Senaite from syenite pegmatite at Tvedalen in the southern part of the Oslo Region, Norway

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Senaite, the plumboan member of the crichtonite group, has been found in a syenite pegmatite in a larvikite quarry at Bjørndalen in the Tvedalen area in the southern part of the Oslo Region. Senaite occurs as well-formed interpenetration twins up to 4×1 mm large with c as the twin axis. The colour is black with a submetallic adamantine lustre. The streak is greenish black. The density is $4.96(1) \, \text{g/cm}^3$ (measured) and $4.93 \, \text{g/cm}^3$ (calculated). The unit cell dimensions found by least squares refinement based on an X-ray diffractogram are (trigonal, space group R3 or R3 or R3 or R3 (a = 10.418(1) Å, c = 20.928(2) Å, V = 1967.1(3) Å³. Chemical analysis yields the structural formula $Pb_{1.13}(Ti_{13.66}Fe_{3.44}^3Fe_{1.22}^3Zn_{1.87}Mn_{0.55}Y_{0.26}Nb_{0.15})_{221.15}O_{38}$ which is in close agreement with the general formula $AM_{21}O_{38}$. Crystallization of senaite, which contains the chalcophile elements Pb and Zn, requires a hydrothermal fluid with an extremely low H_2S fugacity, typically found in syenites, alkali granites and certain hydrothermal veins.

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Senaite is the plumboan member of the crichtonite group with the general formula $AM_{21}O_{38}$ where A is a large cation (Ba, Ca, K, Na, Pb, light REE, Sr, U) and M is mainly Ti and Fe. Other elements (Cr, Mg, Mn, Nb, heavy REE, Sn, V, Zn, Zr) may also enter this position. The predominant cation in the A position determines the mineral name: Ba is lindsleyite, Ca is loveringite, K is mathiasite, Na is landauite, Pb is senaite, REE and U are davidite, Sr is crichtonite. There is, however, considerable substitution in both the A and M positions.

The structure of senaite, which was solved by Grey & Lloyd (1976), may be regarded as a nine-layer close-packed oxygen framework but with one of the anion sites in this framework occupied by the large A cation. The senaite M cations occupy octahedral and tetrahedral interstices between the oxygen layers. Senaite and its relationship to the crichtonite group were treated by Rouse & Peacor (1968) and Grey et al. (1976).

Hussak & Prior (1896) described senaite as a new species occurring as an accessory mineral in the diamond-bearing gravels from the Diamantina area in Minas Gerais, Brazil. Other, but similar findings have been made in the same area and a brief review of these localities has been given by Cassedanne (1986), who also described an *in situ* occurrence: quartz veins in a shear zone in quartzite at Fazenda Guariba, Minas Gerais.

Zinc- and yttrium-group-bearing senaite has been described from an alkali metasomatic granite pegmatite at St. Peters Dome, Colorado, USA (Foord et al. 1984). Complex members of the crichtonite group, including strontian senaite and cerian strontian senaite have been described from alpine fissures in Switzerland and Italy (Stalder & Bühler 1987). Senaite is briefly mentioned from syenite pegmatites at Mont St. Hilaire, Quebec, Canada (Mandarino & Anderson 1989).

In April 1989, a black, well-crystallized mineral embedded in analcime was found in a syenite pegmatite in a larvikite quarry at Bjørndalen (UTM map reference NL497451) in the Tvedalen area in the southern part of the Oslo Region, Norway. Using X-ray diffractometry and qualitative X-ray spectrometry it was subsequently identified as senaite. The Bjørndalen larvikite quarry is thus one of the few senaite localities hitherto reported and the second occurrence of senaite in a syenite pegmatite. Senaite is a new species to add to the long list of minerals from the syenite pegmatites of the Oslo Region which were thoroughly treated by Brøgger (1890). An updated mineral list has been published by Raade et al. (1980).

Occurrence

The senaite-bearing syenite pegmatite dike is

approximately 40-50 cm thick, but the extension is not known due to quarrying. Senaite was restricted to a local part of the pegmatite dike, which has now been removed by the quarry operation. The mineral assemblage includes albite, magnetite, senaite, hambergite, zircon, ilmenite (approximately 67 mol% ilmenite, 33 mol% pyrophanite), bastnäsite-(Ce), parisite-(Ce), fluorite, natrolite, cancrinite and analcime. These minerals belong to the hydrothermal stage of the pegmatite formation and fill up to fist-sized spaces between larger microcline individuals which constitute the main part and first stage of the pegmatite formation together with ferropargasitic hornblende, biotite, magnetite, nepheline (partly altered to natrolite) and wöhlerite.

Morphology, physical properties

Senaite from the Bjørndalen dike occurs as wellformed interpenetration twins up to 4×1 mm large with c as the twin axis, and the twin individuals are rotated 30° relative to each other about this axis. The twin individuals show great variation in size. A typical senaite twin crystal is shown in Fig. 1. The principal forms are pinacoid $\{0001\}$, hexagonal prism $\{10\bar{1}0\}$ and rhombohedron $\{2\bar{1}\bar{1}2\}$. Other rhombohedrons are sometimes present. The prism faces are somewhat striated and uneven.

Senaite from Minas Gerais, Brazil occurs as millimeter-sized, pseudocubic rhombohedrons, sometimes complexly twinned, or as platy crystals up to 1 cm wide (Cassedanne 1986). Senaite crystals from Colorado are developed as prisms modified by pyramids and pinacoids (Foord et al. 1984) and show a strong resemblance to the senaite twin individuals from the Bjørndalen dike. Senaite from Mont St. Hilaire, Canada is reported as trillings up to 0.5 mm in diameter (Mandarino & Anderson 1989).

Bjørndalen senaite is black with a submetallic adamantine lustre. The streak and powder are greenish black. No cleavage is observed. The density was determined at 22°C on 0.5647 g (by the pycnometer method with water as the immersion medium) to be 4.96(1) g/cm³ which is close to the calculated value of 4.93 g/cm³ based on the chemical composition, the measured unit cell volume and Z=3.

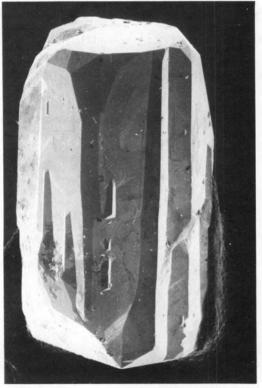


Fig. 1. SEM photo of a twinned senaite crystal (approximately 1 mm long) from Bjørndalen, Tvedalen, Oslo Region.

X-ray crystallography

Senaite from the Bjørndalen dike was run on a Philips PW1700 diffractometer with step size 0.01° $2\Theta s^{-1}$ using $CuK\alpha_1$ ($\lambda = 1.54059 \text{ Å}$) radiation, graphite monochromator and Si (NBS 640a) as internal standard. The X-ray powder diffraction data are given in Table 1. All of the lines are satisfactorily indexed in space group R3 or R3 (hexagonal cell) as given by Grey & Lloyd (1976) and the unit cell dimensions were calculated by least squares refinement using the program by Appleman & Evans (1973) and modified by Benoit (1987). The unit cell dimensions for the Bjørndalen senaite are a = 10.418(1) Å, c =20.928(2) Å, V = 1967.1(3) Å³. The X-ray powder diffraction pattern for Bjørndalen senaite is more complicated than that reported for senaite from Dattas, Minas Gerais, Brazil (Rouse & Peacor 1968) (reported in PDF 20–1048) and St. Peters Dome, Colorado, USA (Foord et al. 1984) (Table 1) where several of the low-intensity reflections are lacking in the data set and some

Table 1. X-ray powder diffraction data for senaites. 1. Bjørndalen, Tvedalen, Oslo Region (this work). Unit cell dimensions: a = 10.418(1) Å, c = 20.928(2) Å. 2. Dattas, Minas Gerais, Brazil (Rouse & Peacor 1968) (PDF 20-1048). Unit cell dimensions: a = 10.42(5) Å, c = 20.86(1) Å. 3. St. Peters Dome, Colorado, USA (Foord et al. 1984). Unit cell dimensions: a =10.448(2) Å, c = 21.036(5) Å.

| | 1 | | | 2 | | 3 | |
|--------|---------|---------------------------|----------------------------|---------------------------|---------|---------------------------|---------|
| hkl | I/I_0 | d _(obs) (Å) | d _(calc) (Å) | d _(obs) (Å) | I/I_0 | d _(obs) (Å) | I/I_0 |
| 101 | 8 | 8.28 | 8.285 | 8.27 | 20 | | |
| 003 | 5 | 6.96 | 6.976 | | | | |
| 012 | 5 | 6.83 | 6.833 | | | | |
| 110 | 15 | 5.20 | 5.209 | | | 5.21 | 15 |
| 021 | 12 | 4.41 | 4.410 | | | 4.418 | 10 |
| 113 | | | 4.174 | 4.17 | 25 | 4.155 | 10 |
| 202 | 11 | 4.14 | 4.143 | | | | |
| 015 | 12 | 3.795 | 3.797 | 3.78 | 20 | 3.813 | 15 |
| 006 | 6 | 3.486 | 3.488 | | | | |
| 024 | 69 | 3.415 | 3.417 | 3.43 | 90 | 3.428 | 50 |
| 122 | 14 | 3.239 | 3.242 | 3.25 | 5 | 3.248 | 15 |
| 205 | 34 | 3.067 | 3.068 | 1 | 20 | 3.081 | 45 |
| 300 | 28 | 3.007 | 3.007 | 3.04 | 20 | 3.012 | 30 |
| 116 | 100 | 2.898 | 2.898 | 2.894 | 100 | 2.914 | 100 |
| 214 | 68 | 2.856 | 2.857 | | | 2.869 | 65 |
| 107 | 15 | 2.839 | 2.838 | | | | |
| 303 | 56 | 2.759 | 2.762 | 2.763 | 25 | 2.772 | 65 |
| 125 | 30 | 2.643 | 2.644 | 2.644 | 20 | 2.654 | 30 |
| 220 | 21 | 2.604 | 2.604 | | | 2.611 | 20 |
| 131 | 32 | 2.485 | 2.485 | 1 | | 2.490 | 60 |
| 223 | 43 | 2.438 | 2.440 | 2.468 | 50 | 2.441 | 40 |
| 306 | | 21.00 | 2.278 | 1 | | 2 | |
| 208 | | | 2.263 | 2.265 | 50 | | |
| 134 | 59 | 2.257 | 2.257 | , | | 2.264 | 45 |
| 315 | 45 | 2.148 | 2.148 | 2.146 | 50 | 2.155 | 95 |
| 119 | 7 | 2.124 | 2.123 | 2.1.0 | | | |
| 128 | 5 | 2.075 | 2.076 | | | | |
| 321 | 4 | 2.061 | 2.060 | | | | |
| 1.0.10 | 3 | 2.041 | 2.039 | | | | |
| 232 | 4 | 2.030 | 2.030 | | | | |
| 045 | 3 | 1.985 | 1.986 | 1.981 | 75 | 1.975 | 10 |
| 410 | 16 | 1.968 | 1.969 | 21702 | , . | 21,7,0 | |
| 324 | 35 | 1.924 | 1.925 | | | 1.932 | 30 |
| 137 | | | 1.919 | 1.914 | 5 | | |
| 413 | 10 | 1.986 | 1.895 | | | | |
| 0.1.11 | | | 1.862 | 1 052 | - | | |
| 235 | 9 | 1.856 | 1.855 | 1.852 | 5 | 1.862 | 10 |
| 318 | 40 | 1.808 | 1.808 | 1.804 | 40 | 1.817 | 80 |
| 407 | 8 | 1.799 | 1.800 | | | | |
| 2.1.10 | 11 | 1.784 | 1.784 | | | | |
| 0.0.12 | 6 | 1.744 | 1.744 | | | | |
| 330 | 3 | 1.737 | 1.736 | | | | |
| 416 | 31 | 1.715 | 1.715 | 1.713 | 40 | 1.721 | 20 |
| 054 | 7 | 1.706 | 1.706 | | | | |
| 505 | 6 | 1.657 | 1.657 | 1 | _ | 1 | _ |
| 1.1.12 | | | 1.654 | 1.656 | 5 | 1.663 | 5 |
| 244 | 8 | 1.621 | 1.621 | • | | , | |
| 1.3.10 | 46 | 1.605 | 1.605 |) | | 1.616 | 45 |
| 152 | - | | 1.601 | 1.603 | 70 | | |
| 425 | 6 | 1.579 | 1.579 | , | | | |
| 336 | 10 | 1.554 | 1.554 | 1.551 | 20 | 1.557 | 10 |
| | - | | | | - | | |

Table 1 (contd.).

| | 1 | | | 2 | | 3 | |
|--------|---------|------------------------|----------------------------|---------------------------|---------|---------------------------|---------|
| hkl | I/I_0 | d _(obs) (Å) | d _(calc) (Å) | d _(obs) (Å) | I/I_0 | d _(obs) (Å) | I/I_0 |
| 514 | 9 | 1.548 | 1.548 | | | | |
| 3.1.11 | 18 | 1.515 | 1.515 | , | | 1.523 | 15 |
| 155 | | | 1.511 | 1.508 | 20 | | |
| 3.0.12 | | | 1.509 | J | | | |
| 600 | 4 | 1.503 | 1.504 | | | | |
| 3.2.10 | 4 | 1.472 | 1.472 | | | | |
| 603 | 5 | 1.468 | 1.470 | | | | |
| 2.1.13 | 4 | 1.456 | 1.456 | | | | |
| 2.2.12 | | | 1.449 | 1 447 | 70 | | |
| 520 | 43 | 1.445 | 1.445 | 1.447 | 70 | 1.449 | 40 |
| 434 | 5 | 1.427 | 1.427 | • | | | |
| 2.0.14 | | | 1.419 | 1 | 10 | | |
| 523 | 5 | 1.415 | 1.415 | 1.415 | 10 | | |
| 345 | 4 | 1.398 | 1.398 | - | | | |
| 606 | 9 | 1.382 | 1.381 | 1.380 | 10 | | |
| 1.2.14 | 4 | 1.370 | 1.369 | | | | |
| 1.3.13 | 5 | 1.354 | 1.354 | | | | |

closely spaced lines are reported as single lines. In addition, there are also variations in the intensities of various lines in the reported X-ray diffraction data sets. This was also observed by Foord et al. (1984) on different samples even within the same locality (St. Peters Dome, Colorado, USA). He points out that some of these variations may be due to orientation effects, differences in chemistry and degree of order. From the significant differences in the various X-ray diffraction patterns, there is reason to believe that senaite exists in several polytypes, as pointed out by Metelo (1968). The lack of weak reflections may, however, be due to slight metamictization because senaite from both Colorado and Minas Gerais contains about 0.1–0.3% ThO₂. Foord et al. (1984) and Cassedanne (1986), however, state that there is no evidence of metamictization in their senaites. Cassedanne (1986) reports that Xray powder diffraction patterns of near-surface samples of senaite are blurred. Alteration obviously has a significant effect on the physical properties of senaite. All investigations on senaite from Minas Gerais, Brazil, have been done on material from alluvial deposits, with exception of the in situ locality by Cassedanne (1986).

Chemical composition

Senaite from the Bjørndalen quarry was analysed

Table 2. Chemical composition of senaite from Bjørndalen, Tvedalen, Oslo Region.

| | Wt% of oxides | Number of atoms based on 38 O | | |
|--------------------------------|------------------|-------------------------------|-------|--|
| TiO ₂ | 56.1 | Ti | 13.66 | |
| SnO_2 | trace | | | |
| Nb_2O_5 | 1.0 | Nb | 0.15 | |
| Y_2O_3 | 1.5 | Y | 0.26 | |
| Fe ₂ O ₃ | 14.1 | Fe ³⁺ | 3.44 | |
| FeO | 4.5 | Fe ²⁺ | 1.22 | |
| MnO | 2.0 | Mn | 0.55 | |
| ZnO | 7.8 | Zn | 1.87 | |
| PbO | 13.0 | Pb | 1.13 | |
| Total | 100.0 | | | |

by energy dispersive X-ray spectrometer (Tracor standardless, "total composition" analysis, i.e. recalculation and summation to 100%) in a JEOL scanning electron microscope. This method showed no significant zoning or inhomogeneity in the analysed crystal fragments. Y and Nb were analysed by X-ray fluorescence spectrometry (ARL 8240+) using synthetic standards. Material for X-ray fluorescence spectrometry and wet chemical analysis was obtained by repeated separations using heavy liquids and acid treatments. Fe²⁺ was determined by titration with K₂Cr₂O₇. The analytical results are recalculated to a total of 100.0% and shown in Table 2. No other elements have been detected in concentrations above ~0.1%.

Calculation of the structural formula for the Bjørndalen senaite on the basis of 38 oxygens yields $Pb_{1.13}(Ti_{13.66}Fe_{3.44}^3Fe_{1.22}^2Zn_{1.87}Mn_{0.55}Y_{0.26}Nb_{0.15})_{\Sigma 21.15}O_{38}$ which agrees well with the general formula $AM_{21}O_{38}$. An excess of A atoms is common in both senaites and loveringite and may be due to the possibility of extra A atoms occupying the twofold, partially unfilled anion site O(7) (Gatehouse et al. 1978). An excess of 0.15 (0.7%) M atoms is ascribed to analytical inaccuracy.

The Bjørndalen senaite with 7.8 wt% ZnO is among the Zn-richest senaites hitherto found together with the species from St. Peters Dome, Colorado (average 7.05 wt% ZnO) and Dattas, Minas Gerais (7.7 wt% ZnO) (Foord et al. 1984).

Discussion

Because of the chalcophility of both Pb and Zn,

crystallization of senaite requires a hydrothermal fluid with an extremly low H₂S fugacity, typically found in syenites, alkali granites and certain hydrothermal veins. This is consistently with both the Bjørndalen occurrence and the other senaite occurrences reported (Foord et al. 1984; Cassedanne 1986; Stalder & Bühler 1987; Mandarino & Anderson 1989).

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