

# Zinc- and Y-group-bearing senaite from St Peters Dome, and new data on senaite from Dattas, Minas Gerais, Brazil

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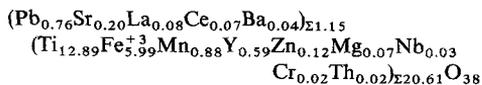
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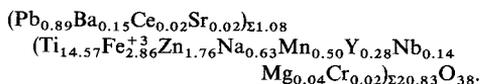
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**ABSTRACT.** A Zn- and Y-group-bearing senaite, formulated as  $AM_{21}O_{38}$ ,  $(Pb_{0.63}Na_{0.46}Ba_{0.11})_{E1.20}(Ti_{14.64}Fe_{2.16}^{+2}Zn_{1.74}Fe_{1.00}^{+3})_{Y\text{-group}}REE_{0.70}Mn_{0.38}Nb_{0.20}Sn_{0.03}Zr_{0.03}Th_{0.02}U_{20.9}O_{38}$ , a member of the crichtonite group, is a newly characterized phase associated with murataite at the St Peters Dome area, Colorado. The Zn- and Y-group-bearing senaite is uranium-free and non-metamict, but otherwise is comparable to known senaites and davidites in X-ray diffraction pattern, symmetry, and structure. The REE distribution shows a strong dominance of Y and the Y-group REE which are present in  $M(1)$ . Megascopically, the mineral is black, submetallic, and opaque; in polished section it appears to be white and moderately bright compared with murataite. Cleavage is absent but twinning on {5270} is present.

Senaite and hitherto unreported zinc-bearing senaite from Dattas, Diamantina, Minas Gerais, Brazil, have the following respective structural formulas as determined by electron microprobe:



and



In the description of the complex oxide murataite,  $(Na,Y)_4(Zn,Fe^{+2})_3(Ti,Nb)_6O_{18}(F,OH)$ , from E1 Paso County, Colorado (Adams *et al.*, 1974), mention was made of an unidentified associated mineral, which was referred to as 'mineral Y'. Mineral Y has now been found to be a Zn- and Y-group-bearing senaite, when formulated from microprobe analyses according to  $AM_{21}O_{38}$  as  $(Pb, Na, Ba)(Ti, Fe^{+2}, Zn, Fe^{+3}, Y, Y\text{-group} REE, Mn, Nb, Zr, Sn, Th)_{21}O_{38}$  (after Gatehouse *et al.*,

1979). It may also be formulated as  $AM_1M_{20}O_{38}$  where the  $M(1)$  octahedral site is emphasized. Fleischer (1983) has formulated davidite as  $(La, Ce)(Y,U,Fe^{+2})(Ti,Fe^{+3})_{20}(O,OH)_{38}$  and senaite as  $Pb(Ti,Fe,Mn)_{21}O_{38}$ . This mineral, like murataite, is found in close association with riebeckite, astrophyllite, and quartz in a small pegmatite in the Pikes Peak biotite granite batholith of Colorado. The St Peters Dome area of the batholith continues to supply unusual mineral phases from rocks derived by an elaborate sequence of chemically changing, metasomatic processes. The pegmatite, initially a part of the biotite granite phase, was probably modified by the Mount Rosa alkali granite unit, which is a subsequently emplaced variant. The appearance of the mineral in a hand specimen so closely resembles that of murataite that distinction between the two species is virtually impossible. The Zn- and Y-group-bearing senaite is, however, more abundant than murataite in the pegmatite. It occurs in larger crystals, as much as several centimetres across, and is more commonly found in euhedral crystals. Some euhedral crystals up to 1 mm or so in length have been found. Figs. 1a and b show two euhedral crystals. The hexagonal (rhombohedral) morphology is clearly evident and the terminations of the crystals show rhombohedral pyramidal faces in addition to the pedion {0001}. The crystals show evidence of compromise growth surfaces and growth lines perpendicular to *c*. The length/diameter ratio is in the range 5:1 to 10:1.

Visual distinction between the two species may be made with the petrographic microscope, as murataite fragments are translucent on thin edges, while the Zn- and Y-group-bearing senaite is opaque. The mineral is unusual for a senaite

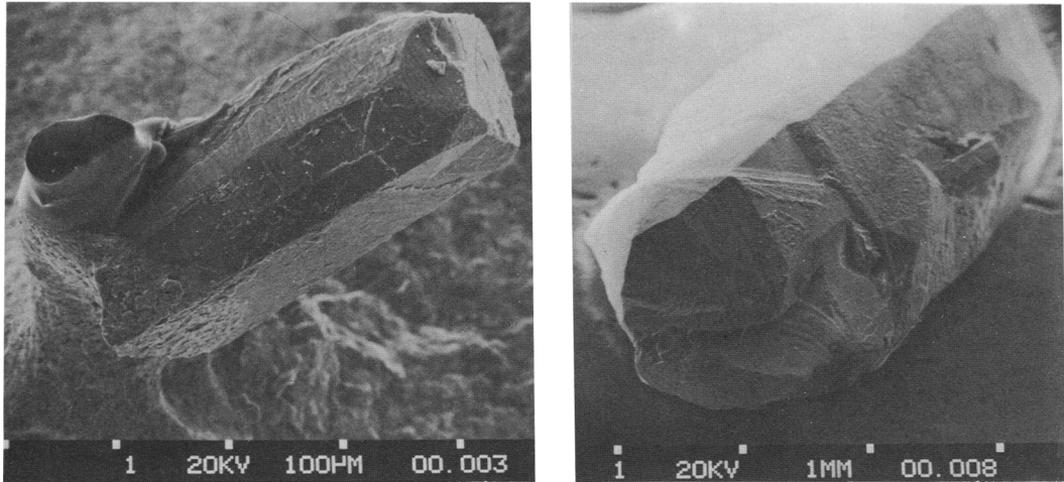


FIG. 1. Scanning electron photomicrographs of Zn- and Y-group-bearing senaite crystals showing: (a, left) development of prism, pyramid, and pedion faces and (b, right) prism faces and compromise growth surfaces. Scales indicated by white marker dots.

because it is Zn- and Y-group-bearing and high in  $\text{TiO}_2$ . Like other senaites, it is non-uranian and non-metamict. The Zn component is not surprising when it is recalled that much of the unusual assemblage of these pegmatites has a general Zn-rich character (Adams *et al.*, 1974). MacDonald and Saunders (1973) have found that the astrophyllite from St Peters Dome contains 1.88%  $\text{ZnO}$ , the most Zn-enriched of all astrophyllites studied. Pb is also enriched in this province.

Senaite, first described from Brazil by Hussak and Prior (1898), was subsequently reported (erroneously as davidite) from Nezilovo, Macedonia, Yugoslavia, by Vujanovic (1970). The third occurrence is that at St Peters Dome, El Paso County, Colorado.

Since 1906, when the name davidite was given to a black mineral from South Australia by Mawson (1906), similar material has been found in a relatively few other localities, but is the most abundant member of the crichtonite group. Also, the various occurrences suggest a mineral species of rather diverse cation composition, a feature that for some time caused some reservations about its validity (Dixon and Wylie, 1951; Whittle, 1959). For example, a brief review of the composition of specimens from various world-wide occurrences shows U to vary, Y, Sr, Pb, and REE concentrations to range widely, and Ba, Cr, and V to be present in some samples.

Pabst (1961) carried out a study of davidites from all localities then available, and with X-ray procedures showed that the mineral was indeed

reputable, with consistent diffraction patterns and structure. On the basis of new analyses, he also formulated davidite with 36 oxygens as  $\text{Y}_6\text{Z}_{15}\text{O}_{36}$ , with  $Z = 3$ . Senaite and davidite presently are placed in the crichtonite group of minerals—a group of minerals of like character but of widely varying chemical composition.

The recent sequence of papers on the minerals of the crichtonite group (Grey and Lloyd, 1976; Grey *et al.*, 1976; Grey and Gatehouse, 1978; Gatehouse *et al.*, 1978; Gatehouse *et al.*, 1979; and Kelly *et al.*, 1979) has done much to clarify the chemical, structural, and crystallographic relations between the individual members. The crichtonite group at present contains davidite, senaite, crichtonite, lovingite, and landauite and is given the general formula of  $\text{AM}_{21}\text{O}_{38}$  by Grey *et al.* (1976) and Gatehouse *et al.* (1979) where  $A = \text{Ca}$ , light REE, Pb, Sr, Na, K, etc., and  $M = \text{Ti}$ , Fe, Mn, Zn, heavy REE, U, Cr, V, and others. Senaite contains dominant Pb in the A site; davidite, Ce-group REE; crichtonite, Sr; lovingite, Ca; and landauite, Na (Gatehouse *et al.*, 1979). While davidite was formerly stated to contain appreciable or dominant U in the A site (Butler and Hall, 1960; Davydova and Shaposhnikov, 1966), Gatehouse *et al.* (1979) have shown that U is present in the M(1) octahedral site. An unusual rhenium-bearing senaite-crichtonite has recently been described by Sarp *et al.* (1981) which contains two A atoms rather than one. This mineral was thought to have affinities to magnetoplumbite which may be represented as  $\text{A}_2\text{M}_{24}\text{O}_{38}$  to emphasize the similarity to ferrous

senaites  $\text{AM}_{24}\text{O}_{38}$  (Rouse and Peacor, 1968). However, Grey *et al.* (1976) have shown that ferrous senaite, R3, has the same structure as ilmenite.

The chemistry of the senaite from St Peters Dome is particularly interesting and of significant importance when its analysis is compared with those of other members of the crichtonite group. This particular material not only contains substantial Zn, but in addition approximately stoichiometrically equal amounts of Pb and total REE. The REE present, however, all belong to the Y-group, and based on the nomenclature proposed by Gatehouse *et al.* (1978) for members of the crichtonite group and on the findings of Gatehouse *et al.* (1979), the material from St Peters Dome may be considered a Zn- and Y-group-bearing senaite. Microprobe analyses show the mineral to be chemically somewhat inhomogeneous. This senaite marks the third reported occurrence of the mineral.

The senaite (DGM/DNPM No. 1651) from Dattas, Diamantina, MG, Brazil, is a senaite with a crichtonite component. Included with it is a Zn- and Na-bearing senaite.

*Occurrence and associations.* Zn- and Y-group-bearing senaite at St Peters Dome, Colorado, occurs as a black, vitreous, submetallic component in a small, unzoned pegmatite of the Pikes Peak batholith in which the mineral murataite (Adams *et al.*, 1974) was found. The mineral is in crystal clusters to irregular granular masses up to 2 cm across. Crystal surfaces have a dull matt finish, while freshly broken surfaces resemble ilmenite. The powder and streak are black.

The small pegmatite in which these two rare minerals are found is like so many pegmatoid bodies in the Pikes Peak batholith which are unimposing and commonly noticed only by the scatter of coarse, fragmental, white quartz and pink and white feldspar in the surface grus of the biotite granite host. A general study of the pegmatites of the Mt Rosa and St Peters Dome area was made by Gross and Heinrich (1966).

The pegmatites of the batholith, some large and well known for their uncommon mineral assemblages, are clustered randomly over the approximately 2,800 km<sup>2</sup> surface of the batholith. Generally, each cluster has minor mineral assemblage variations that make it somewhat distinct from others.

The pegmatites of South Cheyenne Canyon, under the east face of St Peters Dome, one of which includes the Zn- and Y-group-bearing senaite and murataite site, are one of these clusters. They are probably initial dike components of the widespread, main batholithic mass of coarse biotite granite (age 1030 Ma, Barker *et al.*, 1975). Into this flood of biotite granite later episodes of alkali granite magmas were intruded at several root centres. The Mt Rosa riebeckite-astrophyllite granite, one of the alkali complexes, is a few kilometers west of the senaite-bearing pegmatite, and many small satellite bodies and dykes of the Mt Rosa-type granite are scattered around

the main mass of the late intrusive. The pegmatites are in the earlier biotite granite and appear to be partly to totally overprinted by an assemblage more related to Mt Rosa alkali granite, so they have strong aspects of both granite pegmatite and alkali granite pegmatite. Some of the pegmatites are close to the Mt Rosa centre and are dominated by Na-Zr-Th metasomatism. Further away, as in the area of the senaite-murataite pegmatite, more of the biotite granite pegmatite characteristics are discernible. For example, beryl, calcite-siderite, minerals of the light REE, and large biotite books, typical of the granite pegmatites, are found, or more commonly are represented by second-cycle and pseudomorphous minerals. In the area of the senaite-murataite pegmatite, zircon, riebeckite, and astrophyllite form large single crystals to large, intergrown crystal clusters. Along with these conspicuous minerals an assemblage of less common minerals includes the Zn- and Y-group-bearing senaite, murataite, xenotime, thorite, plumbopyrochlore, cyrtolite, bastnäsité, Nb-rutile, and genthelvite. Commonly, the dark mineral clusters are unevenly altered in several ways. The riebeckite is generally intergrown with or partly converted to the Na-pyroxene, acmite, or aegirine. In places the large crystals are altered and replaced by drusy, clear zircon or a red, layered assemblage of bertrandite and quartz. In other places the riebeckite is a grey alteration product containing inclusions of rutile and resembling 'rinkite'. Some commonly oriented blebs of amphibole are distributed in coarse quartz as if silica is a replacing agent as well. Zn- and Y-group-bearing senaite is found in these dark mineral clusters in contact with astrophyllite, murataite, and xenotime. Some of these relations appear to be replacement associations. Coarsely crystalline feldspar as well as the amphibole crystals also show corrosion effects at places where the clusters have formed. At these sites, cavities of 1–2 cm formed, and these are partly filled with free-growing zircon clusters, Zn- and Y-group-bearing senaite, thorite, finely jackstrawed, bladed albite, and octahedrons of plumbopyrochlore. Zn- and Y-group-bearing senaite is also found shrouded by a coating of granular pyrochlore. The paragenetic sequence of the minor mineral assemblage is not everywhere consistent.

The metasomatic fluids began a sequence of changes initially by supplying the Na, Zr, and Zn to form the Na amphibole (Zn-bearing), zircon, astrophyllite, and perhaps Nb-rutile. Addition of Y-group elements, Nb and Th were also required. Murataite formed edges of large astrophyllite crystals and together with xenotime, thorite, etc., invaded the peripheral zones of riebeckite and astrophyllite. The Na-amphibole involved in these minor mineral assemblages always seems to be an intergrowth of riebeckite and acmite-aegirine.

Zn- and Y-group-bearing senaite seems to invade and separate murataite but also encloses xenotime and thorite. Plumbopyrochlore seems to be a late phase everywhere, and at places it is associated with zircon crystal clusters without other minerals. Zircon is a very common mineral in these two-cycle pegmatites, is a dominant associate with the Zn- and Y-group-bearing senaite, and has a grey, translucent, pseudo-octahedral form, finely zoned in the core portions with less zoned overgrowth rims. A late episode of zircon crystallization is also suggested by

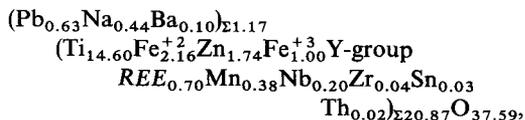
occurrences of small, scattered zircon crystals in the small masses of late, finely jackstrawed albite. The zircon is radioactive and may contain a small amount of Th. Sparse genthelvite is found in many of the small pegmatites of the area and seems to be an early phase in the metasomatic reforming of the granite pegmatites, which may have initially contained small amounts of beryl. The genthelvite also contains significant amounts of Fe and Mn.

The geology, mode of occurrence, and associated minerals with the Dattas senaite have been described by Hussak and Prior (1898).

**Chemistry.** Electron microprobe analyses were carried out on eight different samples of Zn- and Y-group-bearing senaite from St Peters Dome, and five analyses on the senaite and Zn-bearing senaite from Dattas, MG, Brazil. One sample of davidite from Olary, South Australia, was also analysed and the analyses are shown in Tables I and II.

Analyses were carried out on an ARL EMX SM microprobe\* using combined wavelength-dispersive and energy-dispersive detectors. Operating conditions were 15 kV accelerating voltage, 30 nA sample current, and 10  $\mu\text{m}$  beam diameter. Standards included both analysed natural and synthetic phases. Data reduction was done by least squares because concentrations in standards selected for each element were near those of the unknown. FeO was determined separately by wet chemical methods by Edythe Engleman on a portion of specimen D. The values for FeO and  $\text{Fe}_2\text{O}_3$  for the remaining seven samples are calculated values using microprobe determinations for total Fe and the ratio of  $\text{FeO}/\text{Fe}_2\text{O}_3$  calculated from the determination on D. Total water, 0.20%, was also determined for sample D (Edythe Engleman, analyst; microcoulometric moisture analysis). Fluorine was determined by Johnnie Gardner (specific ion electrode method) to be less than 0.05%.

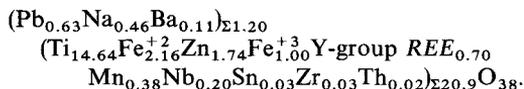
Calculations of the structural formula for analysis D using the observed density (4.74  $\text{g}/\text{cm}^3$ , micro-pycnometer) and the measured unit cell volume (1988.7  $\text{\AA}^3$ ) for a hexagonal cell seems to formulate well as  $AM_{21}O_{38}$  with  $Z = 3$ . Placing the REE (dominantly Y group) into the  $M$  position rather than the  $A$  position results in



which agrees well with the general formula  $AM_{21}O_{38}$  as determined from a structure determination for senaite (Grey and Lloyd, 1976) and for

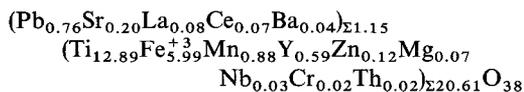
\* Mention of this instrument is for descriptive purposes only and does not constitute endorsement by the US Geological Survey.

davidite by Gatehouse *et al.* (1979). Calculation of the structural formula on the basis of 38 oxygens and the chemical analysis only (for  $AM_{21}O_{38}$ ) yields

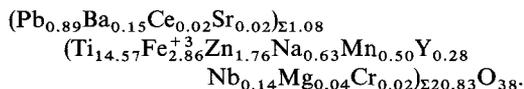


As there is an excess of approximately 0.2  $A$  atoms the possibility that it occupies the twofold anion site O(7), as suggested for loveringite by Gatehouse *et al.* (1978), must be considered.

The structural formula (average of four analyses) for the senaite from Dattas, MG, Brazil on the basis of 38 oxygens and the chemical analysis only (with all Fe expressed as  $\text{Fe}_2\text{O}_3$ ) was



and that for the zinc-bearing senaite was



The density was determined (by micro-pycnometer with water as the immersion medium) on about 570 mg of sample D to be 4.74  $\text{g}/\text{cm}^3$ . A second determination on 790 mg yielded 4.67  $\text{g}/\text{cm}^3$ . The average of three determinations (by Berman microbalance with toluene as the immersion medium) on samples of D ranging from 7.1 to 17.05 mg was 4.727  $\text{g}/\text{cm}^3$ . A sample of senaite (DGM/DNPM No. 1654) from Cipó, Brazil (sample B), gave a density of 4.64  $\text{g}/\text{cm}^3$  (micro-pycnometer) using 360 mg.  $D_{\text{calc}}$  for senaite D using our measured cell volume (1988.7  $\text{\AA}^3$ ) and the molecular weight calculated from the microprobe analysis for 36 oxygens (following the formulation of Pabst, 1961) is 5.02  $\text{g}/\text{cm}^3$ .  $D_{\text{calc}}$  on the basis of 38 oxygens using the measured cell volume and molecular weight is 5.29  $\text{g}/\text{cm}^3$ .

Fleischer (1983) has given the formula of davidite as  $(\text{La,Ce})(\text{Y,U,Fe}^{+2})(\text{Ti,Fe}^{+3})_{20}(\text{O,OH})_{38}$ , which implies a splitting of the  $M$  site. The St Peters Dome senaite formulates well according to this scheme. As indicated by Gatehouse *et al.* (1978, 1979) it appears that the separation of the REE is best made by having the light REE (Ce-group, with larger ionic radii) present in the  $A$  site and the heavy REE (Y-group, with smaller ionic radii) present in the  $M(1)$  site. Fleischer (1983) has given the formula of senaite as  $\text{Pb}(\text{Ti,Fe,Mn})_{21}\text{O}_{38}$  which does not indicate the substitution of the Y-group REE into the  $M(1)$  site along with Zn. Based on the available chemical analyses for the REE distribution and the structural crystallography, the dual

Table I. Electron microprobe analyses for zinc and Y-group-bearing senaite from St. Peters Dome, Colorado, and davidite from Olary, South Australia

Oxides (wt.%)	Specimen								Average of first seven analyses	Davidite, Olary, South Australia (present work)	Davidite, Olary, South Australia (Gatehouse <i>et al.</i> , 1978)
	"D"	"P"	"T"	"U"	"P"	"T"	"V"	"U"			
PbO	7.27	7.15	7.20	7.31	7.47	7.19	8.14	7.54	7.39	0.62	0.69
FeO	8.02	7.90	8.04	9.53	8.16	7.74	7.69	9.47	8.15	**	**
ZnO	7.32	7.42	7.20	5.86	6.86	7.32	7.40	6.89	7.05	<0.1	n.d.
Ce <sub>2</sub> O <sub>3</sub>	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.10	3.23	3.06
Y <sub>2</sub> O <sub>3</sub>	2.04	1.74	1.66	1.52	1.38	1.75	2.02	1.96	1.73	2.32	1.86
Gd <sub>2</sub> O <sub>3</sub> *	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dy <sub>2</sub> O <sub>3</sub>	0.53	0.49	0.60	0.60	0.62	0.60	0.00	0.52	0.49	0.05	n.d.
Ho <sub>2</sub> O <sub>3</sub>	0.17	0.17	0.12	0.31	0.21	0.16	0.19	0.23	0.19	0.06	n.d.
Er <sub>2</sub> O <sub>3</sub>	0.96	0.72	0.51	1.52	1.06	0.78	0.75	1.07	0.90	0.52	n.d.
Tm <sub>2</sub> O <sub>3</sub>	<0.1	<0.1	<0.1	0.21	<0.1	<0.1	<0.1	<0.1	0.03	<0.1	n.d.
Yb <sub>2</sub> O <sub>3</sub>	1.39	1.29	1.56	2.28	1.43	1.37	(1.4)	1.49	1.53	0.42	n.d.
Lu <sub>2</sub> O <sub>3</sub>	0.3	0.2	<0.1	0.6	0.4	0.4	<0.1	0.4	0.27	0.1	n.d.
CaO	<0.04	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.3	0.23
BaO	0.84	0.90	0.77	0.73	0.69	0.90	1.08	0.70	0.84	2.20	n.d.
SnO <sub>2</sub>	0.25	<0.1	0.39	<0.1	<0.1	<0.1	0.20	0.83	0.12	<0.1	n.d.
MnO	1.41	1.63	1.45	1.03	1.58	1.56	1.61	0.80	1.47	0.16	0.04
ZrO <sub>2</sub>	0.22	0.20	0.26	0.15	0.24	0.18	0.27	0.19	0.22	0.07	0.07
ThO <sub>2</sub>	0.26	0.16	0.15	0.18	0.13	0.24	(0.2)	0.31	0.19	0.18	0.05
SiO <sub>2</sub>	0.02	0.02	0.03	0.03	0.03	0.04	(0.03)	0.02	0.03	0.09	n.d.
Na <sub>2</sub> O	0.74	0.69	0.69	0.57	0.63	0.71	0.77	0.62	0.69	<0.1	n.d.
TiO <sub>2</sub>	60.27	60.72	59.83	57.87	60.08	60.99	61.20	55.85	60.10	50.19	51.74
Fe <sub>2</sub> O <sub>3</sub>	4.13	4.13	4.20	4.99	4.26	4.05	3.94	4.95	4.24	**	**
Nb <sub>2</sub> O <sub>5</sub>	1.37	1.46	1.61	2.66	1.61	1.34	2.02	3.98	1.66	<0.1	n.d.
H <sub>2</sub> O (total)	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RE <sub>2</sub> O <sub>3</sub> + Y	5.49	4.71	4.55	7.14	5.20	5.16	4.46	5.77	5.24	10.93	8.62
Totals	97.81	97.09	96.37	98.05	96.94	97.42	99.01	97.92	97.39	---	---
as Fe <sub>2</sub> O <sub>3</sub>	13.04	12.91	13.14	15.58	13.32	12.65	12.49	15.47	13.30	27.63	25.30
Totals	98.7	97.97	97.27	99.11	97.84	98.28	99.87	98.97	98.3	97.27†	98.35††

\* - determined to be 0.08 weight percent for "D" by six-step emission spectrographic analysis.  
n.d. - not determined.  
(X.xx) - estimated from previous six analyses.  
\*\* - total Fe expressed as Fe<sub>2</sub>O<sub>3</sub>.  
† - including 6.67 wt.% U<sub>3</sub>O<sub>8</sub>, 3.35 wt.% La<sub>2</sub>O<sub>3</sub>, 2.88 wt.% U<sub>2</sub>O<sub>5</sub>, 0.51 wt.% HfO<sub>2</sub>, 1.21 wt.% Cr<sub>2</sub>O<sub>3</sub>, 0.22 wt.% Al<sub>2</sub>O<sub>3</sub>, 0.35 wt.% Nd<sub>2</sub>O<sub>3</sub>, 0.1 MgO, 0.02 wt.% SrO.  
†† - including 4.9 wt.% U<sub>3</sub>O<sub>8</sub>, and 4.23 wt.% La<sub>2</sub>O<sub>3</sub>.

Table II. Electron microprobe analyses for senaite and zinc-bearing senaite, Dattas, Diamantina, M.G., Brazil

Oxides (wt.%)	Specimen number					Average of first four analyses	Senaite, Dattas* (Grey <i>et al.</i> , 1976)
	1	2	3	4	5		
PbO	8.7	9.8	8.9	8.9	10.7	9.08	9.21
FeO†	(22.8)	(22.8)	(23.2)	(23.0)	(11.1)	---	8.53
ZnO	0.6	0.5	0.5	0.5	7.7	0.53	---
Ce <sub>2</sub> O <sub>3</sub>	0.6	0.5	0.6	0.7	0.2	0.60	0.07
La <sub>2</sub> O <sub>3</sub>	0.8	0.4	0.7	0.7	0.0	0.65	0.06
Y <sub>2</sub> O <sub>3</sub>	3.3	3.6	3.6	3.7	1.7	3.55	0.86
CaO	n.d.	n.d.	n.d.	n.d.	n.d.	---	---
BaO	0.3	0.3	0.3	0.3	1.2	0.3	---
MnO	3.0	3.4	3.5	3.4	1.9	3.33	4.08
ZrO <sub>2</sub>	n.d.	n.d.	n.d.	n.d.	n.d.	---	0.09
ThO <sub>2</sub>	0.3	0.3	0.3	0.3	0.5	0.3	0.12
Na <sub>2</sub> O	---	---	---	---	1.05	---	---
TiO <sub>2</sub>	54.2	55.2	55.2	54.9	62.6	54.88	58.68
Fe <sub>2</sub> O <sub>3</sub> ††	25.3	25.3	25.7	25.6	12.3	25.48	16.20
Nb <sub>2</sub> O <sub>5</sub>	0.2	0.3	0.2	0.2	1.0	0.22	---
SrO	1.1	1.1	1.1	1.1	0.1	1.1	0.20
HfO <sub>2</sub>	0.15	0.15	0.15	0.15	0.08	0.15	0.02
Cr <sub>2</sub> O <sub>3</sub>	0.12	0.09	0.09	0.09	0.09	0.10	0.16
V <sub>2</sub> O <sub>5</sub>	n.d.	n.d.	n.d.	n.d.	n.d.	---	0.70
Totals (all FeO)	96.17	98.44	98.34	97.94	98.87	---	---
Totals (all Fe <sub>2</sub> O <sub>3</sub> )	98.67	100.94	100.84	100.54	100.07	100.27	98.98

\* - Includes Al<sub>2</sub>O<sub>3</sub> 0.05%, HfO<sub>2</sub> 0.13%  
† - Total Fe as FeO  
†† - Total Fe as Fe<sub>2</sub>O<sub>3</sub>

site occupancy of the combined REE is fairly certain. The non-metamict, rhenium-bearing senaite-crichtonite described by Sarp *et al.* (1981) has two cations in the A position instead of one as in the general formula AM<sub>21</sub>O<sub>38</sub>, and has been

interpreted as either a new species or an intermediate between crichtonite-senaite and magneto-plumbite.

As shown by Gatehouse *et al.* (1978), the formula for loveringites with excess A cations may be

generalized as  $A_{3-x}\square_xM_3O_{36}$ , where  $\square$  = vacancy. Pabst (1961), using chemical analyses and specific gravity determinations to determine unit-cell compositions for davidites, consistently obtained between 35 and 36 oxygens per unit cell. In the case of the Zn- and Y-group-bearing senaite from St Peters Dome some of the Na (0.2 atoms) constituting an *A* site excess may be occupying anion site O(7) as suggested by Gatehouse *et al.* (1978). The number of cations assigned to the *M* position can be increased by considering more of the Fe as being present as FeO rather than as  $Fe_2O_3$ .

The chemistry is consistent in five specimens of the Zn- and Y-group-bearing senaite shown in Table I; the remaining three (Y, L, and U) are aberrant in the following aspects: In the small cation position, among the components  $Fe^{+3}$ , Nb, and Ti, an increase in Ti generally shows a corresponding decrease in  $Fe^{+3}$ , or total Fe for that matter. The slopes of the ratios of Ti with Fe, and Fe + Nb are 0.66 to 0.7 (fig. 2). However, specimens Y and U are

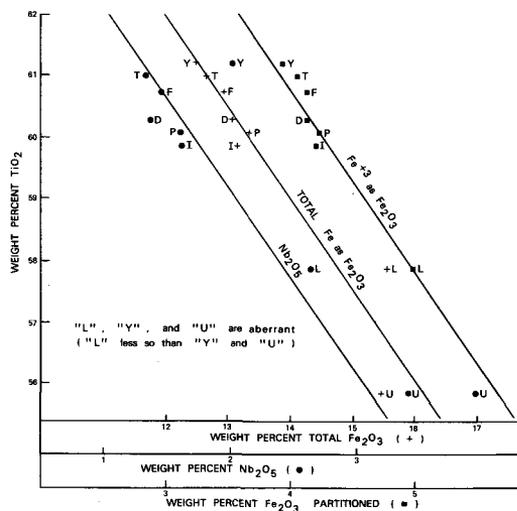


FIG. 2. Elements in 'small cation' position:  $TiO_2$  vs.  $Nb_2O_5$ ,  $Fe_2O_3$  partitioned, and total Fe as  $Fe_2O_3$  for Zn- and Y-group-bearing senaite. Values are in wt. %.

conspicuous; high  $Nb_2O_5$  in Y, and high  $Nb_2O_5$  and low  $Fe_2O_3$  in U. All other specimens conform closely to the straight line trends.

If the combined  $FeO + MnO$  values, having a range of 1.3 wt. %, are plotted against the REE, Zn, and Pb respectively, specimens Y, L, and U are conspicuous (fig. 3). However, the average of the total ( $RE_2O_3 + ZnO + PbO$ ) shows a narrow range of 0.5 wt. %.

It is worth noting the reported distribution of FeO and  $Fe_2O_3$  in the various minerals of the crichtonite group. From available analyses in the literature it appears that davidite may have  $Fe_2O_3 \geq FeO$  or  $Fe_2O_3 \leq FeO$  (Hayton, 1960; Arribas, 1963; Ablanov, 1966). Senaite appears to have FeO dominant over  $Fe_2O_3$ . Crichtonite and landauite contain  $Fe_2O_3$  in excess of FeO. The  $FeO/Fe_2O_3$  ratio for loweringite has not yet been determined, and the same is true for the rhenium-containing senaite-crichtonite described by Sarp *et al.* (1981). The  $FeO/Fe_2O_3$  ratio for the St Peters Dome Zn- and Y-group-bearing senaite is about 2:1.

The distribution of the REE in the Zn- and Y-group-bearing senaite from St Peters Dome is similar to that of the associated murataite in that the Y-group REE (principally Y itself) are dominant. This is in agreement with the senaite from Dattas and in distinct contrast to reported davidites where the Ce-group is dominant. The dominance of the heavy REE in the St Peters Dome Zn- and Y-group-bearing senaite reflects the individual chemistry of the pegmatite host in which yttrium minerals are dominant (murataite, xenotime, Y in zircon, Y in astrophyllite). The REE distribution in davidite (Butler and Hall, 1960; Hayton, 1960; Neumann and Sverdrup, 1960; Butler, 1961; Welin and Uytenbogaardt, 1963) and other members of the crichtonite group frequently shows an unusual double hump pattern with light and heavy REEs present, but with a deficiency of those in the intermediate range. Other davidites in the literature may show a dominance of La + Ce group REE. The senaite from Diamantina, MG, Brazil, however, shows (Grey *et al.*, 1976, and this paper) a dominance of the heavy REE. Depending on the local geochemical conditions, and amounts of the REE present, davidite may have a dominance of the light REE or may show the unusual double hump distribution.

The REE distribution pattern for loweringite (Gatehouse *et al.*, 1978) showed a double hump to be present with maxima at La and Ho. The unusual double hump REE pattern was interpreted (also noted and commented on by previous authors) as evidence that the REE are entering two distinct sites in the structure. The chondrite-normalized REE distribution patterns for davidites (fig. 4) showed the same double maxima as for loweringite (Campbell and Kelly, 1978). Because two sites are available (large cation and small cation positions), depending on the availability of the REE at the time of crystal growth, the crystal may show a dominant light REE distribution pattern or a double hump pattern such as found by Gatehouse *et al.* (1978) and Butler and Hall (1960) as well as by

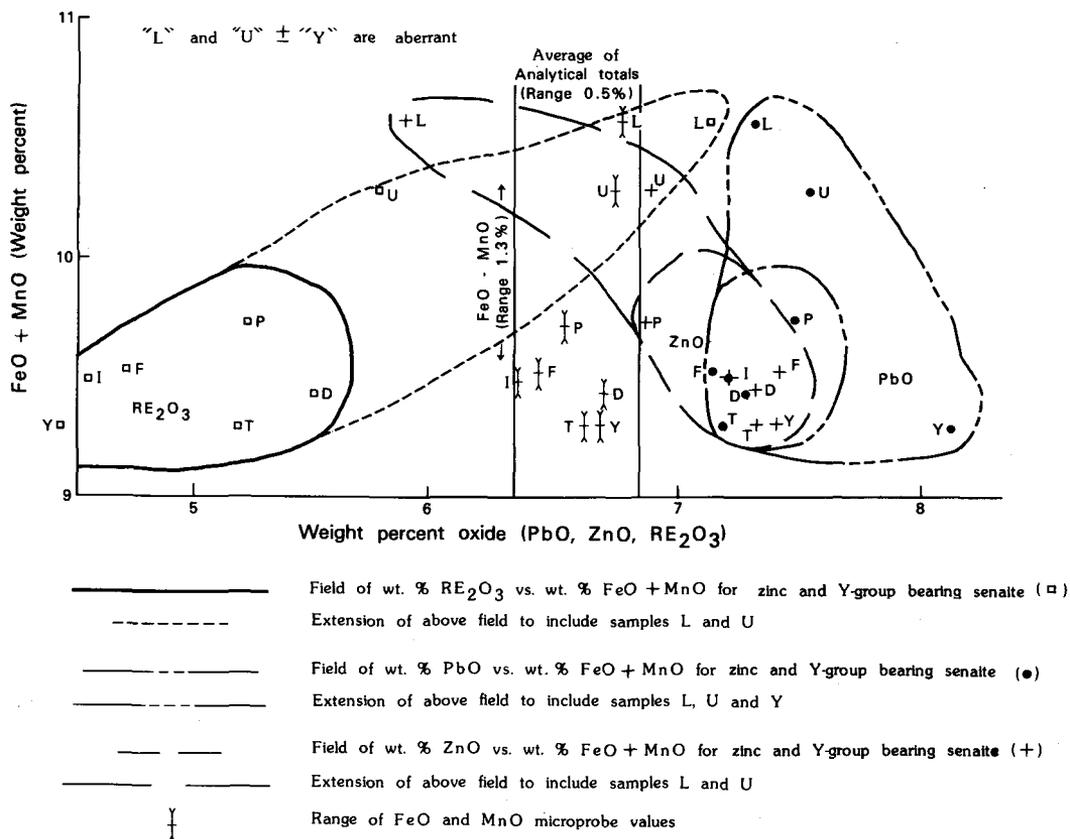


FIG. 3. PbO, RE<sub>2</sub>O<sub>3</sub>, and ZnO vs. FeO + MnO for Zn- and Y-group-bearing senaite. Values are in wt. %.

Neumann and Sverdrup (1960). Details on the CNR plotting method are given in Hanson (1978).

A six-step semiquantitative emission spectrographic analysis made of specimen D (Nancy M. Conklin, analyst) yielded the following (in wt. %): Fe 7, Mg < 0.002, Ca none, Ti > 20, Si 0.2, Al 0.7, Na 0.5, K none, Mn 1.5, Ba 1.5, Nb 1, Pb 7, Sn 0.15, Sr 0.005, Y 3, Zn 7, Zr 0.2, Th 0.2, Yb 1.5, Gd 0.07, Dy 0.7, Ho 0.2, Er 0.7, Tm 0.3, Lu 0.3. No other elements were detected at respective limits of detection. The results from this analysis (converted to oxides) are comparable to the microprobe determinations. The first seven microprobe analyses have been averaged and are presented in Table I.

A new analysis of the davidite from Olary, South Australia, is also presented in Table I. Agreement between the analysis presented here and that of Gatehouse *et al.* (1978) is good for those elements which are in common. We have determined additional REE (Dy, Ho, Er, Tm, Yb, and Lu) and Ba, Zn, Sn, Na, and Nb. If the four additional

elements (Cr, Al, V, and Hf) determined by Gatehouse *et al.* (1978) are added to our total, the new total becomes 102.09%.

Microprobe analyses of the senaite and Zn-bearing senaite from Dattas, MG, Brazil, are given in Table II, along with an average of the four analyses of senaite and the analysis from Grey *et al.* (1976). The 'davidite' from Nezilovo, Macedonia, with 11.83% PbO (Vujanovic, 1970) is actually a senaite if the nomenclature of Gatehouse *et al.* (1979) is followed.

*X-ray diffraction data.* Samples of Zn- and Y-group-bearing senaite from St Peters Dome were examined by both powder diffraction and single-crystal X-ray methods. Both 57.3 and 114.6 mm Gandolfi photographs were made from the various crystal grains. Precession camera photographs (Mo-K $\alpha$  radiation, Zr-filter) of a euhedral crystal similar to those shown in figs 1a and b confirmed the hexagonal (rhombohedral) symmetry shown morphologically and indicated possible space

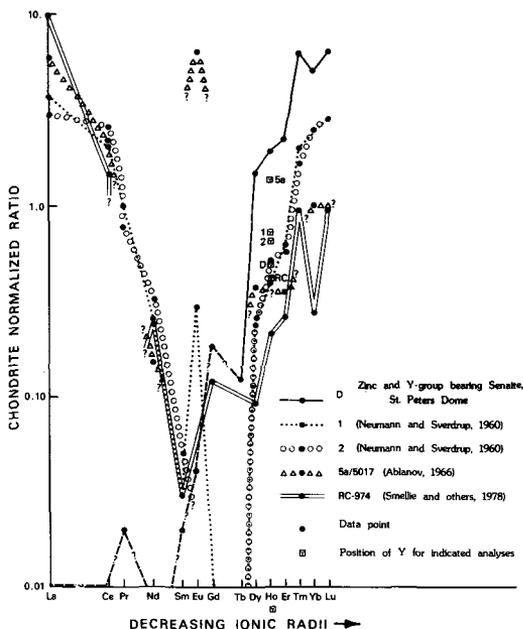


FIG. 4. Chondrite-normalized ratio (CNR) plot for selected davidites from the literature and Zn- and Y-group-bearing senaite from St. Peter's Dome, Colorado.

groups  $R\bar{3}$  or  $R3$ . Preliminary measurements of  $a = 10.36$  and  $c = 20.91$  Å from the precession films (0 to 2nd level) were later refined to  $a = 10.448(2)$  and  $c = 21.036(5)$  Å by powder diffraction techniques (LiF internal standard, graphite monochromatized  $\text{Cu-K}\alpha_1$  radiation,  $\frac{1}{2}^\circ/\text{min.}$ ,  $\frac{1}{2}$  inch/min., twenty-seven reflections used). The single-crystal photographs show sharp spots with no evidence of incipient metamictization. Twinning on  $\{52\bar{7}0\}$  was also observed and is identical to that reported by Pabst (1961) for material from Arizona and Norway.

Table III contains cell data for senaites and davidites from various locations, including determinations made for Zn- and Y-group-bearing senaite, davidite from Arizona, davidite from Tuffan, Norway, and davidite from Olary, South Australia. Data for other members of the crichtonite group are also shown. As pointed out by Gatehouse *et al.* (1979), there is a strong correlation between  $a_{rh}$  and the  $M(1)$ -O bond length for members of the crichtonite group. The A-site cation appears to have little or no effect on the cell dimensions.

Table IV contains X-ray diffraction data for five samples of Zn- and Y-group-bearing senaite from St. Peter's Dome, davidite from Arizona, and three samples of davidite from the Congo. Differences in peak positions and intensities of lines are readily

Table III. Cell parameters for members of the crichtonite group

Species, locality and source	$a_{\text{hex}}^0$	$c_{\text{hex}}^0$
zinc and Y-group-bearing senaite, "D," St. Peter's Dome, Colo. (this paper). Non-metamict	10.448(2)	21.036(5)
senaites, Dattas, Diamantina, Minas Gerais, Brazil (Rouse and Peacor, 1968)	10.42±.05	20.86±0.1
senaites, Diamantina region, Minas Gerais, Brazil (Grey and Lloyd, 1976). USNM R7241	10.393(2)	20.811(5)
rhenium-bearing senaite-crichtonite, ? locality (Sarp <i>et al.</i> , 1981)	10.44	20.82
davidite, Pima Co., Ariz. (this paper)	10.389(2)	20.875(5)
davidite, Pandora prospect, Quitjotoa Mtns., Pima Co., Ariz. (Gatehouse <i>et al.</i> , 1979). USNM R12472	10.376(4)	20.910(9)
davidite (average of 11 determinations on Arizona material and six on Norwegian material) (Pabst, 1961)	10.37±.02	20.87±.02
davidite, Tuffan, Norway (this paper)	10.380(4)	20.976(16)
davidite, Olary, South Australia (this paper)	10.32(7)	20.90(2)
davidite, Kirumba, Kivu, Congo (Van Wambeke, 1968). Non-metamict	10.41±.03	21.00±.06
davidite, Vishnevye Mtns., Urals, USSR (Shabin <i>et al.</i> , 1963). Non-metamict	10.405	20.88
crichtonite, Dauphine region, France (Grey <i>et al.</i> , 1976). USNM B18195	10.374(3)	20.746(6)
landauite, Burpala massif, USSR (Grey and Gatehouse, 1978). USNM 14009	10.366(7)	20.77(1)
lovingite, Jemberiana intrusion, Western Australia (Kelly <i>et al.</i> , 1979). USNM 143350	10.337(6)	20.677(12)

seen between the US material and the three samples from Kirumba, Congo. No one film made of the St. Peter's Dome Zn- and Y-group-bearing senaite contained all of the lines reported, and the same is true for the non-metamict Kirumba davidite and for the Australian davidites studied by Whittle (1959). X-ray powder data for senaite from Dattas, MG, Brazil, are given in Rouse and Peacor (1968). In general, the intensities of various lines are similar but do show some substantial variation. Some of this variation may be due to orientation effects, but much is probably due to differences in both chemistry and degree of order. All of the lines for all samples can be satisfactorily indexed on the hexagonal (rhombohedral) cell chosen by Pabst (1961). Additional diffraction lines representing  $d$ -values lower than 1.449 Å were noted, but these are not included in Table IV.

The powder patterns for davidite and senaite are 'more similar' to each other than to those of landauite, crichtonite, or lovingite. The rhenium-rich (2.63 wt. %  $\text{Re}_2\text{O}_3$ ) senaite-crichtonite described by Sarp *et al.* (1981) shows powder data very similar to davidite and Zn- and Y-group-bearing

Table IV. X-ray powder diffraction data for zinc and Y-group-bearing senaite and selected davidites

Zinc and Y-group-bearing senaite St. Peters Dome, Colorado										Davidite* Pima Co., Arizona		Davidite** Kirumba, Kivu, Congo							
hkil	I/I <sub>0</sub>	d <sub>obs</sub>	d <sub>calc</sub>	Specimen					heated sample		non-metamict								
				h <sub>1</sub> l <sub>1</sub>	h <sub>2</sub> l <sub>2</sub>	h <sub>3</sub> l <sub>3</sub>	h <sub>4</sub> l <sub>4</sub>	h <sub>5</sub> l <sub>5</sub>	d <sub>obs</sub>	I/I <sub>0</sub>	Sample 11	Sample 22	Sample 24						
1011	---	---	---	---	8.4	---	8.4	---	---	---	---	---	---	---	---	---	---	---	---
0003	---	---	---	---	6.95	---	6.9	6.9	6.86	18	---	---	---	---	---	---	---	---	---
1120	15	5.21	5.22	5.25	5.25	---	5.25	5.3	5.21	15	5.20	---	---	---	---	---	---	---	---
0221	10	4.418	4.423	---	4.9?	4.2	4.4?	---	---	---	---	---	---	---	---	---	---	---	---
1123	10	4.156	4.156	---	4.15	4.15	4.15	4.15	4.18	24	4.12	6	4.10	3	---	---	---	---	---
0115	15	3.813	3.813	3.78	3.81	---	3.80	3.80	3.81	7	3.77	10	3.76	10	3.75	8	---	---	---
0278	50	3.428	3.430	3.43	3.43	3.4	3.42	3.42	3.42	72	3.38	44	3.38	11	3.37	23	---	---	---
2131	---	---	---	---	---	---	---	---	---	---	---	---	3.355	2	---	---	---	---	---
1232	15	3.248	3.252	---	3.24	3.21	3.23	---	3.21	20	---	---	---	---	---	3.20	7	---	---
2025	45	3.081	3.081	3.08	3.07	3.06	3.08	3.09	3.065	50	3.05	32	3.055	36	3.04	35	---	---	---
3030	30	3.012	3.016	3.00	3.00	3.00	3.00	3.01	3.000	40	2.985	36	2.982	20	2.97	10	---	---	---
1126	100	2.914	2.911	2.90	2.90	2.90	2.90	2.91	2.895	100	2.890	80	2.873	42	2.878	42	---	---	---
2134	65	2.869	2.867	2.85	2.85	2.84	2.85	2.86	2.850	60	2.838	69	2.838	69	2.822	35	---	---	---
3033	65	2.772	2.771	2.76	2.76	2.75	2.76	2.78	2.755	22	2.752	25	2.749	45	2.728	16	---	---	---
1235	30	2.654	2.654	2.65	2.65	2.64	2.65	2.66	2.640	33	2.634	30	2.627	38	2.619	5	---	---	---
2240	20	2.611	2.612	2.60	2.60	2.59	2.60	2.61	2.595	18	2.594	5	2.583	4	---	---	---	---	---
1341	60	2.490	2.492	2.49	2.49	2.48	2.49	2.50	2.480	38	2.473	100	2.470	26	2.460	49	---	---	---
2243	40	2.441	2.441	2.43	2.43	2.43	2.43	2.45	2.429	25	2.427	30	2.421	13	2.421	19	---	---	---
1344	45	2.264	2.265	2.26	2.26	2.26	2.26	2.27	2.248	50	2.252	60	2.247	33	2.241	54	---	---	---
3145	95	2.155	2.155	2.15	2.15	2.14	2.15	2.16	2.139	40	2.139	65	2.141	65	2.141	100	---	---	---
1238	---	---	---	---	---	---	2.09	---	2.072	5	2.068	5	2.070	6	---	---	---	---	---
10110	---	---	---	---	---	---	2.03	---	2.029	5	---	---	2.034	12	---	---	---	---	---
0425	10	1.975	1.975	1.97	1.97	1.965	1.97	1.975	1.982	12	1.963	9	1.955	3	---	---	---	---	---
3234	30	1.932	1.931	1.93	1.93	1.92	1.925	1.925	1.919	25	1.915	15	1.916	15	1.908	6	---	---	---
02210	---	---	---	---	1.90	---	1.89	---	1.897	5	---	---	---	---	1.886	4	---	---	---
2355	10	1.862	1.862	1.86	1.86	1.85	1.855	1.86	1.849	10	1.848	13	---	---	---	---	---	---	---
3178	80	1.817	1.816	1.815	1.815	1.815	1.81	1.82	1.803	38	1.806	29	1.802	40	1.801	5	---	---	---
21310	---	---	---	---	1.79	1.79	1.79	---	1.780	12	1.778	8	---	---	---	---	---	---	---
00012	---	---	---	---	---	---	---	---	1.741	<5	---	---	---	---	---	---	---	---	---
6136	20	1.721	1.720	1.72	1.715	1.715	1.715	1.715	1.708	22	1.711	13	1.710	14	1.708	3	---	---	---
5055,11212	5	1.663	1.662	1.66	1.66	1.66	1.66	1.67	1.652	12	1.654	5	---	---	1.648	66	---	---	---
13410	45	1.616	1.612	1.615	1.615	1.61	1.61	1.617	1.601	40	1.603	25	1.601	78	1.600	40	---	---	---
4265	---	---	---	---	1.58	1.58	---	1.59	1.572	<5	---	---	1.575	100	1.574	7	---	---	---
3366	10	1.557	1.560	1.555	1.555	1.555	1.55	1.56	1.548	10	1.552	9	---	---	---	---	---	---	---
31511	15	1.523	1.521	1.52	1.52	1.52	1.515	1.525	1.509	15	1.535	6	---	---	---	---	---	---	---
32510	---	---	---	---	---	---	---	---	1.467	5	---	---	1.466	2	---	---	---	---	---
5270	40	1.449	1.449	1.449	1.447	1.445	1.445	1.45	1.439	40	1.443	38	1.441	42	1.439	35	---	---	---

\*Pabst (1961).  
 \*\*Van Wambeke (1968).  
 \*\*\*Nickel-filtered, graphite monochromatized CuK<sub>α1</sub> radiation (1.54051 Å). Intensities estimated visually. d-Values calculated for a hexagonal cell for which a = 10.448 Å, and c = 21.037 Å.

senaite. Because of lack of material, the pattern for loveringite is a calculated pattern (Kelly *et al.*, 1979) from single-crystal data. The patterns for crichtonite, landauite (Portnov *et al.*, 1966), and loveringite are very distinct from those of Zn- and Y-group-bearing senaite.

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