	0.9890(11)	0.40(13)
O(5)	6	O	0.3892(11)	0.4856(10)	0.1364(11)	0.34(14)
O(6)	6	O	0.7056(10)	0.2420(10)	0.0722(11)	0.28(13)
O(7)	2	O	0.2138(7)	0.2138(7)	0.2138(7)	0.13(22)

*Scattering curve contributions, from composition in Table 1a, normalized to 1.0. Minor amount of Zn accounted for by Fe curve, Nb and Zr not accounted for.

**Note reversal of order of Y,Z c.f. that in senaite (Grey & Lloyd 1976) resulting from opposite direction of unique axis in data collection.

TABLE 3. LANDAUITE - INTERATOMIC DISTANCES (Å) 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]	2.211		M(2) - O(5)	[3]	1.950		M(0) - O(2)	[6]	2.800	
				- O(7)		2.004		- O(6)	[6]	2.845	
O(1) - O(1)^{1}	[6]	3.07	87.78*	O(5) - O(5)^{1}	[3]	3.24	112.22	O(2) - O(6)	[6]	2.78	59.00
- O(1)^{11}	[6]	3.19	92.22	- O(7)	[3]	3.17	106.56	O(2) - O(2)	[6]	2.77	59.24
								O(6) - O(6)	[6]	2.86	60.23
								O(2) - O(6)^{1}	[6]	2.91	61.94

	Distance	O-M-O angle		Distance	O-M-O angle		Distance	O-M-O angle
M(3) octahedron			M(4) octahedron			M(5) octahedron		
M(3) - O(4)	1.935		M(4) - O(2)	1.893		M(5) - O(1)	1.842	
- O(2)	1.954		- O(1)	1.945		- O(4)	1.891	
- O(3)	1.963		- O(6)	1.963		- O(3)	1.910	
- O(4)^{1}	2.026		- O(3)	1.999		- O(5)	2.022	
- O(7)	2.022		- O(6)^{1}	2.003		- O(6)	2.035	
- O(2)^{1}	2.084		- O(5)	2.034		- O(5)^{1}	2.113	
O(4) - O(4)^{1}	2.70	86.11	O(1) - O(6)	2.58	81.62	O(5) - O(5)^{1}	2.59	77.43
- O(2)	2.72	82.78	O(5) - O(3)	2.60	80.14	- O(3)	2.60	80.20
O(7) - O(2)	2.67	81.19	- O(6)	2.61	81.70	O(6) - O(1)	2.58	83.31
- O(2)^{1}	2.67	84.44	- O(1)	2.70	85.43	- O(5)	2.61	80.24
O(2) - O(2)^{1}	2.77	86.48	O(2) - O(6)	2.78	91.01	O(1) - O(5)	2.80	89.84
O(4) - O(7)	2.81	88.06	O(1) - O(3)	2.83	91.90	O(4) - O(6)	2.79	90.53
- O(3)	2.86	91.66	O(6) - O(6)^{1}	2.86	92.10	O(3) - O(5)^{1}	2.83	91.82
- O(2)^{1}	2.89	91.99	O(2) - O(1)	2.84	95.56	- O(4)	2.85	97.12
O(4) - O(3)^{1}	2.83	93.11	- O(3)	2.89	95.72	O(1) - O(4)	2.82	98.27
O(3) - O(7)	2.89	93.17	- O(6)^{1}	2.91	97.78	- O(3)	2.93	102.65
- O(2)	2.97	98.42	O(6)^{1}- O(3)	2.87	92.76	O(5)^{1}- O(4)	2.89	95.03
O(4)^{1}-O(2)^{1}	2.98	100.22	- O(5)	2.93	93.19	- O(6)	2.96	91.22

Metal-Metal distances**

M(1) - M(5)	c	3.602	M(2) - M(5)	c	3.401	M(0) - M(4)	c	3.354
- M(4)	c	3.805	- M(5)^{1}	c	3.465			
			- M(4)	c	3.483			
M(3) - M(3)^{1}	e	2.895	M(4) - M(5)	e	2.929	M(5) - M(5)	e	3.227
- M(3)^{11}	e	3.026	- M(5)^{1}	e	3.059			
- M(5)	e	3.384	M(4) - M(4)^{1}	c	3.940			
- M(4)	c	3.425	M(4) - M(5)^{11}	e	3.072			
- M(5)^{1}	c	3.463						
- M(4)^{1}	c	3.559						
- M(5)^{11}	c	3.648						
- M(4)^{11}	c	3.559						

Standard deviations for M-M, M-O, and O-O are 0.004, 0.009 and 0.015 Å respectively and for angle O-M-O 0.4 degrees.

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

DESCRIPTION OF THE STRUCTURE

The structure determined here for landauite bears no relationship to the structure obtained by Nikolayeva & Belov (1970), whose model was characterized by two types of cation polyhedra, square pyramids and elongated octahedra. They assigned tetravalent titanium atoms to the 5-coordinated sites and Ti^{3+}, Zn^{2+}, Fe^{2+} and Mn^{3+} to the 6-coordinated sites. Pairs of square pyramids shared edges, then linked by corner-sharing into infinite chains, $[Ti_2O_6]_\infty$, whereas the octahedra shared faces and also linked into infinite double chains by corner-sharing. By comparison, the structure described here has the small cations in tetrahedral and octahedral coordination and the polyhedra articulate only by edge- and corner-sharing. One possible explanation is that the crystal selected from the landauite specimen for single-crystal analysis by Nikolayeva & Belov (1970) was not landauite. As was discussed earlier, the sample of "landauite" as received contained three grains of other minerals.

A representation of the structure for landauite, given in Figure 1, shows layers of polyhedra parallel to $(001)_{\text{hex}}$ for three consecutive sequences of metal-atom arrangements. The anions are in a close-packed array and have a stacking sequence hexagonal, hexagonal, cubic (*hhc*...) along $[001]_{\text{hex}}$. Within the cubic close-packed layers, Na (and K, Pb) atoms are ordered into one in every thirteen anion sites, *M*(0) (Fig. 1). The hexagonal close-packed layers contain oxygens only. Between pairs of hexagonal close-packed layers, metal atoms *M*(1) and *M*(3) occupy isolated and edge-shared octahedral sites, respectively. The *h-M-h* layer is shown unshaded in Figure 1. The edge-shared $M(3)O_6$ octahedra form interconnected 12-membered rings with an $M(1)O_6$ octahedron at the centre of each ring. Between adjacent cubic and hexagonal anion layers, *h-M-c*, metals *M*(4) and *M*(5) alternate in edge-shared octahedral sites linked into six-membered hexagonal rings, and metals *M*(2) occupy tetrahedral sites. As seen in Figure 1, the hexagonal rings of octahedra are interconnected via corner-sharing with the basal oxygens of the $M(2)O_4$ tetrahedra. The polyhedra in the adjacent *h-M-h* and *h-M-c* layers connect only via corner-sharing whereas between pairs of *h-M-c* layers, the octahedra in the six-membered rings are linked by edge-sharing. Landauite is isostructural with senaite and crichtonite; other diagrams of the structure and more detailed descriptions are given in papers on these minerals (Grey & Lloyd 1976; Grey *et al.* 1976).

METAL-ATOM ORDERING IN LANDAUITE

In the structure refinement, scattering curves for manganese, zinc and titanium neutral atoms were used for sites *M*(1), *M*(2) and *M*(4)+*M*(5), respectively, and a composite titanium/iron curve was used for site *M*(3). The number of different metals, all with similar atomic numbers, precluded site-occupancy refinement; the sensible thermal parameters obtained for *M*(1)–*M*(5), (Table 2), and the close agreement between the refined average metal-oxygen bond lengths and the values calculated using Shannon & Prewitt's (1969) ionic radii tables, justify the proposed ordering scheme. Thus we have *M*(1)–O= 2.211Å (*cf.*, Mn^{2+}–O=2.19Å), *M*(2)–O=1.964Å (*cf.*, Zn^{2+}–O (tetrahedral)=1.97Å), and *M*(4)–O=1.973Å, *M*(5)–O=1.969Å (*cf.*, Ti^{4+}–O=1.97Å).

On the basis of the proposed ordering scheme, an ideal end-member composition for landauite can be given as $Na[MnZn_2(Ti,Fe)_6Ti_{12}]O_{38}$,where the Ti/(Ti+Fe) ratio in site *M*(3) is a function of the ferrous to ferric iron ratio. It conforms to the general composition proposed also for crichtonite, senaite, davidite and loveringite, $AM_{21}O_{38}$, where *A* = large cations, Na, K, Ca, Sr, Pb, R.E., and *M* = small cations, Ti, Fe, Cr, V, Zn, Mn *etc.* (Gatehouse *et al.* 1978).

A comparison of the ideal composition for

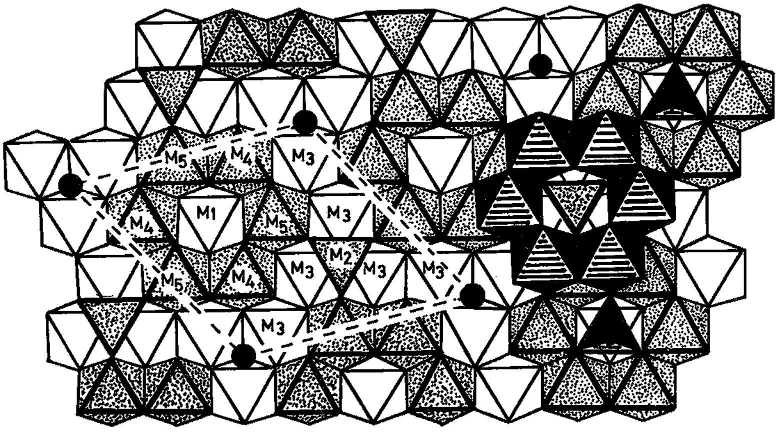

FIG. 1. Representation of three consecutive $(001)_{\text{hex}}$ layers of polyhedra in landauite, viewed along $[001]_{\text{hex}}$. Only part of the third layer (heavy shading) is shown for clarity. The hexagonal unit-cell edges, *a* and *b*, are shown by the dashed lines. The small filled circles represent sodium atoms. The atom labels *M*(1) to *M*(5) correspond to those given in Table 2.

landauite with that determined from the chemical analysis, Table 1a, reveals some important differences; the latter has a large cation sum, ΣA, greater than one, and a small cation sum, ΣM, less than 21. The low value for ΣM may be simply due to an incorrect assumption that the Fe^{3+}/Fe^{2+} ratio is equal to that obtained by explained in this way. Ions such as Na^+, K^+ and Portnov *et al.* (1966) on a bulk landauite sample. However, the large ΣA value cannot be explained in this way. Ions such as Na^+, K^+ and Pb^{2+} are too large to occupy the interstitial sites $M(1)$ to $M(5)$; we must consider the possibility that these ions substitute into more than one anion site. One possibility, that the extra 0.08 A cations replace oxygen at site O(7), is supported by the observation that the thermal parameter for O(7), 0.13, is considerably smaller than the B values for the other oxygens, 0.28 to 0.53. (Both anion sites $M(0)$ and O(7) lie on three-fold axes; Pabst (1961) has discussed the possibility that these sites are oxygen-free in the related mineral davidite.) A refinement was in fact carried out with 0.08 (Na,K,Pb) replacing oxygen in O(7), which resulted in the B value for O(7) increasing to 0.37. The presence of large cations in site O(7) is also consistent with a ΣM value less than 21; M cations in sites $M(2)$ and $M(3)$ bond to anion O(7), and if this is occupied by sodium ($M(2)$–Na and $M(3)$–Na $\simeq$ 2Å), then the surrounding sites $M(2)$ and $M(3)$ will be empty. The ratio of empty M sites to cation-occupied O(7) sites is 4:1. However, because of the uncertainty in the Fe^{3+}/Fe^{2+} ratio in the grain studied, this could not be checked quantitatively.

A further complication regarding O(7) is that it has an unusally high electrostatic valence sum. On the basis of the ideal composition proposed above, a value of 2.25 is calculated; this value is modified only slightly if we consider the real composition (Table 1a). This oversaturation of O(7) is a feature common to the crichtonite group of minerals; it is reflected in $M(2)$–O(7) and $M(3)$–O(7) bonds that are longer than the average $M(2)$–O and $M(3)$–O values (Table 3).

Landauite as a member of the crichtonite group

We have previously commented on the fact that both senaite and crichtonite contain lead and strontium as the main A cations, and that the mineral names should apply to phases which contain *dominant* lead and *dominant* strontium, respectively (Grey *et al.* 1976). We find, from a recent microprobe analysis on the related mineral mohsite, that an equal number of atoms of lead and strontium occur as the main A cations. Thus, mohsite, as a member of the senaite-crichtonite series (Gatehouse *et al.* 1978), does not warrant a new name. Consistent with such a nomenclature scheme, landauite would be classed as a sodium-dominant member of the crichtonite group.

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