Chemistry of aenigmatite from Vesterøya, Larvik plutonic complex, Norway

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Introduction

Aenigmatite, general formula $Na_2Fe^{2+}{}_5TiSi_6O_{20}$, typically occurs in the syenitic pegmatites of the eastern part of the Larvik plutonic complex, especially at Vesterøya and other localities in the vicinity of Sandefjord (Larsen et al. 2010). A detailed study of aenigmatite from Vesterøya, by electron-microprobe analysis, single-crystal structure refinement and Mössbauer spectroscopy, was published by Grew et al. (2008). The two average analyses of Grew et al. (2008) and the analysis of aenigmatite from Buer, Vesterøya, by Åsheim et al. (2008) represent the only complete chemical data reported so far on aenigmatite from the Larvik plutonic complex.

Electron-microprobe analyses of aenigmatite from Vesterøya, performed by the present author more than 32 years ago, are presented here. They were for some time thought to be lost, but have recently been retrieved. In spite of their age, these analyses are of high quality. Since the exact locality of the sample analysed by Grew et al. (2008) is not known (the authors believe that it is most likely from the Vindal-Buer area), the publication of the old analytical data on samples from identified localities seems to be justified.

A thin section of a sample from the lower pegmatite dyke at Vøra, Vesterøya, was analysed. Here, aenigmatite occurs both as cores in aegirine crystals and as discrete grains in microcline. Three small aenigmatite grains embedded in epoxy were analysed from each of two additional localities: the upper dyke at Vøra and a pegmatite at Vindal.

Analytical details

Energy-dispersive analyses were performed in October and November 1978 with an ARL-EMX electron microprobe at Sentralinstituttet for industriell forskning (Oslo). The operating voltage was 15 kV and the probe current 0.35 nA. The probe standards were diopside for Si, Mg and Ca, jadeite for Al and Na, rutile for Ti, fayalite with 2.5 wt% Mn for Fe and Mn, and K-feldspar for K. A rhodonite standard was used for Mn in the analyses marked VN2-1, VN2-2 and VN2-3 in Table 1. The counting data were converted to weight-percent oxides by a procedure described by Bence & Albee (1968), using the program PROBECOR developed by Kari Thoresen. Ferric iron was calculated with the program PYROX, based on a charge-balance method described by Neumann (1976).

The analyses of Grew et al. (2008) include ZnO, Cr_2O_3, ZrO_2 and Nb_2O_5, generally at levels of 0.0*x* wt% and below. These elements were not considered in the present study. Åsheim et al. (2008) report the concentrations of 42 (!) trace elements in aenigmatite from Østre Brattholmen, Langesundsfjord, and from Buer and Urderåsen, Vesterøya. The elements with the highest concentrations (100 ppm = 0.01 %) are: Li (88 to 220 ppm), Ni (384 ppm from Urderåsen only), Zn (641 to 1070 ppm), Zr (558 to 775 ppm), Nb (428 to 490 ppm) and Ce (178 from Urderåsen only).

Results

The results of 13 single-point analyses are presented in Table 1. The structural formulae are calculated on 14 cations and 20 negative charges.

The mean of four analyses on aenigmatite cores in aegirine from the lower dyke at Vøra gives the following empirical formula:

$(Na_{2.00}K_{0.03})_{\Sigma 2.03}(Fe^{2+}_{4.07}Mn_{0.66}Fe^{3+}_{0.10}Mg_{0.05}Ca_{0.05}Ti_{0.03})_{\Sigma 4.96}Ti_{1.00}$
$(Si_{5.86}Al_{0.08}Fe^{3+}_{0.06})_{\Sigma 6.00}O_{20}$,

as compared to the empirical formula based on three analyses of individual grains of aenigmatite also from the lower dyke at Vøra:

$(Na_{1.91}Ca_{0.06}K_{0.03})_{\Sigma 2.00}(Fe^{2+}_{4.07}Fe^{3+}_{0.44}Mn_{0.25}Mg_{0.17}Ca_{0.08})_{\Sigma 5.01}(Ti_{0.89}Fe^{3+}_{0.11})_{\Sigma 1.00}$
$(Si_{5.63}Al_{0.21}Fe^{3+}_{0.16})_{\Sigma 6.00}O_{20}$.

The aenigmatite that forms cores in aegirine is characterised by very high contents of MnO compared to the other variety, and its contents of Fe_2O_3, Al_2O_3, MgO and CaO are lower, whereas the contents of TiO_2 and SiO_2 are slightly elevated. These differences are quite consistent, as can be seen from the individual analytical data in Table 1.

The mean of three analyses of aenigmatite from the upper dyke at Vøra results in the following empirical formula:

$(Na_{1.94}K_{0.04}Ca_{0.02})_{\Sigma 2.00}(Fe^{2+}_{3.88}Fe^{3+}_{0.50}Mn_{0.29}Mg_{0.20}Ca_{0.13})_{\Sigma 5.00}(Ti_{0.94}Fe^{3+}_{0.06})_{\Sigma 1.00}$
$(Si_{5.54}Fe^{3+}_{0.20}Al_{0.26})_{\Sigma 6.00}O_{20}$.

This composition is very close to that of the individual grains of aenigmatite in microcline from the lower dyke at Vøra.

Finally, the empirical formula of aenigmatite from Vindal, based on the mean of three analyses, is:

$(Na_{1.85}Ca_{0.12}K_{0.03})_{\Sigma 2.00}(Fe^{2+}_{3.88}Fe^{3+}_{0.42}Mg_{0.34}Mn_{0.22}Ca_{0.12})_{\Sigma 4.98}Ti_{1.01}$
$(Si_{5.43}Al_{0.30}Fe^{3+}_{0.27})_{\Sigma 6.00}O_{20}$.

Compared to the three formulae of aenigmatite from Vøra reported above, the Vindal mineral has lower Na_2O, MnO and SiO_2, but higher MgO, CaO and Al_2O_3. The relatively high Fe_2O_3 content is comparable to the results for individual grains from the lower Vøra dyke and the upper Vøra dyke sample.

Discussion

The Vøra locality and its minerals have been dealt with by Raade & Larsen (1980), Andersen et al. (1996) and Larsen (2010). Aenigmatite is described as a late-formed, magmatic mineral, roughly contemporaneous with amphiboles and later than the primary generation of aegirine. The thin section examined here, from the lower dyke at Vøra, reveals two generations of aenigmatite with distinct chemical signatures. One of them, occurring as cores in primary aegirine, is probably the oldest and has a remarkably high content of MnO. The results of four electron-microprobe analyses of the coexisting aegirine were published by Larsen & Raade (1997). It has a low content of MnO (0.36 to 0.53 wt%) compared to that of the enclosed aenigmatite, and relatively low contents of CaO (0.51 to 0.60 wt%) and Al_2O_3 (0.55 to 0.63 wt%) compared to most aegirines from syenitic pegmatites in the Larvik plutonic complex (Larsen & Raade 1997). The TiO_2 content is quite high at 1.97 to 2.22 wt%.

The chemical data published by Grew et al. (2008), especially the relatively low MnO and high Al_2O_3 contents, are comparable with the chemistry of the Vindal aenigmatite presented here. Also the analytical data of Åsheim et al. (2008) on the Buer aenigmatite resembles those of Grew et al. (2008). Consequently, it seems safe to conclude that the material studied by them most likely originates from the Vindal-Buer area on Vesterøya.

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Table 1. Electron-microprobe analytical data (wt%) of aenigmatite from Vøra and Vindal, Vesterøya, Larvik plutonic complex.

	Vøra (lower dyke) cores in aegirine				**Vøra (lower dyke)** single grains in microcline			**Vøra (upper dyke)**			**Vindal**		
	VN-1	VN-4	VN2-1	VN2-2	VN-2	VN-3	VN2-3	VO-1	VO-2	VO-3	VIN-1	VIN-2	VIN-3
Na_2O	7.38	7.38	7.24	7.21	7.04	7.02	6.79	7.01	7.05	7.08	6.54	6.74	6.62
K_2O	0.16	0.16	0.18	0.20	0.19	0.15	0.21	0.21	0.18	0.21	0.18	0.16	0.18
MgO	0.21	0.21	0.24	0.24	0.74	0.77	0.86	0.89	0.99	1.00	1.63	1.53	1.64
CaO	0.35	0.35	0.35	0.35	0.95	0.92	0.97	0.98	0.96	1.00	1.66	1.43	1.67
MnO	5.72	5.92	5.20	5.36	2.15	2.07	1.93	2.35	2.40	2.36	1.75	1.86	1.81
FeO	34.06	34.30	34.97	34.77	33.62	34.13	35.04	31.91	33.57	32.30	32.52	32.00	32.57
Fe_2O_3	2.31	1.24	1.35	1.32	7.51	6.52	5.88	8.00	6.86	8.04	5.95	6.95	6.40
Al_2O_3	0.42	0.65	0.43	0.41	1.23	1.25	1.26	1.27	1.18	1.13	1.82	1.66	1.83
SiO_2	41.54	41.78	41.56	41.37	39.52	39.68	39.75	38.30	39.68	38.82	37.81	37.67	38.16
TiO_2	9.68	9.82	9.60	9.76	8.26	8.34	8.36	8.74	8.70	8.88	9.32	9.46	9.25
Sum	101.83	101.81	101.12	100.99	101.21	100.85	101.05	99.66	101.57	100.82	99.18	99.46	100.13
Na	2.012	2.008	1.986	1.981	1.934	1.933	1.869	1.956	1.927	1.952	1.826	1.878	1.831
K	0.029	0.029	0.032	0.036	0.034	0.027	0.038	0.039	0.032	0.038	0.033	0.029	0.033
Mg	0.044	0.044	0.051	0.051	0.156	0.163	0.182	0.191	0.208	0.212	0.350	0.328	0.349
Ca	0.053	0.053	0.053	0.053	0.144	0.140	0.148	0.151	0.145	0.152	0.256	0.220	0.255
Mn	0.681	0.704	0.623	0.643	0.258	0.249	0.232	0.286	0.287	0.284	0.213	0.226	0.219
Fe^{2+}	4.005	4.026	4.138	4.122	3.985	4.054	4.160	3.840	3.958	3.841	3.916	3.847	3.885
Fe^{3+}	0.244	0.131	0.143	0.141	0.801	0.697	0.628	0.866	0.728	0.860	0.645	0.752	0.686
Al	0.070	0.108	0.072	0.068	0.205	0.209	0.211	0.215	0.196	0.189	0.309	0.281	0.308
Si	5.840	5.863	5.880	5.864	5.601	5.637	5.642	5.511	5.595	5.521	5.443	5.415	5.443
Ti	1.024	1.037	1.021	1.041	0.881	0.891	0.892	0.946	0.923	0.950	1.009	1.023	0.992
Sum	14.000	14.000	14.000	14.000	14.000	14.000	14.000	14.000	14.000	14.000	14.000	14.000	14.000