Chemical composition of catapleiites from the syenite pegmatites in the Larvik plutonic complex, Norway

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Introduction

Catapleiite was described as a new mineral from Låven island in the Langesundsfjord district by Weibye (1850). The name, however, was used by him already the year prior to the formal description (Weibye 1849a,b). A comprehensive description of the mineral, with special emphasis on the crystallography, was given by Brøgger (1890). Bollingberg et al. (1983) presented a chemical analysis of a catapleiite from Eikaholmen. No further studies have been done on catapleiite from the syenite pegmatites in the Oslo Region.

Brøgger (1890) distinguished between two varieties of catapleiite: "Gewöhnlicher Katapleït" (normal catapleiite, calcium-sodium-catapleiite) and "Natronkatapleït" (sodium catapleiite). In modern mineralogical terms, however, both varieties are treated as catapleiite. The mineral forms an isomorphous series with calcium catapleiite (Portnov 1964), in which catapleiite, $Na_2ZrSi_3O_9 \cdot 2H_2O$, is the sodium end-member, and calcium catapleiite, $CaZrSi_3O_9 \cdot 2H_2O$, is the calcium end-member. The sodium dominant catapleiite is relatively common in alkaline rocks and associated pegmatites and hydrothermal veins, while calcium catapleiite has been found at just a few localities worldwide (Gaines et al. 1997).

Minerals of the catapleiite - calcium catapleiite series have been found at about 20 different localities of syenite pegmatites in the Larvik plutonic complex, most of them in the Langesundsfjord district. Catapleiite occurs both as a primary, magmatic mineral, and as a hydrothermal, late stage mineral. The primary catapleiite is a typical accessory mineral in pegmatites which approach agpaitic mineralogy. The chemistry of the catapleiites from the Larvik plutonic complex is poorly known. It is therefore of interest to analyse a number of samples in order determine the extent of solid solution in catapleiites.

The samples

1. Østre Brattholmen, Langesundsfjord district: Pale reddish brown plates of catapleiite, 2 cm across, embedded in feldspar.
2. Bjerke, Lille Arøya, Langesundsfjord district: Dark reddish brown plates of catapleiite, 1-2 cm across, embedded in eudialyte and feldspar.
3. Eikaholmen, Langesundsfjord district:: Reddish brown plates of catapleiite, up to 10 cm across, embedded in feldspar.
4. Vesle Arøya, Langesundsfjord district: Bluish grey thick plates of catapleiite. "Natronkatapleït", collected by Brøgger in 1884, Naturhistoriska Riksmuseet (Stockholm), catalogue no. 253913.
5. Låven island, Langesundsfjord district: Pale brownish red plates of catapleiite, 1 cm across, embedded in feldspar.
6. Skutesundskjærene (southern islet), Langesundsfjord district: Pale dirty yellow plates of catapleiite, up to several cm across, embedded in feldspar.
7. Skutesundskjærene (northern islet), Langesundsfjord district: Pale yellowish white plates of catapleiite, 2 cm across, embedded in feldspar.

8. Barkevikskjær, Langesundsfjord district: Greyish white plates of catapleiite, 1-2 cm across, embedded in feldspar.
9. Kjeøya, Langesundsfjord district: Dark reddish brown plates of catapleiite, up to 5 cm across, embedded in feldspar.
10. Lysebo, Larvik: Pale reddish brown plates of catapleiite, 2 cm across, embedded in feldspar.
11. Bratthagen, Kvelde: Pale reddish brown plates of catapleiite, 2 cm across, embedded in feldspar.
12. Vardåsen larvikite quarry, Malerød, Larvik: Aggregates up to 5 mm across, composed of thin platelets of dark reddish brown catapleiite, in vugs in feldpar associated with analcime, natrolite, gonnardite, gaidonnayite and hochelagaite.
13. Agnes, Stavern: Globular aggregates composed of thin plates of pale greyish yellow catapleiite. The globules are up to 10 mm across, and occur in vugs in feldspar associated with albite, analcime and calcite.
14. Håkestad larvikite quarry, Tjølling: Transparent, yellow, platy crystals up to 3 mm across, freely crystallized in vugs in analcime, associated with natrolite and chlorite.
15. Buer, Vesterøya, Sandefjord: Pale reddish brown plates, 2-4 mm across, embedded in feldspar, aegirine and chlorite.
16. Vøra, Vesterøya, Sandefjord: Reddish brown, anhedral grains up to 5 mm across, embedded in a very fine-grained matrix of catapleiite, quartz and bastnäsite.

Catapleiite samples 1-11 belong to the magmatic stage of pegmatite formation, while samples 12-16 belong to the late, hydrothermal stage of pegmatite formation.

Chemical composition

Catapleiites from the Larvik plutonic complex were analysed by a JEOL 5600 LV scanning electron microscope equipped with a Tracor energy dispersive X-ray spectrometer. The net intensities were corrected for atomic number effect, absorption and fluorescence. The reported oxides were normalized to 100 % and finally corrected for 9.0 wt.% water, which is the theoretical content of water of crystallization for $Na_2ZrSi_3O_9 \cdot 2H_2O$. The actual water content was determined as loss on ignition at 1000° C for 8 catapleiites (samples no. 2, 3, 4, 5, 7, 8, 9 and 10). The values range from 9.2 wt.% to 9.8 wt.%, which are close to the theoretical water content. The results are given in Table 1.

Most of the catapleiites from the Larvik plutonic complex have a notable Ca substition for Na, according to the scheme 2Na Ca. The sum of Na and Ca atomic proportions usually amounts to 1.4 - 1.8 only, thus indicates vacancies among the Na-Ca atomic positions. The general chemical formula for catapleiites can be written (Na,Ca,)$_2ZrSi_3O_9 \cdot 2H_2O$. The primary catapleiites generally contain 20 mol-% to 30 mol-% calcium catapleiite (Table 1). There are, however, a few exceptions: The samples from Vesle Arøya (Brøgger's "Natronkatapleït"), Bratthagen and Lysebo (both from within the lardalite area) are rather pure catapleiites, with calcium catapleiite contents of 3 mol-%, 2 mol-% and 1 mol-%, respectively, and are thus the purest catapleiites hitherto found in the Larvik plutonic complex.

Minor amounts of Fe and Al are present in most of the samples. The hydrothermal catapleiites from Vardåsen, Buer and Vøra, however, have notable Fe and Al contents. As shown by Bollingberg et al. (1983), catapleiite from Eikaholmen contains minor amounts of Mg, Al, K, Ti, Mn, Fe, Sr, Nb, Y and Hf. The same minor elements have been detected by semiquantitative analyses on several other catapleiites from the Langesundsfjord district during this study.

The catapleiite from Vardåsen occurs as extremely thin plates in parallell oriented aggregates. The platelets vary from 2 μm to 10 μm in thickness. Each platelet shows strong zonation, by which the catapleiite core is encrusted by a Ca-rich catapleiite

(Fig. 1). The latter mineral is the most Ca-rich catapleiite hitherto found in the Larvik plutonic complex, with 33 mol-% calcium catapleiite.

The catapleiite from Vøra occurs as anhedral grains with a solid, outer rim of catapleiite and a porous core of zircon (Fig. 2). The aggregates have been formed by the action of sodium rich hydrothermal solutions upon primary zircon crystals. Catapleiite crystallized in the rim, while skeletal remains of the zircon still exist in the core.

Catapleiite as a hydrothermal decomposition product of eudialyte has been observed at the Bjørndalen quarry in Tvedalen. It occurs as very fine-grained, pale brown masses up to several centimeters across. No further investigations, however, have been done on this mineral.

Conclusion

All catapleiites from the Larvik plutonic complex are sodium dominant catapleiites. Most of the primary catapleiites generally contain 20 mol-% to 30 mol-% calcium catapleiite, except catapleiites from Vesle Arøya (Brøgger's "Natronkatapleït"), Bratthagen and Lysebo (both from within the lardalite area), which are rather pure catapleiites with calcium catapleiite contents of 3 mol-%, 2 mol-% and 1 mol-%, respectively. Hydrothermal catapleiites may contain from 10 mol-% to 33 mol-% calcium catapleiite. Catapleiite as a hydrothermal alteration product of zircon and eudialyte has been observed.

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Table 1. Chemical composition (in weight-%) for catapleiites from the Larvik plutonic complex, atomic proportions calculated on the basis of 9 oxygens (not including oxygen in H_2O), and mol-% of calcium catapleiite (Ca cat) and catapleiite (cat).

	1	2	3	4	5	6	7	8	9
SiO_2	43.9	44.0	44.3	44.0	44.9	44.2	43.9	44.1	44.4
ZrO_2	32.0	31.7	32.0	32.1	31.1	32.3	32.2	32.5	32.2
Al_2O_3	0.2	0.2	0.2	0.0	0.7	0.0	0.0	0.2	0.1
Fe_2O_3	0.2	0.4	0.0	0.1	0.0	0.0	0.2	0.1	0.0
CaO	4.6	4.8	5.2	0.9	5.5	4.7	5.2	4.6	5.1
Na_2O	10.2	10.0	9.2	13.9	8.8	9.8	9.6	9.5	9.1
H_2O	9.0*	9.4	9.6	9.8	9.3	9.0*	9.3	9.2	9.5
Total	99.9	100.5	100.5	100.8	100.3	100.0	100.4	100.2	100.4
Si	2.94	2.94	2.96	2.96	2.98	2.96	2.94	2.95	2.97
Zr	1.05	1.03	1.04	1.05	1.00	1.05	1.05	1.06	1.05
Al	0.01	0.01	0.02	0.00	0.05	0.00	0.00	0.02	0.01
Fe	0.01	0.02	0.00	0.01	0.00	0.00	0.01	0.01	0.00
Ca	0.33	0.34	0.37	0.06	0.39	0.34	0.37	0.33	0.37
Na	1.32	1.30	1.19	1.81	1.14	1.27	1.24	1.24	1.18
Ca cat	20	21	24	3	25	21	23	21	24
cat	80	79	76	97	75	79	77	79	76

	10	11	12a	12b	13	14	15	16
SiO_2	45.9	44.5	47.1	45.5	45.3	43.4	44.5	44.7
ZrO_2	33.6	32.7	31.3	28.0	31.6	32.3	29.5	31.3
Al_2O_3	0.1	0.0	0.9	2.5	0.2	0.0	0.2	0.2
Fe_2O_3	0.1	0.0	0.4	0.6	0.2	0.1	2.5	1.1
CaO	0.3	0.4	2.4	6.8	2.6	2.4	5.4	6.2
Na_2O	10.9	13.4	9.0	7.7	11.2	12.8	9.0	7.4
H_2O	9.0*	9.0*	9.0*	9.0*	9.0*	9.0*	9.0*	9.0*
Total	99.9	100.0	100.1	100.1	100.1	100.0	100.1	99.9
Si	3.04	2.98	3.07	2.96	3.01	2.93	2.96	2.97
Zr	1.09	1.07	0.99	0.89	1.02	1.06	0.96	1.01
Al	0.01	0.00	0.07	0.19	0.02	0.00	0.01	0.02
Fe	0.01	0.00	0.02	0.03	0.01	0.01	0.12	0.05
Ca	0.02	0.03	0.17	0.48	0.19	0.18	0.38	0.44
Na	1.40	1.74	1.13	0.97	1.44	1.68	1.16	0.96
Ca cat	1	2	13	33	12	10	25	31
cat	99	98	87	67	88	90	75	69

* theoretical content of water of crystallization for $Na_2ZrSi_3O_9 \cdot 2H_2O$

1. Østre Brattholmen
2. Bjerke, Lille Arøya
3. Eikaholmen
4. Vesle Arøya
5. Låven island
6. Skutesundskjærene (southern islet)
7. Skutesundskjærene (northern islet)
8. Barkevikskjær
9. Kjeøya
10. Lysebo
11. Bratthagen

12a (core). Vardåsen quarry
12b (rim). Vardåsen quarry

13. Agnes, Stavern
14. Håkestad quarry, Tjølling
15. Buer, Vesterøya
16. Våra, Vesterøya

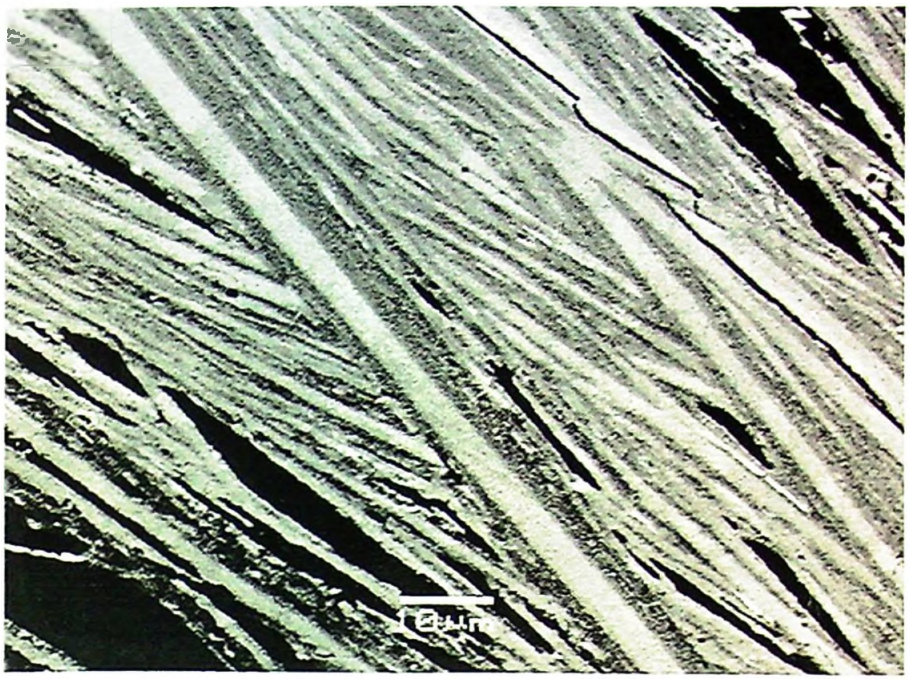

Fig. 1. SEM image of catapleiite platelets from Vardåsen, Malerød. The platelets are cut perpendicular to the *c*-axis. The zoning of each platelet is clearly visible; pale grey in the core, dark grey in the outer zone (calcium enrichment). Scale bar 10 μm.

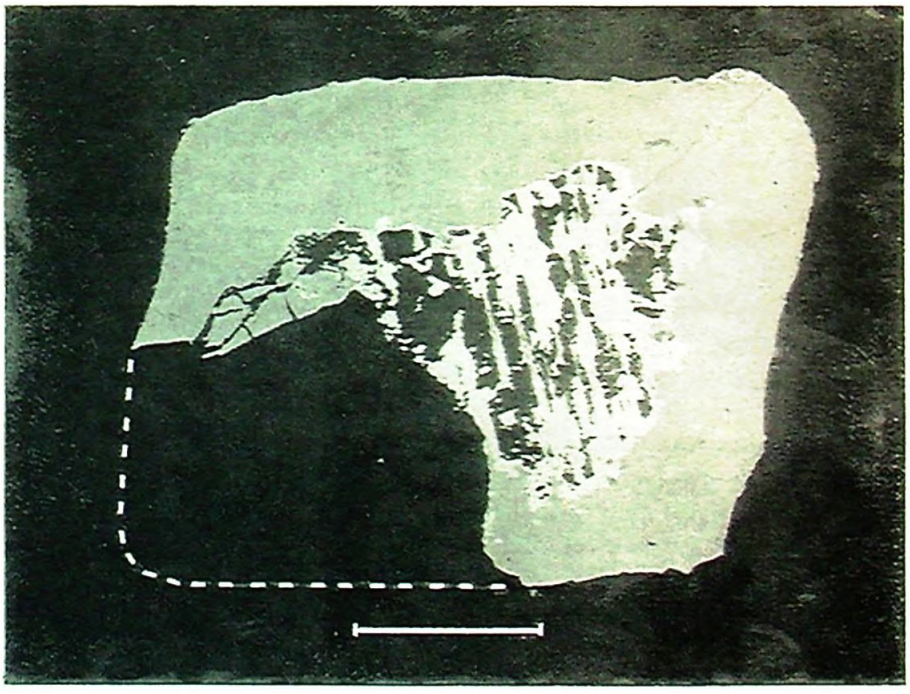

Fig. 2. SEM backscatter image of an aggregate showing catapleiite (medium grey) in the rim and skeletal remains of zircon (pale grey) in the core. The somewhat distorted tetragonal outline of the primary zircon crystal is evident, although lower left quarter is missing. From Vøra, Vesterøya, Sandefjord. Scale bar 1 mm.