Delindeite and lourenswalsite, two new titanosilicates from the Magnet Cove region, Arkansas

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Abstract

Delindeite and lourenswalsite are two new barium titanosilicate minerals found as microscopic crystals in miarolitic cavities in nepheline syenite in the Diamond Jo quarry, Hot Spring County, Arkansas. Delindeite is found as aggregates of flake-like crystallites in compact spherules, light pinkish grey in colour, with a resinous, pearly lustre. The flakes are biaxial positive with average $n \sim 1.813$; the measured density is 3.3 g/cm^3. Electron diffraction revealed a monoclinic unit cell in space group $C2/m$ or subgroup, with $a = 21.617(13), b = 6.816(5), c = 5.383(3)$ Å, $\beta = 94.03(5)°$ (refined from X-ray powder data). The strongest X-ray lines are (hkl, d_{obs}, I_{rel}): (200, 10.80, 100); (311, 3.54, 24); ($\bar{6}$01, 3.083, 28); (601, 2.888, 31); ($\bar{2}$21, 2.806, 20); (910, 2.262,18). The crystals are submicroscopically twinned on (100) and also produce additional continuous diffraction streaks parallel to a^*, which double the b and c axes. The formula derived from electron and ion probe analyses (H$_2$O by difference), as constrained by density and molar volume data, is approximately (Na,K)$_{2.7}$(Ba,Ca)$_4$(Ti,Fe,Al)$_6$Si$_8$O$_{26}$(OH)$_{14}$, with Na > K, Ba $\gg$ Ca, Ti $\gg$ Fe,Al; $Z = 1$. Lourenswalsite occurs as very thin hexagonal plates in rosettes, silver grey to light brownish grey in colour. The crystals are biaxial negative with very low $2V$ angle. Indices of refraction are $n_\alpha = 1.815$, $n_\beta \approx n_\gamma = 1.840$; the measured density is 3.17 g/cm^3. X-ray and electron diffraction show a sharp pseudohexagonal lattice with $a = 5.244$ Å, but extremely diffuse diffraction streaks normal to the $hk0$ plane. In these streaks a period of 20.5 Å can be discerned. A hexagonal unit cell with $a = 5.244(2)$ Å, $c = 20.49(3)$ Å can be refined from the powder diffraction data but does not account for some lines, probably because of extreme layer disorder as shown by precession single-crystal patterns. The strong X-ray powder lines are (002, 10.22, 20); (—, 3.93, 20); (111, 2.608, 100); (300, 1.5145, 80); (220, 1.3111, 25). The formula given by microprobe analyses, constrained by density and molar volume data, is approximately (K,Ba)$_2$(Ti,Mg,Ca,Fe)$_4$(Si,Al,Fe)$_6$O$_{14}$(OH)$_{12}$ with K > Ba, Ti $\gg$ (Mg,Ca,Fe), Si > Al > Fe; $Z = 1$. These minerals are formed under oxidizing weathering conditions, and iron is assumed to be in the Fe^{3+} state.

Introduction

THE Magnet Cove region near Hot Springs, Arkansas has long been famous for its titanium-bearing minerals. Since the classic work of J. Francis Williams (1891) few comprehensive mineralogical studies of the deposits have been carried out, although it is now becoming apparent that the mineralogy is very complex and includes many rare and new mineral species. For example, kassite, CaTi$_2$O$_4$(OH)$_2$, has recently been found at the Diamond Jo quarry and described by Evans et al. (1986) as the first occurrence outside the USSR. The manganese analogue of astrophyllite, kupletskite, has frequently been found at the 3M mine in Little Rock as well as at the Diamond Jo quarry in Hot Spring County. Here we describe two new titanosilicate minerals from Diamond Jo, delindeite and lourenswalsite.

In the syenite at Diamond Jo, Williams (1891)

cited the presence of orthoclase, nepheline, can-crinite, aegerine, biotite, sodalite, sphene, magnetite, pyrite, fluorite, hematite, and calcite. Erickson and Blade (1963), who have made the most detailed geologic study of the Magnet Cove alkalic complex, also list Ti-garnet, apophyllite, pseudowavellite, analcime, apatite and perovskite. Besides these, sixteen others have been found: albite, arfvedsonite, taeniolite, monticellite, natrolite, pectolite, baryte, barytocalcite, brookite, sphalerite, labuntsovite, kupletskite, astrophyllite, kassite, and the two new barium titanosilicates delindeite and lourenswalsite described in this paper.

Occurrence

Perhaps the best and most interesting exposure in the Magnet Cove region is in the Diamond Jo quarry in Hot Spring County, Arkansas. The quarry lies on the south edge of the Magnet Cove alkalic complex, in a zone of xenolith-bearing garnet–pseudoleucite syenite in contact with a coarse-grained nepheline syenite which rims the complex. The nepheline syenite in the quarry contains innumerable vugs and miaroles ranging up to 10 cm across, lined with many different mineral species. The two new barium titanosilicate minerals occur in these vugs, but only in a limited area of the quarry face a few metres across where the syenite is especially rich in cavities. Pyroxene in the vugs ranges from compositions near the diopside–hedenbergite join through aegerine–augite to acmite, with corresponding variations in colour. Pyroxene, sphene, pectolite, baryte, sphalerite, K-feldspar and labuntsovite are especially well crystallized. Labuntsovite, $K_4Na_4Ba_2(Ti,Nb,Fe)_9$

$Si_{16}O_{55}(OH)_2 \cdot 6H_2O$, was previously known in North America only from the Green River trona beds of Wyoming and from Mont St. Hilaire, Quebec. Delindeite and lourenswalsite are closely associated with fine platy crystals of baryte and pectolite, and small prismatic crystals of labuntsovite.

Delindeite is named in honour of Henry deLinde of Mabelvale, Arkansas, owner of the Diamond Jo quarry, and a leading amateur mineralogist who has preserved this unique mineral locality. Lourenswalsite is named for Dr Lourens Wals who is of Dutch origin, living in Turnhout, Belgium, and one of the foremost mineral collectors in Belgium. Both names have been approved by the International Commission on New Minerals and Mineral Names.

Delindeite

Description and physical properties. This mineral has a light pinkish grey colour: it occurs as tiny, compact, spherulitic aggregates ranging up to about 1 mm in diameter. The aggregates are composed of micrometre-sized, lath-like or flake-like crystals, which have a resinous, pearly lustre. Delindeite is translucent and biaxial positive, with parallel extinction and negative elongation when lying on the cleavage. In the plane of the cleavage $\{001\}$ $n_\alpha = 1.790(5)$, $n_\beta = 1.825(5)$. Because of the aggregate nature of even the smallest fragments (Fig. 1) and the submicrometre size of individual crystallites, it proved impossible to obtain a reliable measure of n_γ, the index normal to the platelets, but it must be > 1.825. The value calculated from the Gladstone–Dale relationship is 1.982. $2V$ is ob-
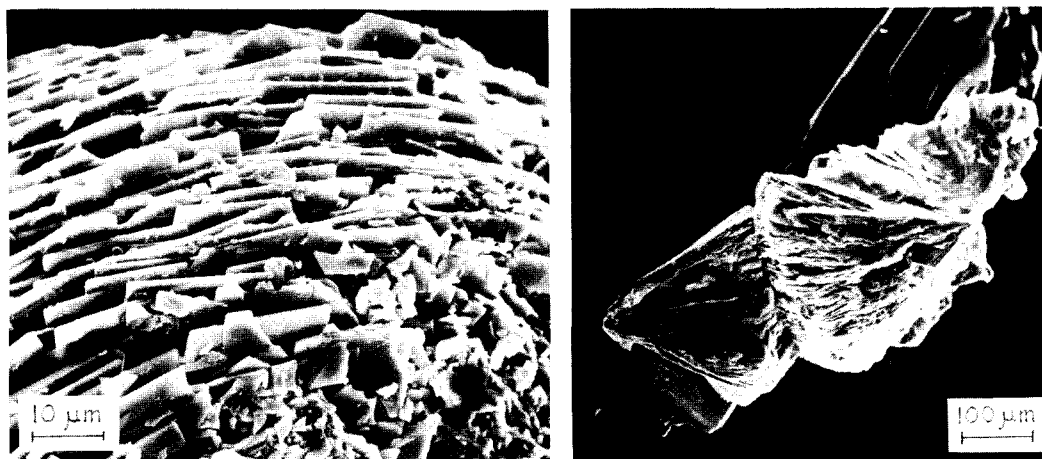

FIG. 1. Scanning electron micrographs of delindeite, on pectolite crystal (right).

served to be moderate, and predicted to be 54° using the calculated n_y. All values are measured with white light. No pleochroism was observed and dispersion was not measured.

The density was measured by flotation using calibrated liquids and found to be 3.3(1) g/cm³. This value is significantly low due to the aggregate nature of the 'grains', and the calculated value of 3.70(1) g/cm³ is to be preferred. The fracture is irregular and the tenacity brittle. The crystallites are quite fragile. Cleavage on {001} is good.

Chemistry. Delindeite was analysed primarily by electron microprobe techniques because of the extremely small amounts of material available and minute crystal size. Analyses were performed on an ARL-SEMQ instrument, using an operating voltage of 15 kV and a beam current of 0.15 μA. A beam diameter of approximately 20 μm was used together with analysis times of 10 seconds, chosen to minimize water loss. Standards used were: (set 1) benitoite for Ba, Ti, and Si, and Kakanui hornblende for Al, Fe, Mg, Ca, K, and Na: (set 2) sphene for Si, Al, and Ti; omphacite for Fe, Mg, Na, and Ca; Kakanui hornblende for K; and benitoite for Ba—all from the U.S. National Museum of Natural History. Analyses were highly reproducible from point to point and on different aggregates, and the two sets gave essentially identical results. The chemical composition of delindeite in Table 1 is the average of 4 points with standard set 1, and 4 points with standard set 2. Corrections to the raw data were made using the standard Bence–Albee factors.

Careful wavelength scans showed that no elements with atomic number greater than 8 other than those listed in the analysis were present in significant amounts (greater than 0.2–0.3 wt. %). The difference between the sum of the analysis and 100% is attributed to H_2O. This assumption was tested by repeated analysis of the same spot with a beam approximately 1 μm in diameter at 0.5 μA. The analysis totals approached 100% with increasing exposure while the ratios of the oxides, except for Na_2O and K_2O, remained essentially constant, thus indicating volatilization of water (presumably) and alkalis.

In order to confirm these observations, ion probe analysis of delindeite was carried out through the kindness of Prof. F. Begemann and Mr S. Specht of the Max-Planck Institut für Chemie, Mainz, Federal Republic of Germany. The instrument used was a CAMECA IMS 3f ion probe; standards employed for Li, Be, B, and H_2O were spodumene, hambergite and synthetic beryl from the collection of the National Museum of Natural History, Smithsonian Institution. The results showed that no significant amounts of any elements were present other than those reported above from electron

microprobe analysis. Specifically, there are only trace amounts of Li and virtually none of the light elements Be, B, C, N, and F, which cannot be detected with the microprobe. The presence of $(OH)^-$ is confirmed, in amounts compatible with the value obtained for water by difference from the microprobe analysis.

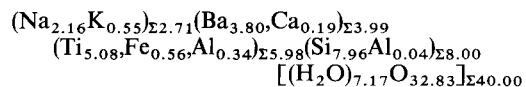Table 1. Electron probe analyses of delindeite and lourenswalsite

Component	Delindeite (wt. pct.)	Lourenswalsite (wt. pct.)	k^a
SiO_2	27.10	28.20	0.208
Al_2O_3	1.10	5.37	0.207
$Fe_2O_3^b$	2.54	6.18	0.268
MgO	absent	1.57	0.200
CaO	0.61	0.81	0.210
K_2O	1.47	5.82	0.196
Na_2O	3.79	absent	0.190
TiO_2	23.02	28.73	0.393
BaO	33.05	11.69	0.128
H_2O (by difference)	7.32	11.63	0.340
Total	100.—	100.—	

Notes:

[a] Molar refractivity from Mandarino (1981).

[b] Calculated as ferric iron (see Discussion).

The analysis yields the following empirical formula, based on 40(O+OH):

$$(Na_{2.16}K_{0.55})_{\Sigma 2.71}(Ba_{3.80},Ca_{0.19})_{\Sigma 3.99}$$
$$(Ti_{5.08},Fe_{0.56},Al_{0.34})_{\Sigma 5.98}(Si_{7.96}Al_{0.04})_{\Sigma 8.00}$$
$$[(H_2O)_{7.17}O_{32.83}]_{\Sigma 40.00}$$

or approximately: $(Na,K)_{2.7}(Ba,Ca)_4(Ti,Fe,Al)_6Si_8$ $O_{26}(OH)_{14}$, with Na > K, Ba ≫ Ca, and Ti ≫ Fe > Al. The total iron is reported in Table 1 as Fe^{3+} (in the absence of wet-chemical or Mössbauer analyses) for reasons described in the Discussion section.

Crystallography. X-ray powder diffraction data for delindeite are listed in Table 2. The data were obtained by the Debye–Scherrer method using Ni-filtered Cu radiation, with Si as an external standard (NBS Ref. Mat. No. 640). Line spacings were measured on a Nonius optical viewer and intensities were obtained from a strip chart made with a Nonius microdensitometer by comparison with a calibrated exposure strip. The powder diffraction data were highly reproducible from among several samples. The nature of the crystals

precluded any single-crystal X-ray diffraction study which is necessary to permit indexing of the powder data, and so recourse was made to electron diffraction techniques.

Individual flakes of delindeite were examined in a Jeol 200B transmission electron microscope operated at 200 keV, and were found to give highly characteristic but complexly twinned diffraction patterns. Fig. 2A shows a centred net found close to the plane of the cleavage flake. The orthogonal spacings observed, measured against a simultaneously recorded gold powder pattern, are 22.1
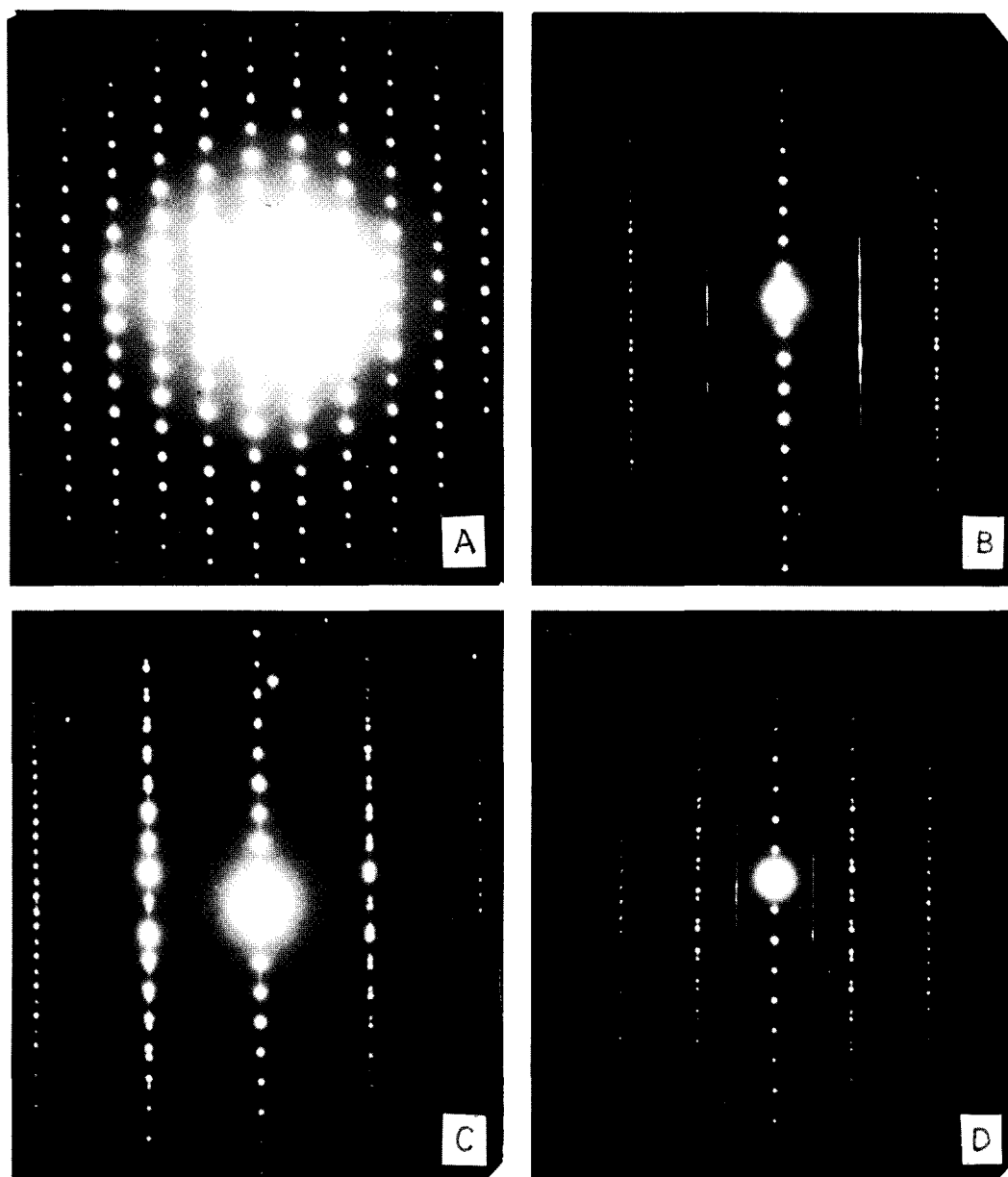

FIG. 2. Electron diffraction patterns of delindeite: (A) $hk0$ net; (B) net containing a^* (vertical) tilted 23° to $hk0$ plane; (C) net tilted 36.5° to $hk0$ plane; (D) net tilted 51.5° to $hk0$ plane.

and 6.9 Å. It was nearly impossible to obtain a diffraction net containing the normal to the cleavage plane, but by tilting the crystal around the long axis in the plane a series of diagonal nets could be registered as seen in Figs 2B, C, and D. These revealed twinning of a sharp lattice on a microscopic scale, and also additional diffuse streaks. In Fig. 3 the reciprocal lattice shown by these patterns is projected along the axis of tilt, to show how the whole lattice can be reconstructed. The resulting sharp crystal lattice is monoclinic in space group $C2/m$ or a corresponding subgroup. The unit cell derived in this way was used to index the powder

data, and the parameters were refined by least-squares analysis. The final results are given in Table 2. These results rule out the possibility of a c-glide plane, although the $h0l$ net could not be directly registered by electron diffraction.

Gladstone–Dale relationship. The Gladstone–Dale relationship between chemical composition, mean index of refraction and density was evaluated for delindeite using the constants of Mandarino (1981). The mean index of refraction n observed for delindeite is > 1.813, although this value is only approximate because of the difficulty of obtaining optical measurements of n_y on these aggregates,
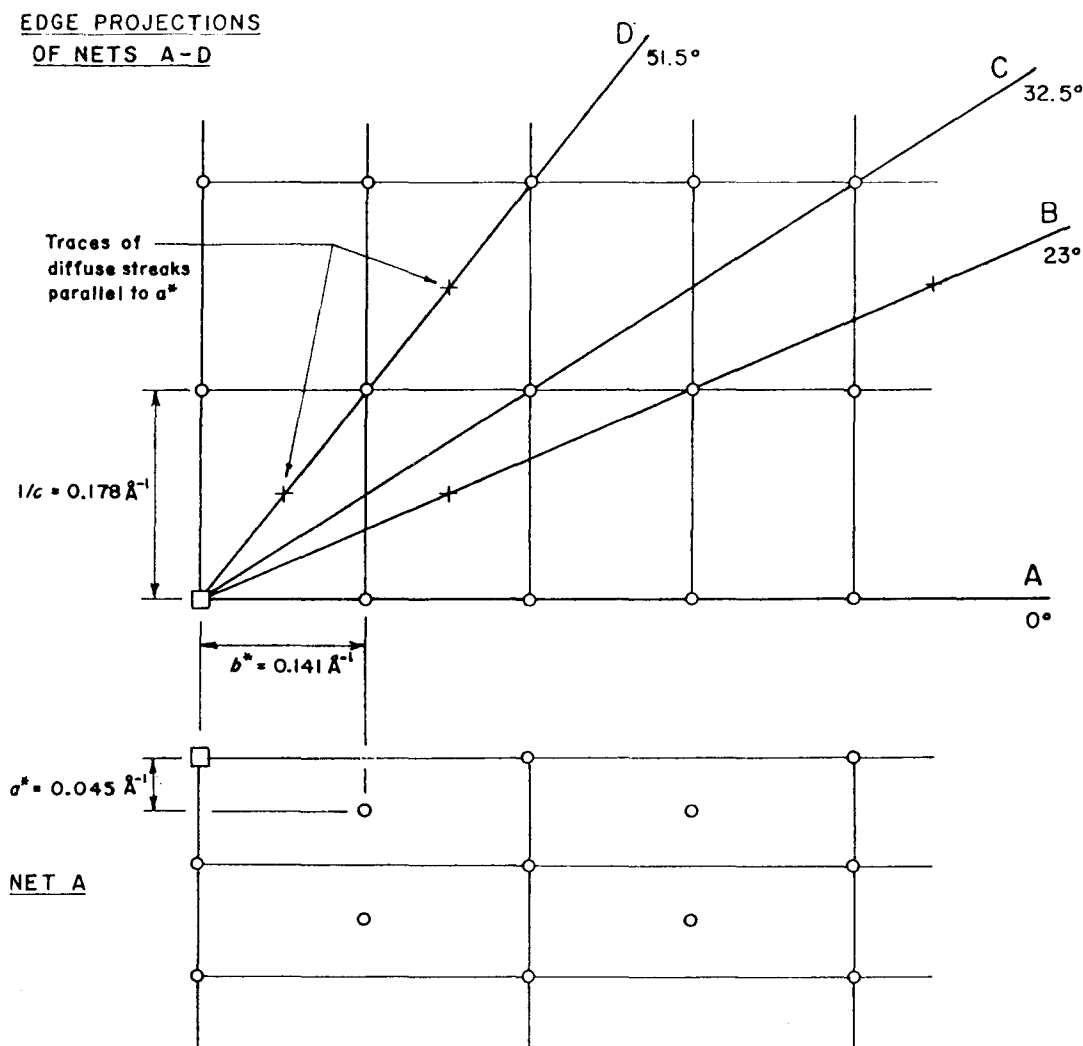

FIG. 3. Interpretation of reciprocal lattice nets of Fig. 2. According to the results of the X-ray powder study the measured reciprocal dimensions shown should be increased by about 4%.

Table 2. X-ray powder data for delindeite

hkl	d(obs)	d(calc)	I	hkl	d(obs)	d(calc)	I
200	10.80	10.78	100	$\overline{4}02$		2.474	
110	6.53	6.50	2	620	2.471	2.473	7
400		5.39		711	2.428	2.425	1
001	5.37	5.37	3	312	2.312	2.313	3
$\overline{2}01$	4.95	4.95	3	910	2.262	2.260	18
310		4.95		130		2.260	
201	4.65	4.68	1	621	2.206	2.206	15
$\overline{1}11$	4.15	4.18	11	10.0.0	2.155	2.156	5
111		4.10		$\overline{2}22$		2.092	
$\overline{3}11$		3.73		$\overline{1}31$	2.089	2.089	12
401	3.69	3.68	13	131	2.076	2.077	10
$\overline{4}01$	3.92	3.95	10	911	2.037	2.036	7
510		3.64		712	1.880	1.881	5
600		3.59		730	1.833	1.829	3
311	3.54	3.55	24	12.0.0	1.807	1.797	1
020	3.41	3.42	5	622	1.776	1.777	3
220	3.255	3.250	10		1.735		2
$\overline{6}01$	3.083	3.089	28		1.711		6
511	2.936	2.933	7		1.695		8
601	2.888	2.894	31		1.670		4
420		2.881			1.646		4
021		2.878			1.630		6
710		2.807					
$\overline{2}21$	2.806	2.807	20				
221	2.753	2.755	16				
800	2.697	2.695	11				
002		2.685					
$\overline{2}02$	2.654	2.649	11				
$\overline{4}21$		2.579					
202		2.563					
$\overline{7}11$	2.532	2.556	4				

Notes:
(1) Least squares analysis of 19 lines yields the monoclinic unit cell parameters: a = 21.617(13)Å, b = 6.816(5)Å, c = 5.383(3)Å, β = 94.03(5)°.
(2) All predicted calculated d spacings to 2.500Å are listed (left columns).

and is necessarily low. Using a density of 3.70 g/cm³ calculated from X-ray data (see Discussion), the parameter $K_p = (n-1)/D$ (Mandarino, 1981), is

thus $K_p = 0.220$. The parameter $K_c = \Sigma(k_i p_i)/100$, is $K_c = 0.234$, based on the analysis of Table 1, which lists the weight percentages p_i and molar refractivities k_i for each component i. The 'compatibility index' $[1-(K_p/K_c)]$ is thus 0.0598, which is on the boundary between Mandarino's 'good' and 'fair' categories; this is very satisfactory considering the difficulty of measuring n_y.

Lourenswalsite

Description and physical properties. The second new barium-titanium mineral, lourenswalsite, is silvery grey to light brownish grey in colour, and occurs as tiny rosettelike clusters of fragile, very thin hexagonal flakes a few micrometers on edge (Fig. 4). The habit is distinct from that of delindeite whose aggregates of flakes are more compact and show no distinct geometric shape.

Lourenswalsite is translucent and optically biaxial negative with extremely low 2V angle; it has parallel extinction and positive elongation when viewed lying on the platy cleavage. The measured indices of refraction (white light) are $n_\alpha = 1.815(2)$, $n_\beta \approx n_y = 1.840(2)$; $2V \approx 0$. Pleochroism is absent and dispersion could not be measured because of the size and habit of the crystals. The lustre is pearly to dull, fracture irregular, tenacity brittle, and the platelets are very fragile. Cleavage is {001} good. The density, measured by flotation in calibrated liquids, is 3.17(2); the calculated density is 3.199(5).

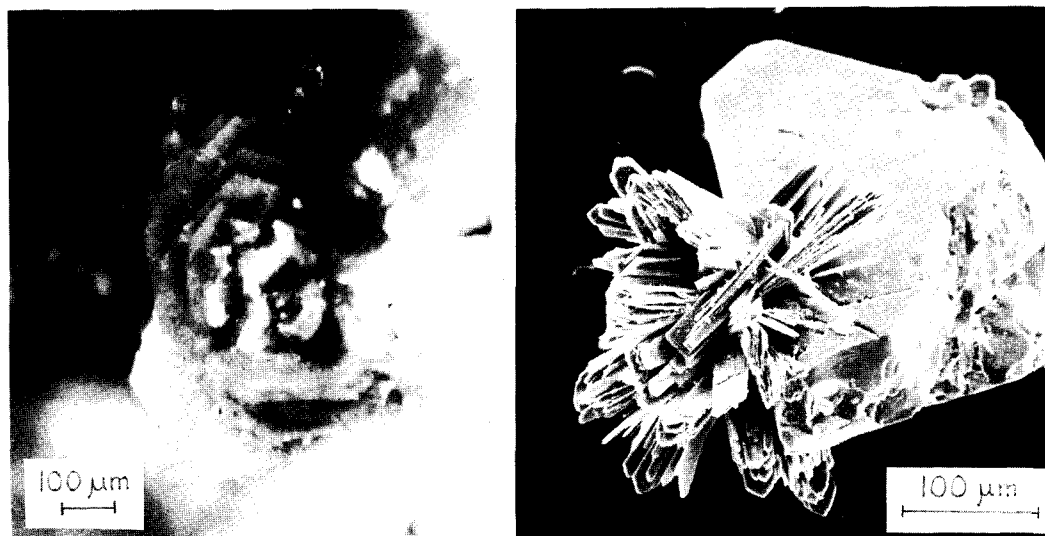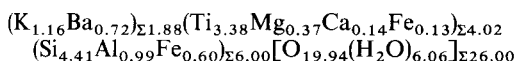*Chemistry.* Lourenswalsite was analysed by elec-

FIG. 4. Light photomicrograph (left), and scanning electron micrograph (right) of lourenswalsite, the latter showing crystal groups perched on a labuntsovite crystal.

tron microprobe techniques, using the same procedure and standards and at the same time as delindeite (see above). Sample preparation and analysis were even more difficult than for delindeite, owing to the extreme thinness and fragility of the crystallites and their high water content. Beam destruction of the material was a constant problem. The chemical analysis of lourenswalsite given in Table 1 is the average of the two analyses considered most reliable, one with each standard set.

As with delindeite, wavelength scans showed that lourenswalsite contains no significant amounts (greater than 0.2–0.3 wt. %) of elements with atomic numbers greater than 8 other than those listed in Table 1. Again, the difference between the sum of the analysis and 100% is assigned to H_2O, for similar reasons. The analysis yields the following empirical formula, based on 26(O + OH):

$(K_{1.16}Ba_{0.72})_{\Sigma1.88}(Ti_{3.38}Mg_{0.37}Ca_{0.14}Fe_{0.13})_{\Sigma4.02}$
$(Si_{4.41}Al_{0.99}Fe_{0.60})_{\Sigma6.00}[O_{19.94}(H_2O)_{6.06}]_{\Sigma26.00}$

or approximately: $(K,Ba)_2(Ti,Mg,Ca,Fe)_4(Si,Al,Fe)_6$ $O_{14}(OH)_{12}$ with K > Ba, Ti ≫ (Mg,Ca, Fe), Si > Al > Fe. Again, the total iron is reported as Fe^{3+}, as explained in the Discussion section.

Lourenswalsite was analysed with the ion probe using the same procedure and standards and at the same time as delindeite. Again the microprobe analyses were confirmed and no significant amounts of any of the lighter elements were detected. The presence of $(OH)^-$, in amounts consistent with the value estimated for water by difference in the microprobe analyses, was also confirmed.

Gladstone–Dale relationship. The Gladstone–Dale relationship for lourenswalsite was evaluated in the same way as for delindeite (see above). The observed mean index of refraction $n = (\alpha + \beta + \gamma)/3 = 1.832$. Thus, $K_p = 0.263$, and $K_c = 0.270$, and the predicted $n = 1.843$, which corresponds to a 'compatibility index' of 0.026, in the 'excellent category' (Mandarino, 1981).

Crystallography. X-ray powder diffraction data for lourenswalsite are listed in Table 3. As with delindeite, a Debye–Scherrer pattern was made with Cu-$K\alpha$ radiation, and also a Gandolfi pattern was obtained from a cluster of two or three crystals. In addition, patterns were made with the focussing Guinier–Hägg camera using Cu-$K\alpha_1$ and Cr-$K\alpha_1$ radiations. The spacing data from these patterns were combined to create Table 3, standardized by the strong reflection at 2.608 Å. The use of an internal standard was avoided in this case, and the data have been referred to the Gandolfi pattern which was well calibrated externally. Intensities were measured on microdensitometer traces of the Guinier–Hägg patterns by comparison with calibrated exposure strips. These patterns were con-

sidered to be least affected by orientation effects. While crystals could be mounted for single-crystal study, the crystals proved to be of very poor quality, and a single, distinct lattice could not be found. In the plane of the crystal plate sharp spots were observed in a hexagonal array in both X-ray precession photographs (Fig. 5A) and electron diffraction patterns. Normal to this plane, except for some fairly sharp reflections on the 00*l* row, only continuous streaks with diffuse intensity concentrations could be found in the precession photographs (Fig. 5B, C) and in electron diffraction. Although the overall X-ray pattern conforms approximately to Laue symmetry 3̄*m*, no rational lattice which accounts for all the maxima along rows normal to the cleavage could be fitted to the pattern. Along the 00*l* row a definite period of ~ 21 Å is present, and this spacing can also be seen in regions along other parallel rows. Other less prominent intensity concentrations along 00*l* do not conform to this period, however. These effects show that this crystal is highly distorted by great layer disorder normal to the hexagonal plate, probably accompanied by complex twinning of a lower symmetry lattice, and perhaps even a second, minor interlayered phase. We can describe the crystallography of lourenswalsite only incompletely in terms of a pseudo-hexagonal lattice with $a = 5.24$ Å, and a normal spacing of $1/c^* = 21$ Å. This lattice could be used to index most of the lines on the powder diffraction pattern (Table 3), yielding a refined unit cell with $a = 5.244(2)$, $c = 20.49(3)$ Å, $V = 488.0(8)$ Å^3, and $Z = 1$. However, certain lines which appear on all powder patterns cannot be indexed by this cell, doubtless because of the extreme layer disorder and
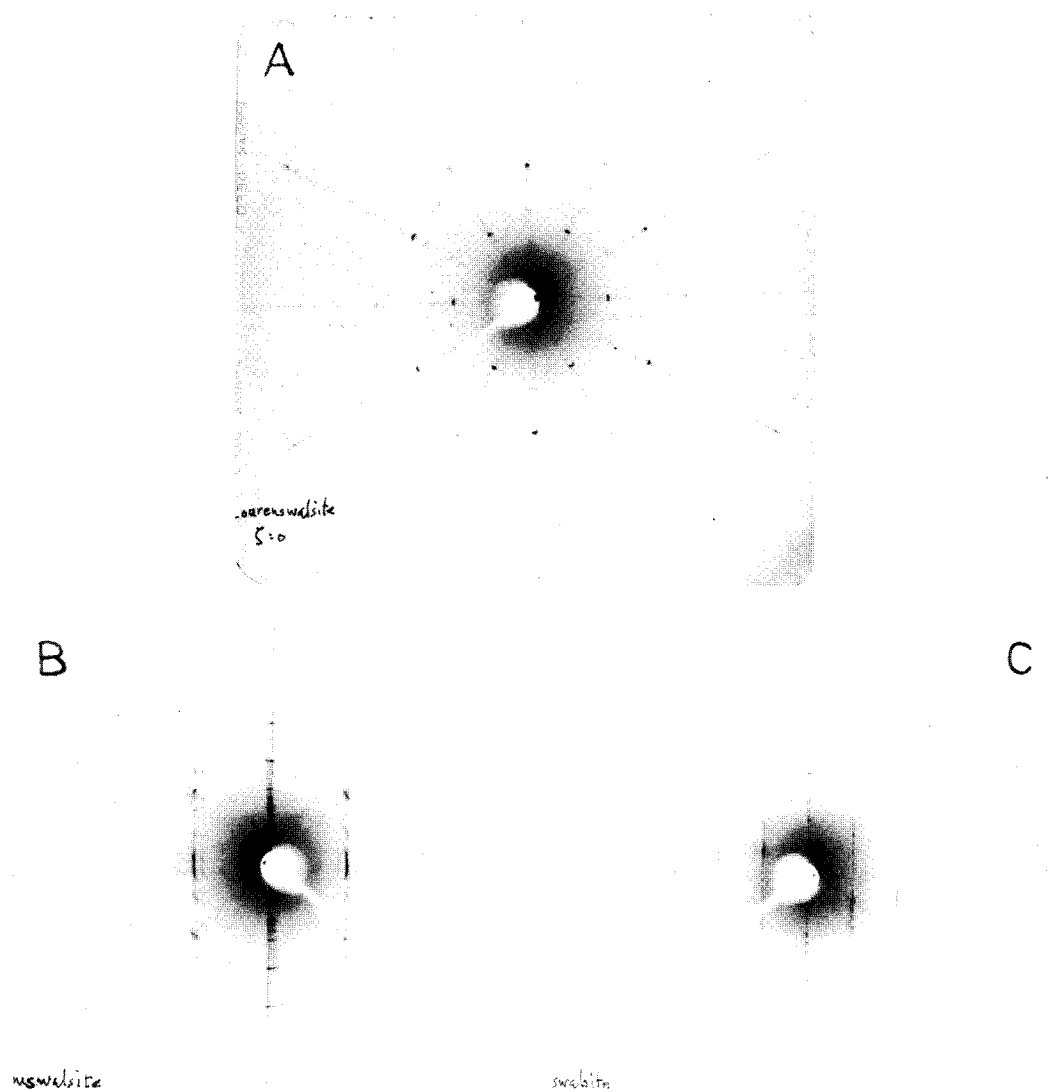
Table 3. X-ray powder data for lourenswalsite

hkl	d(obs)	d(calc)	I/I$_0$	hkl	d(obs)	d(calc)	I/I$_0$
002	10.22*	10.245	20	108	2.228*	2.231	6
100	4.54*	4.541	10	115	2.211	2.209	9
101	4.37	4.434	5			2.185	5
102	4.25	4.152	10	203	2.146	2.155	4
005	4.08*	4.098	15	116	2.086	2.080	3
	3.93		20		1.762		3
103	3.78*	3.782	8			1.744	3
006	3.43*	3.415	15	1.0.11	1.734	1.723	5
105	3.10	3.042	5	210	1.716	1.717	5
	2.97		3	212	1.691	1.693	6
007	2.92*	2.927	3	213	1.678	1.665	7
106	2.65	2.729	10	214	1.633	1.628	5
110	2.62*	2.622	8	1.0.12	1.597	1.598	5
111	2.608*	2.601	100	216	1.551	1.534	8
	2.586		8	300	1.515*	1.514	80
008	2.564*	2.561	15	301	1.508	1.510	12
112	2.533*	2.540	11	220	1.3111*	1.3110	25
113	2.452	2.448	7	308	1.3034	1.3032	6
114	2.390	2.334	6	225	1.2456	1.2487	8
200	2.268	2.270	13	2.0.14	1.2269	1.2302	4
201	2.249*	2.257	16	226		1.2239	

Notes:
(1) Least squares analysis of 15 lines yields the hexagonal unit cell parameters: $a = 5.244(3)$ Å, $c = 20.49(3)$ Å, $V = 488.0(8)$ Å^3, $Z = 1$.
(2) Lines marked with (*) were used for least squares analysis.

FIG. 5. Precession X-ray diffraction patterns of lourenswalsite: (A) $hk0$ net ($\bar{\mu} = 30°$); (B) hhl net ($\bar{\mu} = 20°$; c^* vertical); (C) $h0l$ net ($\bar{\mu} = 20°$). Mo-K radiation (unfiltered).

probable mixed-layering observed on the single-crystal diffraction photographs.

Discussion

Without crystal structure information it is difficult to interpret the chemistry of these complex titanoaluminosilicates. Both are certainly layer structures, but there appear to be no obvious similarities to any known titanosilicate layer types.

The problem consists primarily in finding a rational empirical formula that is consistent with the measured density, optics, and the unit cell volume in terms of atomic volumes. All of these determinants are subject to considerable uncertainties, which aggravate the problem. The density was measured in both cases by a very careful flotation method, through the use of liquid mixtures standardized with calibrated glass beads. A thick aggregate of flakes such as delindeite forms may

give an abnormally low value for the density, but the more open rosettes of lourenswalsite should give a more reliable measure. This circumstance must account for the poorer internal density-cell volume consistency in the former case (see below). Considering the relatively much larger water content of lourenswalsite and the higher barium content of delindeite, the latter might be expected to have a somewhat higher density than that actually measured.

In delindeite the number of the space-filling atoms barium, potassium, and oxygen in the unit cell must conform approximately to the ratio (unit cell volume)/(atom volume of oxygen) $= 791/18 \approx$ 44 atoms/cell (atomic volumes of O, K, and Ba are nearly equal). This is consistent with atomic volumes found in other titanosilicates such as benitoite, $BaTiSi_3O_9$ (17.9 Å), sphene, $CaTiSiO_5$ (18.4 Å), and astrophyllite $(Na,K)_3(Fe,Mn)_7Ti_2Si_8$ $O_{24}(O,OH)_7$ (18.5 Å). This number of $(Ba + K + O)/$ cell yields total cell contents with a formula weight of 1750 (calculated from the analysis), and a density of 3.67 g/cm³. A lower limit to the cell contents is set by the measured density, which leads to a formula weight of 1572 for the full cell contents and 39.5 space-filling $(Ba + K + O)$ atoms/cell, yielding a rather large 20 Å³/atom. If we require that atom-site multiplicities be even integers because of the centered monoclinic cell, at least for the 'framework' atoms, then a reasonable formula can be derived for the cell contents which agrees well with the observed optics and is close to that predicted by the cell volume and volume of space-filling atoms. This formula (given above) is based on 40(O,OH), has 44.35 $(Ba + K + O)$ atoms/cell for atomic volume 17.8 Å³, and gives a formula weight of 1764 and a calculated density of 3.70(1) g/cm³. This is considered acceptable since the density measured on aggregate clumps is almost certainly considerably low. All iron is assumed to be in the ferric state, as these minerals were formed under oxidizing weathering conditions. The alkali cations do not add up rationally, which may not be surprising in view of the pronounced diffuse streaks parallel to a^* on the electron diffraction patterns (Figs. 2, 3), which double the b and c axes, implying the presence of nonstoichiometric vacancies and substitutions.

A similar treatment of the lourenswalsite data, based on the refined cell volume 488.0(8) Å³, predicts approximately 27(Ba + K + O) atoms/cell. The observed density (3.17 g/cm³) yields a formula weight of 932 for the pseudohexagonal cell contents with $(Ba + K + O) = 27.7$. In this case we can rationalize the site occupancies only by splitting the iron atoms between the tetrahedral (Si) and octahedral (Ti) sites; this is permissible if the iron is

again assumed to be in the ferric state as described above. The most probable formula (given above) is then based on 26(O + OH), has 27.88(Ba + K + O) for an atomic volume of 17.5 Å, a formula weight of 940, and yields a calculated density of 3.199(5) g/cm³, which compares well with the measured density. As in the case of delindeite, the number of alkali and alkaline earth cations do not total to integer values, but in view of the extreme disorder shown by the diffraction patterns, such nonstoichiometry of interlayer cations is plausible.

The hexagonal basal network of lourenswalsite $(a = 5.24$ Å) is reminiscent of the mica structures, but the chemistry evidently does not conform to an (Si_4O_{10}) sheet unit. Actually, the hexagonal dimensions are merely characteristic of hexagonal close-packed oxygen layers, which may accommodate some other layer structure completely different from that of the micas. It is unfortunate that the structural chemistry of these two minerals is so poorly understood. Nevertheless, in spite of this situation, delindeite and lourenswalsite are clearly and distinctly defined as new mineral species. They are evidently weathering products of the titaniferous syenite in which they are found in the Diamond Jo quarry, and may be expected to occur in other similar geological settings.

Acknowledgements

References

Erickson, R. L. and Blade, L. V. (1963) *Geochemistry and petrology of the alkalic igneous complex at Magnet Cove, Arkansas.* U.S. Geol. Surv. Prof. Paper 425.

Evans, H. T., Jr., Dwornik, E. J., and Milton, C. (1986) Kassite from the Diamond Jo quarry, Magnet Cove, Hot Spring County, Arkansas: The problem of cafetite and kassite. *Am. Mineral.* **71,** 1045-8.

Mandarino, J. A. (1981) The Gladstone–Dale relationship: part IV. The compatibility concept and its application. *Can. Mineral.* **19,** 441-50.

Williams, J. F. (1891) *The Igneous Rocks of Arkansas.* Arkansas Geol. Surv. Ann. Report for 1890, vol. II.