

A note on some Dalradian stilpnomelanes and their oxidation

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SUMMARY. The widespread ferristilpnomelane in Dalradian metabasites of the south-west Scottish Highlands has usually formed by secondary oxidation of primary ferrostilpnomelane, probably during weathering. Ferrostilpnomelane oxidizes readily in polished thin sections open to the atmosphere over a period of months, and microprobe examination of the resulting ferristilpnomelane suggests a change in the role of potassium in the structure during oxidation.

THE presence of ferristilpnomelane² in the south-west Highland Dalradian was first positively recognized by Wiseman (1934) from a 'keratophyre schist' near Carsaig (fig. 1) (but see also Flett in Peach *et al.*, 1911, p. 77), and subsequently reported in metabasites ('epidiorites') from Castle Sween, Knapdale (Hutton, 1938), from Craignish (Knill, 1960), and from the Loch Awe area (Borradaile, personal communication). Elsewhere in the Dalradian, Mather and Atherton (1965) and Mather (1970) record both ferrostilpnomelane and ferristilpnomelane in lower greenschist facies greywackes of the Upper Dalradian of the Aberfoyle and Dunkeld areas (fig. 1) of the Highland Border, but stilpnomelane has not been recorded in the central, eastern, or north-east Highlands.

Study of Dalradian metabasites (Graham, 1973) has revealed the extensive occurrence of ferristilpnomelane and rare occurrence of ferrostilpnomelane in a variety of greenschist facies metabasites of Tayvallich, Knapdale, and south-east Islay (fig. 1, this study; Graham, 1973, 1974, fig. 2). This note describes the texture and chemistry of these stilpnomelanes, and outlines evidence regarding their present and original oxidation states.

Petrography

Ferrostilpnomelane. The reduced variety, ferrostilpnomelane, has been found in only two metabasites, both from a fresh road-cut near Crinan (fig. 1, this study; detailed location and mode of specimen 25104 in Graham, 1974). In these unfoliated metagabbros, stilpnomelane occurs in plates, fibres, and sheaves intergrown with or enclosed in amphibole porphyroblasts and patches of chlorite, or penetrating plagioclase laths. The stilpnomelane is abundant, the plates and fibres often coarse, and the grain boundaries sharp; there is no indication that ferrostilpnomelane replaces another phase, and the intergrowths clearly show it to belong to the primary metamorphic assemblage.

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² Nomenclature of the stilpnomelane group used here is that followed by Eggleton (1972, p. 693).

Ferristilpnomelane occurs in nonschistose metagabbros from the same road-cut as specimen 25104, and in a variety of other metabasites of the Knapdale-Tayvallich area, all of similar paragenesis and texture to 25104 (e.g., specimen 25035, location and mode in Graham, 1974). In schistose metabasites (typically chlorite + quartz + plagioclase + calcite + sphene, \pm minor or accessory epidote, biotite, or muscovite), ferristilpnomelane plates tend to lie parallel to the primary fabric, although some lie

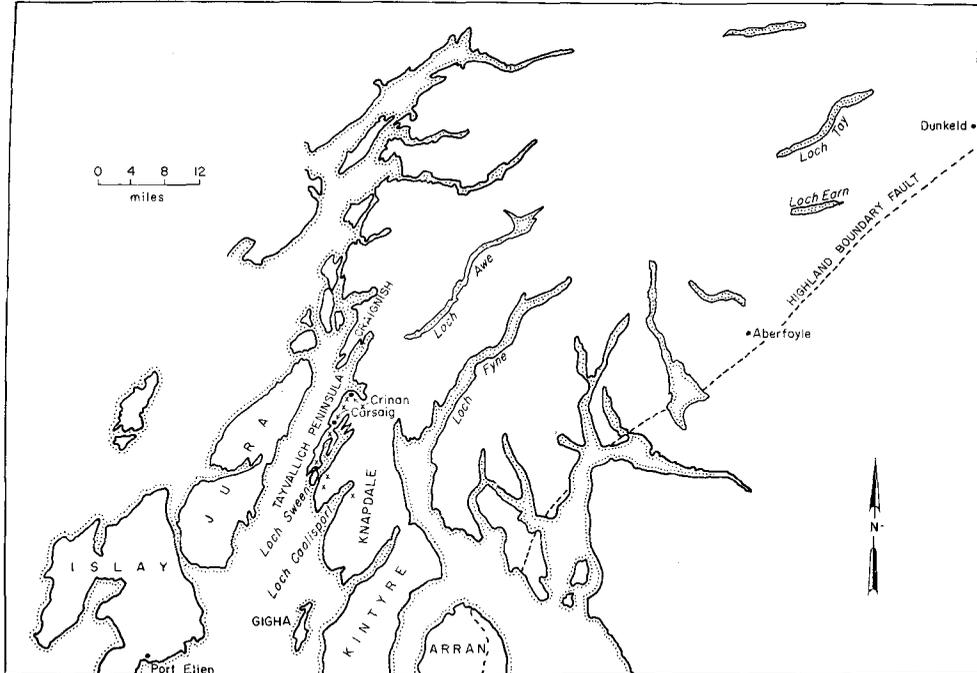


FIG. 1. Map of central and south-west Scottish Highlands showing localities and areas of stilpnomelane occurrence (see text). Stilpnomelane in metabasites of Knapdale and Tayvallich (indicated by X).

across the fabric in radiating sprays or clusters. Brown (1971) has observed that the line of intersection of such clusters of plates generally parallels the prevailing schistosity or lineation.

Mather (1970) has concluded that stilpnomelane textures in low-grade greywackes of the south Highlands, in which stilpnomelane growth bears no relation to rock cleavage, indicate its growth during some late metamorphic event postdating the original prograde metamorphism. However, there is no evidence in the schistose south-west Highland metabasites to suggest that stilpnomelane replaces or is mimetic after chlorite or other phases, or is anything other than an integral and equilibrium member of the primary metamorphic assemblage.

Knill (1960) concluded that stilpnomelane crystallization in the Dalradian schists of Craignish (fig. 1) belongs to the main phase of greenschist-facies crystallization, post-

dating the regional primary slaty cleavage, but predating formation of an early strain-slip cleavage.

Relative stability of ferro- and ferristilpnomelane

A variety of evidence indicates that ferrostilpnomelane rather than ferristilpnomelane was the stable primary metamorphic phase in at least some of the greenschist facies metabasites of the Knapdale area:

Ferrostilpnomelane may show alteration to mud-brown ferristilpnomelane at grain margins and along fractures.

Ferrostilpnomelane- and ferristilpnomelane-bearing metagabbros (e.g. 25104) of otherwise identical mineralogy occur within the same outcrop at Crinan.

Thin sections of fresh ferrostilpnomelane-bearing (essentially ferristilpnomelane-free) metagabbro (25104) revealed partial oxidation of ferrostilpnomelane to mud-brown ferristilpnomelane over a period of 18 months, while the original green ferrostilpnomelane in uncovered, polished sections showed complete alteration and oxidation over the same period (with preservation of the original fabric and texture).

The above evidence is clearly consistent with a secondary origin for ferristilpnomelane through oxidation of primary ferrostilpnomelane in at least some of the south-west Highland metabasites. Other workers have reached similar conclusions for other occurrences of ferristilpnomelane (e.g. Hutton, 1938; Zen, 1960; Brown, 1967), alteration and oxidation occurring probably during weathering (Robinson, 1969; Brown, 1971) through the agency of circulating groundwater, and perhaps also during retrogressive metamorphism or hydrothermal alteration. There is, however, no direct textural or field evidence of any pervasive effect of these latter factors in the Tayvallich-Knapdale area.

The third observation (above) indicates the ease of oxidation of ferrostilpnomelane under atmospheric conditions, without the aid of circulating groundwater, and the preservation of ferrostilpnomelane in 25104 is doubtless attributable to its occurrence in a fresh road-cut. However, experimental data of Nitsch (1970) have demonstrated the stability of highly oxidized ferristilpnomelane at high f_{O_2} (defined by hematite-magnetite) under greenschist facies P - T conditions.

Microprobe analyses of stilpnomelane

Stilpnomelanes were analysed in polished thin section with Cambridge Instruments 'Geoscan' and 'Microscan' electron microprobes, using analysed silicates, pure metals, and stoichiometric oxides as standards, and following methods and correction procedures of Sweatman and Long (1969). The microprobe permits determination only of total iron, here expressed as FeO (Table I).

Problems were encountered in measuring potassium, which in the ferristilpnomelane may show extensive small-scale variation in concentration from point to point and grain to grain. The ferristilpnomelanes of 25104 (Table I), oxidized from primary ferrostilpnomelane, show increasing potassium count rates with time (fig. 2) for any one point within a stilpnomelane plate, while count rates for other major elements remain constant with time at any point. This observation is true *only* of ferristilpnomelane

TABLE I. *Chemical analyses and pleochroism of south-west Highland stilpnomelanes*

	25104* ferrostilpnomelane Crinan‡	25104† ferristilpnomelane Crinan‡	25035 ferristilpnomelane Carsaig‡	25150 ferristilpnomelane Port Ellen, Islay
SiO ₂	46.7	46.0	43.9	46.0
TiO ₂	tr	tr	n.f.	0.5
Al ₂ O ₃	6.0	5.9	7.1	6.2
FeO§	27.7	26.6	28.2	27.8
MnO	0.6	0.5	0.8	0.7
MgO	6.7	6.8	7.6	6.4
CaO	0.2	0.1	0.1	0.2
Na ₂ O	0.5	0.5	0.3	0.5
K ₂ O	3.6	3.2	1.0	2.1
Total	92.0	89.6	89.0	90.4
$\beta \approx \gamma$	apple green	dark brown	dark red-brown	deep red-brown
α	colourless	pale tan	golden yellow	gold

* Analysed August 1971 (before oxidation); average of 2 grains.

† Analysed January 1974 (after oxidation); average of 5 grains..

‡ See Graham (1974, fig. 1) for locality map.

§ Total Fe expressed as FeO.

|| Anhydrous total.

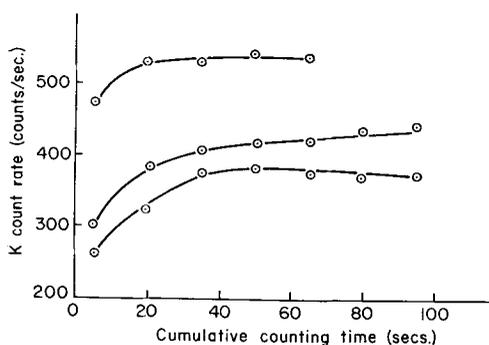


FIG. 2. Typical plots of microprobe count rate for potassium (counts per second averaged over 10 second counts, with 5 second intervals between counts) against cumulative or total counting time, for 3 individual points in ferristilpnomelane grains of 25104 (see text). De-focused beam, 20 kV accelerating voltage.

25104, and persists despite defocusing of the probe beam. While the average K₂O content of ferristilpnomelanes in 25104 is scarcely lower than that of the parent ferrostilpnomelane (Table I), individual points show a wide range of K₂O-contents from 2 to over 5 wt. %.

These observations on 25104 are perhaps explained by the 'boiling off' by the electron beam of 'zeolitic' water within the cavities in the tetrahedral sheet of the stilpnomelane structure (Eggleton, 1972), and the diffusion of potassium from the surrounding material into the volume of stilpnomelane excited by the beam.

Role of potassium in stilpnomelane and in its oxidation

Early studies of stilpnomelane structure suggested a talc-like (Gruner, 1937, 1944) or chlorite-like (Hutton, 1938) layered structure, in which K⁺ ions were located in loosely bound interlayer sheets (Gruner, 1944). Eggleton's (1972) recent elucidation

of the structure implies that K^+ (and Na^+ , Ca^{2+} , H^+) may be located in interlayer sites where it may balance tetrahedral charge deficiency caused by substitution of Al for Si. Alternatively K may perhaps occupy sites within the cavities in the tetrahedral sheet itself.

Stilpnomelane data presented here (ferristilpnomelane 25104 excepted) and by Brown (1971) indicate distinct differences in K_2O between ferro- and ferri-stilpnomelanes consistent with leaching of K during oxidation and weathering. No other conspicuous chemical differences are evident. Such a trend is less than clear in stilpnomelane data compiled by Eggleton (1972, Table IVa) (where K_2O -contents of ferristilpnomelanes may commonly exceed 2 wt. %), although high K_2O concentrations exceeding 4 or 5 wt. % are restricted to the ferrostilpnomelane group, in which Eggleton (personal communication) has noted a rough inverse correlation of potassium content and oxidation ratio.

Although average K_2O in 25104 remained fairly constant during oxidation to ferristilpnomelane, the role of K in the structure clearly changed so that, when the ferristilpnomelane was excited by the electron beam, K was able to diffuse rapidly through the structure, probably via cavities in the tetrahedral sheet after the manner of the 'zeolitic' water (Eggleton, 1972).

Eggleton (1972) shows that oxidation may proceed at the expense of octahedral hydrogen, generating water within the tetrahedral-sheet cavities; e.g. $4Fe^{2+} + 4OH^- + O_2 \rightarrow 4Fe^{3+} + 4O^{2-} + 2H_2O$. The process may perhaps proceed alternatively through release of K^+ to balance excess charge in the octahedral sheet on oxidation of Fe^{2+} to Fe^{3+} . Subsequent loss of potassium from the structure will obviously depend on the chemical environment of oxidation and on the presence of circulating groundwater, the absence of which has prevented removal from ferristilpnomelane 25104 of any K released during oxidation.

While H_2O contents and oxidation ratios of the stilpnomelanes have not been measured (Table I), ferrostilpnomelane 25104 has a significantly higher anhydrous total than the ferristilpnomelanes. The lower ferristilpnomelane totals may be attributed not only to the fact that their Fe_2O_3 content has been calculated as FeO, but perhaps also to increased 'zeolitic' or interlayer water as (OH) decreases during oxidation. Clearly both the above oxidation processes may have proceeded synchronously during oxidation of the stilpnomelane in 25104, and in turn the additional 'zeolitic' water in the tetrahedral sheets (and interlayer sites) may enhance the instability of K in these sites.

It is not clear to what extent potassium is an essential constituent of highly oxidized ferristilpnomelane, though it appears to be essential to the formation of the ferrostilpnomelanes (cf. Brown, 1971, p. 283).

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