

Aegirine of possible authigenic origin in Middle Devonian sediments in Caithness, Scotland

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SUMMARY. An occurrence of aegirine in Middle Devonian lacustrine beds in Caithness is described. The mineral occurs as euhedral to subhedral prismatic crystals within a finely laminated siltstone. Microprobe analyses reveal a remarkably 'pure' composition consisting almost entirely of Na, Fe³⁺, Si, and O. X-ray diffractometry yielded the unit cell data: a 9.657 Å, b 8.800 Å, c 5.296 Å, and β 107.37°. Comparison with other natural aegirine compositions shows marked differences from those of igneous or metamorphic origin but a close similarity to a unique occurrence of authigenic aegirine in the lacustrine Green River Formation of Wyoming, U.S.A. Consideration of the nature of the Caithness occurrence, and comparison of the Devonian Orcadian basin with the Eocene Green River basin indicate similar geological environments. It is suggested that the mineral formed in hypersaline conditions in which sodium may have been derived from contemporaneous alkaline volcanism within the Orcadian basin.

DURING an examination of strata about the Middle Devonian Achanarras fish bed, Caithness, large (up to 2 cm in length) green prismatic crystals were discovered by one of the authors (U. McL. M.) in fine-grained laminated siltstones and mudstones. During preliminary mineralogical examination they were identified as the soda pyroxene aegirine (NaFeSi₂O₆). Because of this very unusual paragenesis a more detailed mineralogical study was made.

To the authors' knowledge, this is the only recorded occurrence of aegirine within the Caithness Flags. The formation, and indeed the flagstone sequence as a whole, is poorly exposed in inland Caithness and the coastal section is often cliffed and inaccessible. This field investigation formed part of a mineral exploration programme so that there could be no exhaustive study to determine whether other occurrences exist. However, the

sequence has been examined in considerable detail in the search for the famous fish fossils for over 150 years, and also for base metal mineralization. Heddle (1880) recorded remarkably few minerals from Caithness in his study of the geognosy and mineralogy. Detailed petrography of the Achanarras limestone (Rayner, 1963; Donovan *et al.*, 1974) found no authigenic minerals other than calcite and dolomite. Turner (1977) notes the development of authigenic magnetite and complex intergrowth of chrome spinels in the Achanarras limestone, but does not mention aegirine.

The one exposure of the aegirine-bearing strata found to date is in a ditch section near the village of Halkirk, Caithness (National Grid Ref. ND 13 58). An exact locality or map is not given until the outcrop can be protected, but parties interested in research on the material should contact the authors.

Geology. Stratigraphically, the horizon of interest lies about 40 m below the limestone that characterizes the base of the Achanarras-Niantd-Sandwick fish-bed cycle, which has been correlated palaeontologically with the Eifelian/Givetian boundary in the Middle Devonian (Miles and Westoll, 1963). Aegirine occurs as a minor constituent of a 30 to 50 cm thick disturbed bed of dark-grey carbonate-rich silt and fine sand contained between undisturbed beds of finely laminated bituminous siltstone and fine sandstone. All lithologies in the vicinity are dark grey to black, which, with the abundant organic material and pyrite, is indicative of the generally reducing environment of deposition of these lacustrine bottom-sediments. Weathering colours of the rocks in outcrop are dull orange, reflecting the ferroan dolomitic nature of the carbonate cement. Adjacent outcrops weather

pale grey to black and have a calcite cement. Further west, generally lower in the succession, a limited number of loose blocks of dark siltstone containing a thin layer of chert nodules up to 5 cm thick were found. They have not been found in outcrop, but in a similar stratigraphic position in Orkney chert layers are present and form characteristic marker horizons 14 m and 59 m below the base of the Sandwick fish bed (Fannin, 1971). These are of syngenetic origin and are considered to have been produced by precipitation of silica gels.

Before final consolidation of the sediment the aegirine-bearing bed was thrown into tight irregular folds and wrinkles and was fractured. Recementation has caused destruction of the original lamination in part, and the resulting bed is crossed by veinlets and irregular patches of quartz accompanied by minute crystals of ankerite. Also present are disseminated grains of pyrite and elongate vug-like pockets containing white calcite and a black, jelly-like hydrocarbon. No other sodic minerals have been located apart from a small number of minute, detrital grains of albite.

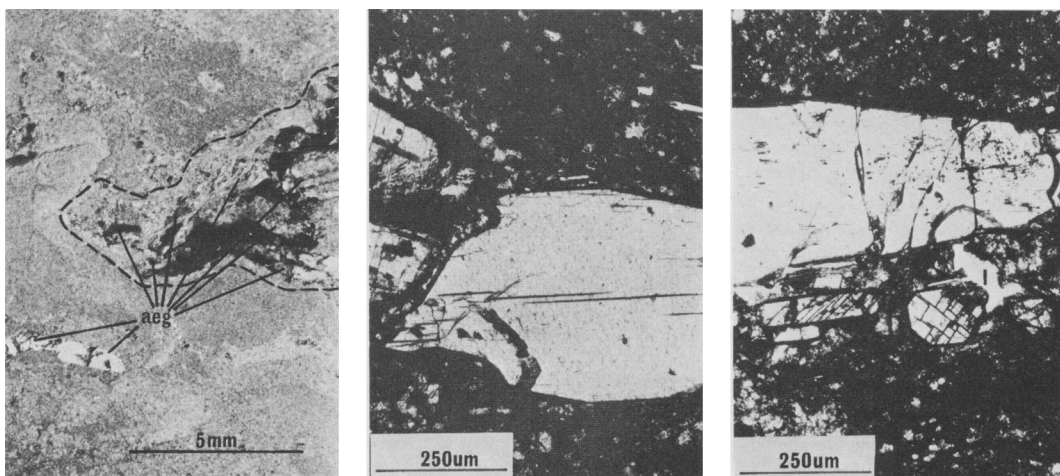
In the Thurso river section through the Achanarras fish-bed cycle and adjacent strata a small number of disturbed horizons are quite well exposed. These appear in part as pseudo-breccias between undisturbed strata. Samples of the material were found to contain fluorite, hydrocarbon, calcite, and baryte, but no aegirine or other sodic phases.

Petrology and mineralogy. The aegirine crystals vary in size, most of the larger ones being of the

order of 3 mm in width and 1 cm long. They are appreciably larger than the grains of the silt to sand grade host material. In many instances they lie parallel to the bedding, often in small groups spread along bedding surfaces. They also occur within small solution cavities (fig. 1) and as individual crystals oriented at large angles to the bedding.

Most of the crystals are notably euhedral, having prismatic forms showing good developments of pinacoid faces and both blunt and sharp-pointed terminations. Several have one or more irregular faces (fig. 2). No intergrowth with the host material has been observed. The crystals vary in colour from leaf green to pale green or colourless. A red coloration is also found, but tends to be centred on limonitic cross fractures and is clearly of secondary formation. Pale-green to colourless zones are frequently bounded internally by surfaces at which occur abrupt transitions to more strongly coloured aegirine. These surfaces do not follow the growth patterns of the mineral, and the weakly coloured zones are believed therefore to be of secondary origin, probably a result of changes in the oxidation state of iron to create an 'acmitic' aegirine as described by Bøggild (1953, p. 273), since no significant compositional difference between the two types of material could be detected (Table II, p. M61). In thin section the mineral is pale green to colourless, sometimes pleochroic to pale pink.

Optical measurements were carried out using a spindle-stage. In view of the high refractive indices involved, McAndrew's (1972) technique was used



FIGS. 1 and 2: FIG. 1 (left). Contorted siltstone in which aegirine prisms (aeg) occur conformably and within an irregular cavity (outlines by dashed line). FIG. 2a (centre). Aegirine prism showing irregular termination, occurring as one of an elongated conformable group of crystals. FIG. 2b (right). Euhedral aegirine crystals of contrasting sizes, occurring within a conformable group of crystals. The light area (1) is a gap in the thin section.

to determine refractive indices in sodium light ($\lambda = 589$ nm) since this method involves a minimum of heating of the volatile high-index immersion liquids. $2V_{\alpha}$ was measured to an estimated error of $\pm 2^{\circ}$ by Joel's (1963) extinction curve method. The results obtained and their estimated errors are: $\alpha = 1.770 \pm 0.002$, $\beta = 1.814 \pm 0.005$, $\gamma = 1.830 \pm 0.005$, $2V_{\alpha} = 61^{\circ} \pm 2^{\circ}$, and $\alpha: [001] = 6^{\circ} \pm 1^{\circ}$. A determination of specific gravity made using a Berman balance gave the result 3.52 ± 0.05 g cm⁻³.

X-ray diffractometer study of a hand-picked concentrate using cobalt radiation (Co- $K_{\alpha 1} = 1.78892$ Å, Co- $K_{\alpha 2} = 1.79021$ Å) and an internal silicon standard (S.R.M. 640 supplied by N.B.S.; $a = 5.43088$ Å) gave d -spacings very close to those reported by Frondel and Klein (1965) for aegirine from the Narsarsuk Complex. By cross-indexing unambiguous reflections the diffraction data were refined using the least-squares programme (BA 1.0) developed by Dr. R. J. Davis of the British Museum (Natural History) to yield: $a = 9.657$ Å, $b = 8.800$ Å, $c = 5.296$ Å, $\beta = 107.37^{\circ}$, $a/b = 1.097$, $c/b = 0.602$; volume of unit cell = 429.64 Å³ and a theoretical density of 3.574 g cm⁻³ (Table I, p. M61).

Ten quantitative analyses for twelve elements were carried out by electron microprobe (analyst J. F. W. Bowles), corrections to the initial data being made by the iterative programme of Mason *et al.* (1969). The results are notably uniform. All are close to an arithmetical average composition of 52.31% SiO₂, 34.32% Fe₂O₃, and 13.96% Na₂O, the only other constituents > 0.01% being MgO (0.6%) and V₂O₃ (0.02%) (Table II, p. M61). Formulae are calculated by the procedure of Yoder and Tilley (1962), the more recent procedure of Cawthorn and Collerson (1974) being found to be unsatisfactory in this case since it produces excesses of Si and Na outside the pyroxene end members.

It may be significant to note that what appears to be the only recorded analysis of aegirine of comparably 'pure' composition (Table III) is quoted by Clarke *et al.* (1969) for aegirine of probably authigenic origin from the Green River Formation (Milton and Eugster, 1959; Bradley, 1964). In contrast, aegirines of the Cnoc nan Cuilean pegmatites in the Ben Loyal Complex (King, 1942) have normal compositions (Table III), and the same applies to igneous and metamorphic aegirines from various sources described by Sabine (1950), Bøggild (1953), Deer *et al.* (1963), and others (Table III, p. M61).

Discussion. Situations in which the sodapyroxenes aegirine and aegirine-augite occur are usually characterized by an association with alkaline igneous or metamorphic rocks. In this case,

however, the sedimentary association and unusual composition of the mineral suggest an uncommon environment of formation.

Aegirine occurs in the suite of sodic authigenic minerals found in the Eocene Green River Formation of Wyoming and Utah, U.S.A. (Milton *et al.*, 1960; Hay, 1963). This formation bears many similarities to the fluvio-lacustrine Devonian sequence of northern Scotland. Even the uraniferous phosphatic horizons of Caithness and Orkney (Michie, 1972) are paralleled by uraniferous horizons in the former area (Love, 1964).

In the Green River Formation the aegirine occurs as prismatic crystals up to a few millimetres in length, found enclosed in shortite and northupite in dolomitic mudstones, which also contain baryto-calcite, analcime, sodic magnesioarfvedsonite, and other authigenic phases (Milton *et al.*, 1960; Milton *et al.*, 1974). Many of these minerals are soluble in water or readily altered with release of sodium, and are recorded only from well cuttings. The Green River beds show features strongly suggestive of alteration of ashes, and this is the genetic model for the origin of the sodic assemblage favoured by Milton *et al.* (1960) and more recently by Surdam and Parker (1972). An origin by alteration of clays as suggested by Keller (1952) for the analcime of the Popo Agie member (Chugwater Formation) of western Wyoming was not supported by these later workers.

During deposition of the Middle Devonian sequence of Caithness the Orcadian basin was a warm, semi-arid, land-locked region containing shallow and somewhat ephemeral lakes (Crampton and Carruthers, 1914). Algal stromatolites are found preserved in dense ferroan dolomites in marginal environments (Fannin, 1969). Such dolomitization in recent sediments is associated with hypersaline conditions (Logan, 1961). It can thus be suggested that evaporitic concentration in the basin led to the development of locally hypersaline conditions marked by dolomitization. Where reactive phases such as volcanogenic crystals, glasses, and gels were present, reactions could have led to formation of authigenic minerals (Surdam and Eugster, 1976).

There is little evidence of Middle Devonian volcanism in Caithness, except for thin (1–2 cm) tuffaceous horizons present within the Achanarras fish-bed cycle of the Thurso River section near the site of the aegirine occurrence and at Niandt on the coast. In Orkney and Shetland, however, alkaline volcanism is evidenced at several horizons including thin tuffs in the Sandwick fish bed (Fannin, 1971). It is thus likely that appreciable quantities of volcanic material rich in sodium would have been available to the basin during this time.

It is concluded that an authigenic origin is compatible with the mineralogy and geology of the occurrence. One objection to this would seem to be the absence from the limited outcrop examined of other more typically authigenic phases. This could be in part a result of the low solubility of aegirine if it be proposed that the changes in the circulation and salinity of waters within the basin in late Middle Devonian times led to re-solution of zeolites and sodic salts.

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Fortey and Michie: Authigenic aegirine (Appendix) M61

Table I

X-ray powder data for aegirine SXR 4205, together with (A) calculated data for synthetic aegirine (Nolan and Edgar, 1963) and (B) calculated data for aegirine from the Narvaasak Complex (Frondel and Klein, 1965).

Halkirk SXR 4205					Halkirk SXR 4205				
A		B		hkl (1)	A		B		
d _{obs} (Å)	d _{calc} (Å)	d _{calc} (Å)	d _{calc} (Å)		d _{obs} (Å)	d _{calc} (Å)	d _{calc} (Å)	d _{calc} (Å)	
6.398	6.365	6.36	6.364	110	1.6590	1.6594	-	1.6585	
4.414	4.428	4.40	4.400	111	1.6346	1.6349	-	223	
3.618	3.612	3.610	3.608	111	1.6116	1.6105	1.610	531	
3.185	3.183	3.181	3.182	220	1.5909	1.5912	1.591	440	
2.989	2.985	2.985	2.985	221	1.5360	1.5362	-	1.5356	
2.903	2.901	2.900	2.900	310	1.5327	1.5311	-	1.5313	
	2.892	2.893	2.893	311					
2.7980	2.7952	-	2.7954	130	1.5267	1.5272	-	1.526	
						1.5259		1.5271	
2.5460	2.5456	2.545	2.5455	131	1.4668	1.4667	-	1.4668	
	2.5350		2.5327	112					
2.5280	2.5273	2.526	2.5240	002	1.3948	1.3976	1.394	260	
						1.3952		531	
2.4728	2.4731	2.458	2.4730	220	1.3281	1.3282	-	712	
2.2561	2.2563	-	2.2540	311	1.2995	1.2995	-	551	
2.1986	2.1986	-	2.2002	040	1.2679	1.2685	-	062	
						1.2675		225	
2.1931	2.1915	2.197	2.1956	112	1.2282	1.2289	-	352	
2.1205	2.1216	2.118	2.1213	330	1.1657	9.657	9.658	9.657	
	2.1183		2.1185	331					
2.0955	2.0949	2.095	2.0950	421	1.1657	8.800	8.795	8.801	
2.0168	2.0172	-	2.0169	041	1.1657	5.296	5.294	5.291	
1.9342	1.9345	-	1.9350	241	cell vol. (Å ³)	429.5	429.1	429.0	
1.8824	1.8822	-	1.8823	511	calc density (g/cm ³)	3.574	3.577	-	
1.8035	1.8043	-	1.8036	510					
1.7283	1.7288	1.728	1.7289	130					

(1) In the calculations of the final results only unambiguously indexed observed d-spacings were used. These are underlined in the (hkl) column.

Table III

Comparison of the averaged microprobe analyses of aegirine from SXR 4305 (1 and 7) with published analyses of aegirines and aegirine-augites from (2) the Assynt Complex (Sabine, 1950), (3) the Ben Loyal Complex (King, 1942), (4) Glen Lui (MacLachlan, 1951), (5) Narvaasak (Seggild, 1953), (6) Kamperdarsak (Seggild, 1953) and (8) the Green River Formation (moll-prop's only; Clarke, Applen and Papicke, 1969).

	1	2	3	4	5	6
SiO ₂	52.31	51.35	51.40	51.68	51.54	51.66
TiO ₂	0.00	0.65	0.01	1.59	0.09	1.60
Al ₂ O ₃	0.00	2.88	1.67	1.28	0.93	1.16
Fe ₂ O ₃	34.32*	25.43	4.32	19.10	8.21	29.23
FeO	-	3.70	8.10	5.17	6.86	1.61
MnO	0.01	0.18	0.27	0.45	0.30	0.72
MgO	0.06	0.58	10.60	4.29	9.10	0.25
CaO	0.00	3.29	21.98	9.56	19.04	1.30
Na ₂ O	13.96	11.65	1.47	7.25	3.43	11.93
K ₂ O	0.01	0.14	tr	n.d.	0.02	0.16
V ₂ O ₅	0.02	0.02	-	-	-	-
ZrO ₂	0.00	nd	-	-	-	-
H ₂ O ^δ	-	0.24	0.29	0.05	0.34	0.26
H ₂ O ^h	-	0.09	-	0.05	0.06	0.01
H ₂ O ^g	-	-	-	nd	0.01	0.01
Total	100.69	100.20	100.11	100.47	99.99	99.98

*Total Fe expressed as Fe₂O₃

	7	8
Si	2.00	2.00
Ti	0.00	
Al	0.00	0.01
Fe	0.99	0.99
Cr	<0.01	nd
Mn	<0.01	nd
Mg	<0.01	0.01
Ca	0.00	nd
Na	1.03	0.95
K	<0.01	nd
V	0.01	
ZM	2.02	1.96

Table II

Microprobe analyses of aegirine in specimen SXR 4205 (analyst J F W Bowles)

Wt %	Grain 1					Grain 2					Average
	1	2	3	4	5	6	7	8	9	10	
SiO ₂	52.90	52.76	52.11	52.63	52.53	52.72	52.20	52.06	51.44	51.79	52.31
TiO ₂	nd	nd	nd	nd	nd	nd	nd	0.01	nd	nd	0.00
Al ₂ O ₃	nd	nd	nd	nd	nd	nd	nd	0.01	0.01	0.01	0.00
Fe ₂ O ₃	34.26	34.34	34.40	34.23	34.27	34.28	34.31	34.41	34.44	34.25	34.32
FeO	0.01	0.02	0.01	nd	0.01	0.01	0.01	0.01	0.02	0.01	0.01
MnO	nd	0.01	0.01	0.01	0.01	nd	nd	nd	0.01	0.01	0.01
MgO	0.09	0.04	0.02	0.04	0.04	0.05	0.10	0.03	0.06	0.12	0.06
CaO	nd	0.01	0.01	nd	0.01	nd	nd	nd	nd	nd	0.00
Na ₂ O	13.77	13.93	13.89	13.88	14.01	13.99	14.08	14.02	14.00	14.03	13.96
K ₂ O	nd	0.01	0.01	0.01	nd	nd	nd	0.01	0.01	0.01	0.01
V ₂ O ₅	0.04	0.02	0.01	0.03	0.01	0.03	0.04	0.01	0.01	0.03	0.02
ZrO ₂	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.00
Total	101.07	101.64	100.47	100.83	100.89	100.08	100.74	100.55	99.99	100.26	100.70
Mol. prop's											
Si	2.009	2.005	1.997	2.006	2.002	2.004	1.995	1.994	1.985	1.991	1.999
Ti	-	-	-	-	-	-	-	-	-	-	-
Al	-	-	-	-	-	-	-	-	-	-	-
Fe ³⁺	0.979	0.982	0.992	0.981	0.983	0.981	0.987	0.992	1.000	0.991	0.987
Fe ²⁺	0.001	0.001	0.001	-	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Mn	-	-	-	-	-	-	-	-	-	-	-
Mg	0.005	0.002	0.001	0.002	0.002	0.003	0.006	0.002	0.004	0.007	0.003
Ca	-	0.001	0.001	-	0.001	-	-	-	-	-	-
Na	1.014	1.027	1.032	1.025	1.035	1.031	1.044	1.041	1.048	1.046	1.034
K	-	-	-	-	-	-	-	-	-	0.001	-
V	0.001	0.001	-	0.001	-	0.001	0.001	-	-	0.001	0.001
Total cations	4.009	4.019	4.024	4.015	4.024	4.021	4.014	4.030	4.038	4.038	4.025
X ¹	1.019	1.030	1.034	1.027	1.038	1.034	1.050	1.043	1.052	1.054	1.037
Y ¹	0.981	0.984	0.995	0.982	0.984	0.983	0.989	0.993	1.001	0.993	0.989
Z ¹	2.009	2.005	1.997	2.006	2.002	2.004	1.995	1.994	1.985	1.991	1.999

* - Total Fe expressed as Fe₂O₃

1 - Formulae calculated by the procedure of Yoder and Tilley (1962)