

# 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  $3.3 \text{ g/cm}^3$ . Electron diffraction revealed a monoclinic unit cell in space group  $C2/m$  or subgroup, with  $a = 21.617(13)$ ,  $b = 6.816(5)$ ,  $c = 5.383(3) \text{ \AA}$ ,  $\beta = 94.03(5)^\circ$  (refined from X-ray powder data). The strongest X-ray lines are ( $hkl, d_{\text{obs}}, I_{\text{rel}}$ ): (200, 10.80, 100); (311, 3.54, 24); (601, 3.083, 28); (601, 2.888, 31); (221, 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 ( $\text{H}_2\text{O}$  by difference), as constrained by density and molar volume data, is approximately  $(\text{Na}, \text{K})_{2.7}(\text{Ba}, \text{Ca})_4(\text{Ti}, \text{Fe}, \text{Al})_6\text{Si}_8\text{O}_{26}(\text{OH})_{14}$ , with  $\text{Na} > \text{K}$ ,  $\text{Ba} \gg \text{Ca}$ ,  $\text{Ti} \gg \text{Fe}, \text{Al}$ ;  $Z = 1$ . 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  $n_x = 1.815$ ,  $n_\beta \approx n_y = 1.840$ ; the measured density is  $3.17 \text{ g/cm}^3$ . X-ray and electron diffraction show a sharp pseudo-hexagonal lattice with  $a = 5.244 \text{ \AA}$ , but extremely diffuse diffraction streaks normal to the  $hk0$  plane. In these streaks a period of  $20.5 \text{ \AA}$  can be discerned. A hexagonal unit cell with  $a = 5.244(2) \text{ \AA}$ ,  $c = 20.49(3) \text{ \AA}$  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  $(\text{K}, \text{Ba})_2(\text{Ti}, \text{Mg}, \text{Ca}, \text{Fe})_4(\text{Si}, \text{Al}, \text{Fe})_6\text{O}_{14}(\text{OH})_{12}$  with  $\text{K} > \text{Ba}$ ,  $\text{Ti} \gg (\text{Mg}, \text{Ca}, \text{Fe})$ ,  $\text{Si} > \text{Al} > \text{Fe}$ ;  $Z = 1$ . These minerals are formed under oxidizing weathering conditions, and iron is assumed to be in the  $\text{Fe}^{3+}$  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,  $\text{CaTi}_2\text{O}_4(\text{OH})_2$ , 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, cancrinite, 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 mioholes 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  $\{001\}$   $n_x = 1.790(5)$ ,  $n_y = 1.825(5)$ . 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  $n_y$ , 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-

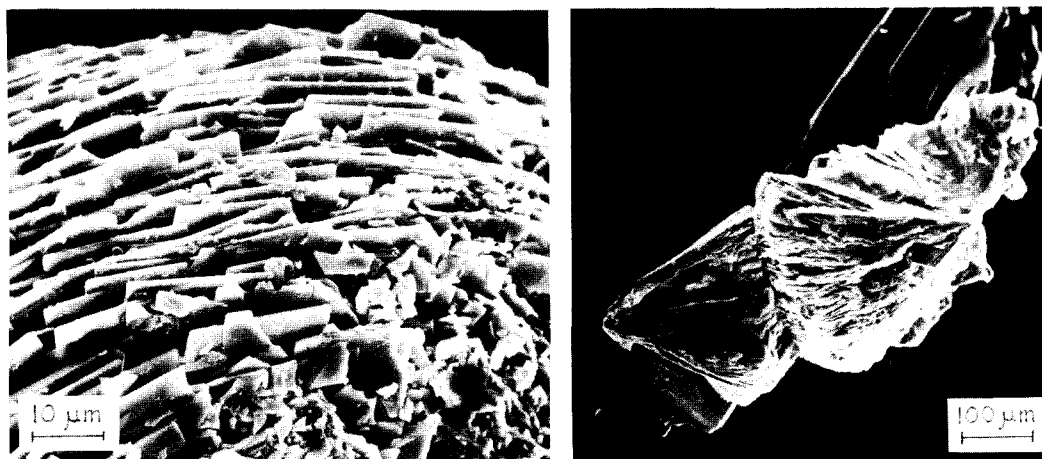


FIG. 1. Scanning electron micrographs of delindeite, on pectolite crystal (right).

served to be moderate, and predicted to be  $54^\circ$  using the calculated  $n_\gamma$ . 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  $3.3(1) \text{ g/cm}^3$ . This value is significantly low due to the aggregate nature of the 'grains', and the calculated value of  $3.70(1) \text{ g/cm}^3$  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-SEM-Q instrument, using an operating voltage of 15 kV and a beam current of  $0.15 \mu\text{A}$ . A beam diameter of approximately  $20 \mu\text{m}$  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  $\text{H}_2\text{O}$ . This assumption was tested by repeated analysis of the same spot with a beam approximately  $1 \mu\text{m}$  in diameter at  $0.5 \mu\text{A}$ . The analysis totals approached 100% with increasing exposure while the ratios of the oxides, except for  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , 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  $\text{H}_2\text{O}$  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  $(\text{OH})^-$  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

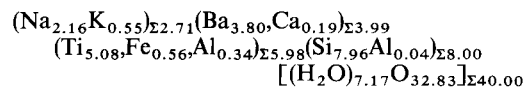
Component	Delindeite (wt. pct.)	Lourenswalsite (wt. pct.)	$k^a$
$\text{SiO}_2$	27.10	28.20	0.208
$\text{Al}_2\text{O}_3$	1.10	5.37	0.207
$\text{Fe}_2\text{O}_3^b$	2.54	6.18	0.268
$\text{MgO}$	absent	1.57	0.200
$\text{CaO}$	0.61	0.81	0.210
$\text{K}_2\text{O}$	1.47	5.82	0.196
$\text{Na}_2\text{O}$	3.79	absent	0.190
$\text{TiO}_2$	23.02	28.73	0.393
$\text{BaO}$	33.05	11.69	0.128
$\text{H}_2\text{O}$ (by difference)	7.32	11.63	0.340
Total	100.00	100.00	

Notes:

<sup>a</sup> Molar refractivity from Mandarino (1981).

<sup>b</sup> Calculated as ferric iron (see Discussion).

The analysis yields the following empirical formula, based on  $40(\text{O} + \text{OH})$ :



or approximately:  $(\text{Na},\text{K})_{2.7}(\text{Ba},\text{Ca})_4(\text{Ti},\text{Fe},\text{Al})_6\text{Si}_8\text{O}_{26}(\text{OH})_{14}$ , with  $\text{Na} > \text{K}$ ,  $\text{Ba} \gg \text{Ca}$ , and  $\text{Ti} \gg \text{Fe} > \text{Al}$ . The total iron is reported in Table 1 as  $\text{Fe}^{3+}$  (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

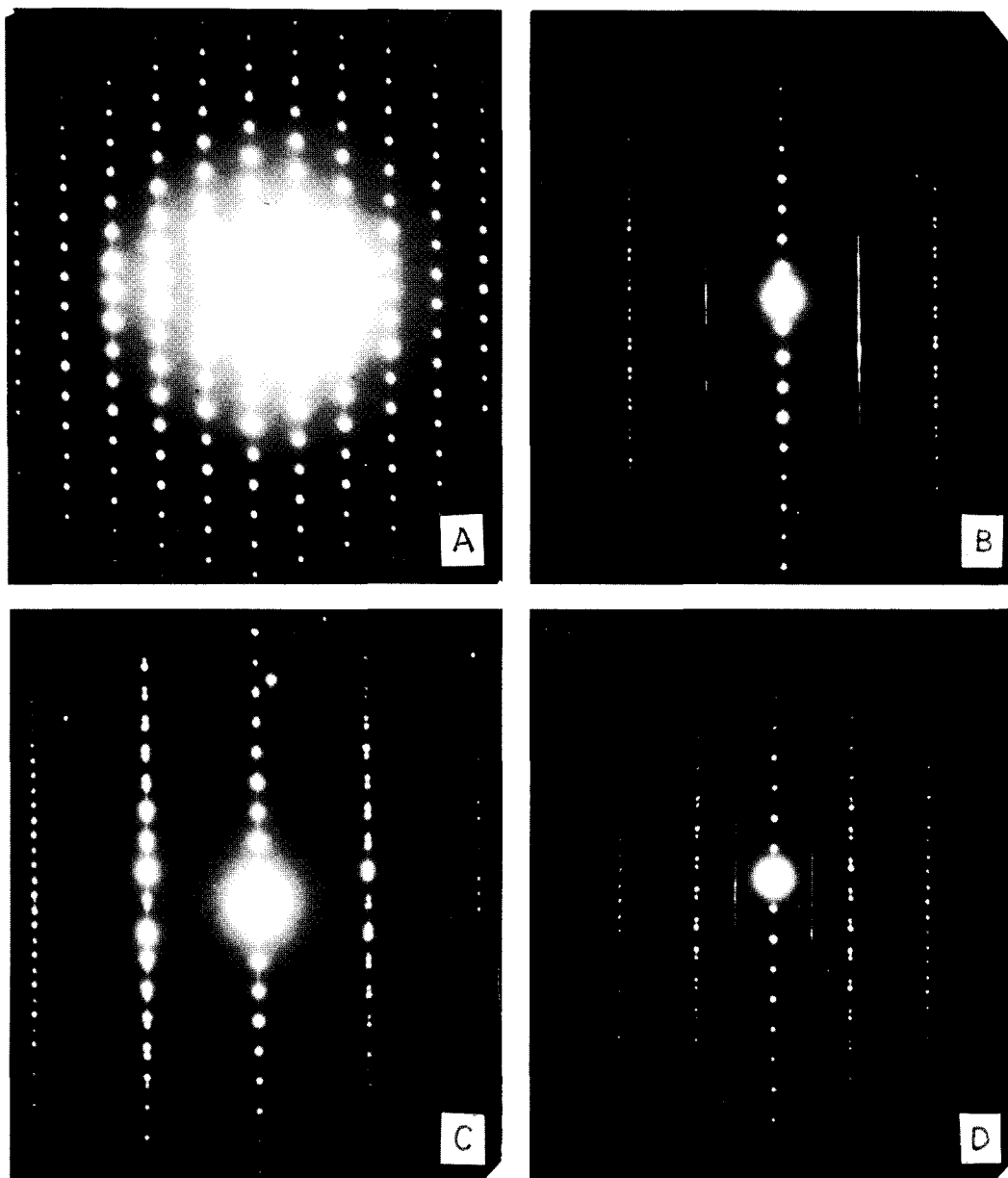


FIG. 2. Electron diffraction patterns of delindeite: (A)  $hk0$  net; (B) net containing  $a^*$  (vertical) tilted  $23^\circ$  to  $hk0$  plane; (C) net tilted  $36.5^\circ$  to  $hk0$  plane; (D) net tilted  $51.5^\circ$  to  $hk0$  plane.

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  $n_x$  on these aggregates,

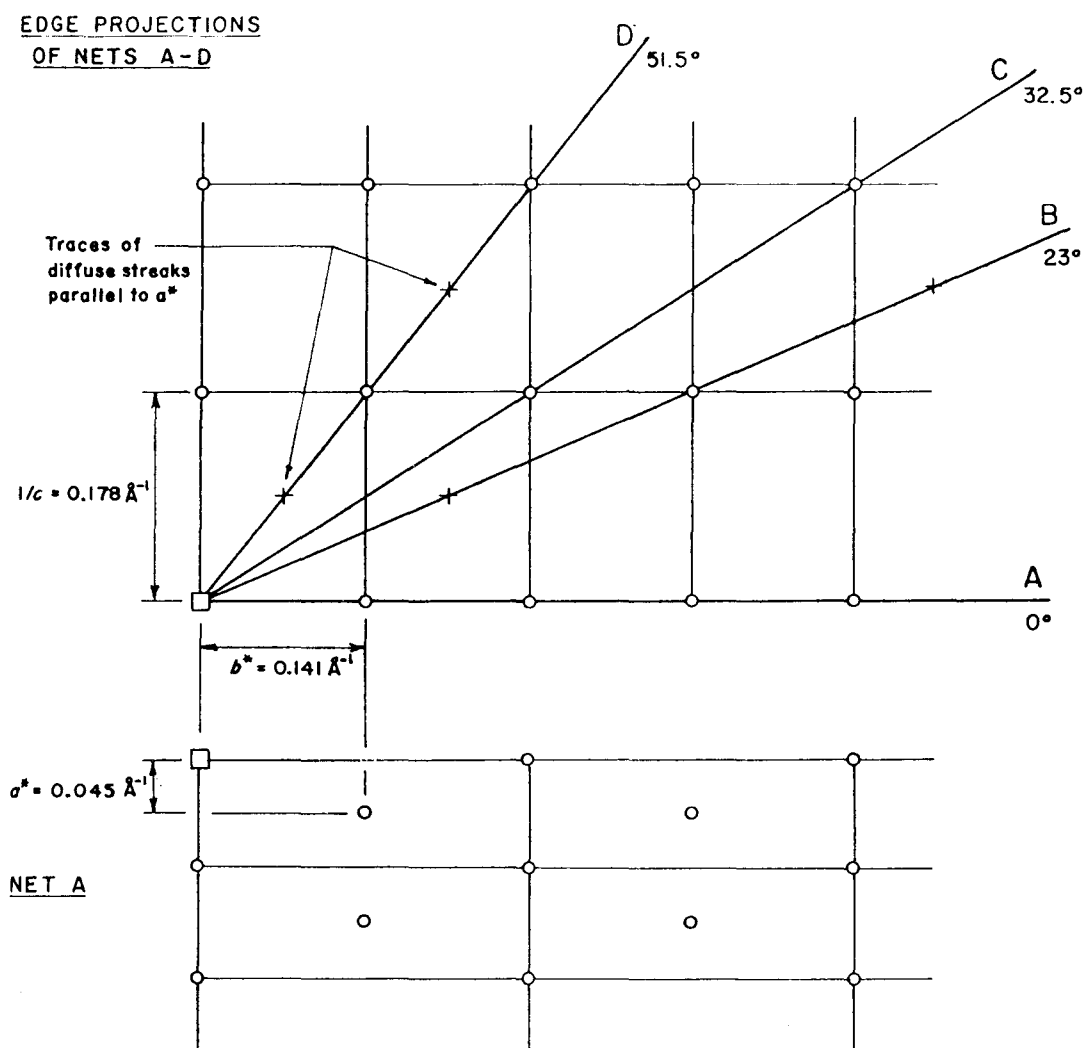


Fig. 3. Interpretation of reciprocal lattice nets of Fig. 2. According to the results of the X-ray powder study the measured reciprocal dimensions shown should be increased by about 4%.

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	402		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
201	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
111	4.15	4.18	11	10,0,0	2.155	2.156	5
111		4.10		222		2.092	
311		3.73		131	2.089	2.089	12
401	3.69	3.68	13	131	2.076	2.077	10
401	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
601	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					
221	2.806	2.807	20				
221	2.753	2.755	16				
800	2.697	2.695	11				
002		2.685					
202	2.654	2.649	11				
421		2.579					
202		2.563					
711	2.532	2.556	4				

## Notes:

- (1) Least squares analysis of 19 lines yields the monoclinic unit cell parameters:  $a = 21.617(13)\text{\AA}$ ,  $b = 6.816(5)\text{\AA}$ ,  $c = 5.383(3)\text{\AA}$ ,  $\beta = 94.03(5)^\circ$ .
- (2) All predicted calculated d spacings to  $2.500\text{\AA}$  are listed (left columns).

and is necessarily low. Using a density of  $3.70\text{ g/cm}^3$  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  $n_x = 1.815(2)$ ,  $n_y \approx n_z = 1.840(2)$ ;  $2V \approx 0$ . 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-

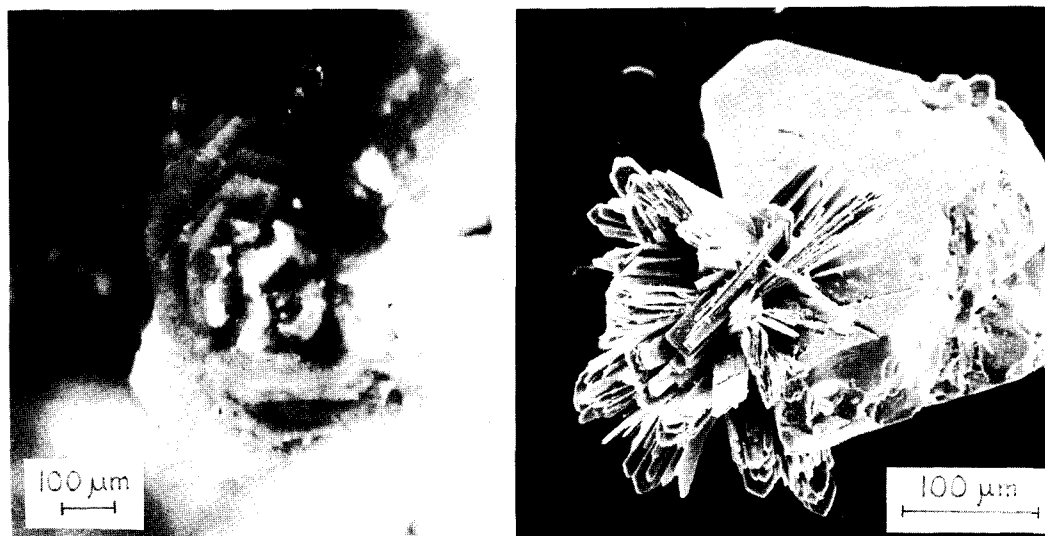


FIG. 4. Light photomicrograph (left), and scanning electron micrograph (right) of lourenswalsite, the latter showing crystal groups perched on a labuntsovite crystal.

