Contribution to the study of ore minerals in some igneous rocks from Assynt.

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Summary. The parageneses of opaque minerals in three Assynt rocks are described. A biotite-diorite dyke-rock of Lewisian age is characterized by a primary igneous assemblage of Fe–Ti oxides, pyrrhotine, and pentlandite. Effects of metamorphism are recognized, particularly in the oxidation of ilmenite in a Lewisian epidiorite dyke-rock. Cromaltite contains a primary assemblage of oxide minerals together with a later hydrothermal sulphide assemblage. Evidence from the opaque minerals cannot be reconciled with a theory of limestone assimilation. The correlation of the distribution of Co, Ni, and Cu in the rocks with the opaque minerals present is considered.

THE following account is presented as a supplement to the existing descriptions of a few selected and well-known rock-types in the Assynt district. It has been customary to discuss the opaque minerals as 'accessory ore minerals', although in the rocks selected they amount to an appreciable proportion of the minerals present. Study of the opaque minerals in the rocks selected has provided some interesting data regarding petrogenesis.

Three rock-types have proved of particular interest: epidiorite from Allt a Mhuilinn; biotite-diorite as described by Teall (1907) from Loch Bad nam Ban, Lochinver; and cromaltite from Ledmore, Assynt. The first two rocks occur as dykes in the Lewisian. The epidiorite is older than the biotite-diorite, and has been subject to metamorphism.

The *epidiorite* has been metamorphosed to a considerable extent. Originally a dolerite, the ferromagnesian constituents in the rock have been altered almost completely into hornblende. The main constituents are now hornblende associated with plagioclase.

The ore paragenesis has been affected by the alterations in an impressive way.

A typical feature of the primary ore content of the epidiorite is the scarcity of ilmenite exsolution lamellae in the magnetite. The magnetite grains are martitized, mainly in an irregular way. The alteration into hematite proceeds from the rim of the grains and from cracks, and only rarely follows the more usual {111} directions (fig. 9). At high magnification (× 500) a fine pattern of unmixing lamellae is seen to be arranged parallel to {100}. This feature possibly corresponds to what Ramdohr (1953) describes as original ulvöspinel dissolved out of magnetite. The presence of ulvöspinel would indicate an excess of FeO in the original magnetite.

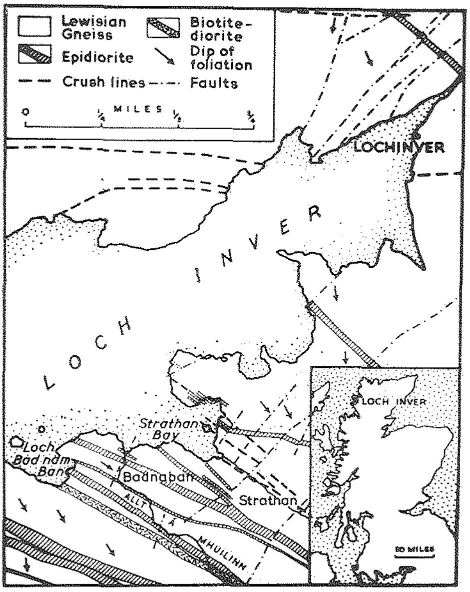


FIG. 1: Geological sketch-map of the dykes on the south shore of Lochinver (after Macgregor and Phemister).

Ilmenite follows magnetite in quantity and frequently is associated with the latter. To a large extent ilmenite has been affected by the alteration which has taken the form of oxidation according to the following reaction:

$$2\,FeTiO_3 + O \rightarrow Fe_2O_3 + 2\,TiO_2.$$

The products of this reaction are fine-grained, mostly symplektic intergrowths of rutile and hematite as illustrated in fig. 9. The grain size of the intergrowth may vary considerably and irregularly within a single grain. It is doubtful in such cases whether the variable coarseness of the rutile–hematite intergrowths can be simply correlated with the temperature of formation. Ramdohr (1940) has emphasized that alteration of this type is frequently a product of metamorphism.

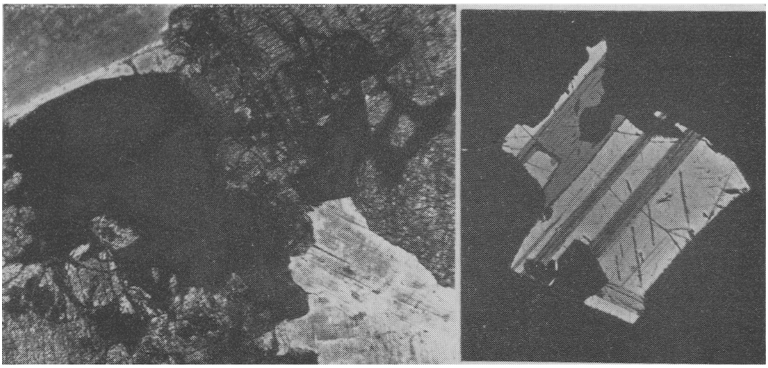
Occasionally the optical orientation of the ilmenite has been taken over by the intergrowth so that all the hematite in a single altered grain shows simultaneous extinction. In grains that are made up of both ilmenite and magnetite, the much lower resistance of the former to decomposition is clearly demonstrated. The magnetite that has survived alteration forms thin lamellae parallel to {0001} in certain ilmenites ('magnetoilmenites'), as illustrated by fig. 10. These lamellae are products of early unmixing, which took place in ilmenites containing both Fe_2O_3 and FeO in excess.

Amongst sulphide minerals only pyrite need be mentioned, occurring in irregular aggregates. In addition very minute grains of pyrite are frequently accumulated along grain boundaries. The latter especially seem to represent a very late formation, possibly due to hydrothermal activity. The comparison of biotite-diorite and epidiorite shows the extent to which alteration affects not only the transparent, but also the opaque minerals.

Biotite-diorite. This rock belongs to a system of dykes that have a NW.–SE. trend and cut Lewisian orthogneisses on the south shore of Lochinver. The emplacement of the biotite-diorite took place during Lewisian times. In hand-specimen the diorite is dark green to black, with many specks of sulphide ore visible macroscopically. In thin sections (fig. 2) the rock is made up of olivine, augite, and biotite, enclosed by plagioclase. The composition of the plagioclase was determined as An_{40}. The texture is distinctly poikilitic. The olivine frequently shows corona structure. All stages of alteration of the augite into hornblende can be observed. If this process proceeds to completion, hornblende and plagioclase remain the main constituents of the rock.

The main features of ore paragenesis are apparent at low magnification. The basic character of the rock is underlined by the occurrence of titanomagnetite. which is the dominant ore mineral and occurs occasionally as euhedral crystals, but mostly in typical skeletal forms filling interstices between the silicate minerals. It has obviously been formed after the crystallization of most silicates. The common distribution of titanomagnetite in this position within the crystallization sequence of coarse-grained igneous rocks has been stressed by Ramdohr (1940). The sizes of the titanomagnetite grains range mostly between 0·1 and

0·4 mm., but in some cases reach 1 mm. The comparatively high Ti-content in the titanomagnetite has to a certain extent been unmixed as ilmenite lamellae. These lamellae occur partly in the well-known arrangement transecting the whole grain in a pattern parallel to {111} of the magnetite (fig. 3). In some instances the ilmenite forms broad, patchy lamellae with rounded boundaries. This type of unmixing is rather rare and its genetical significance is not yet fully understood.



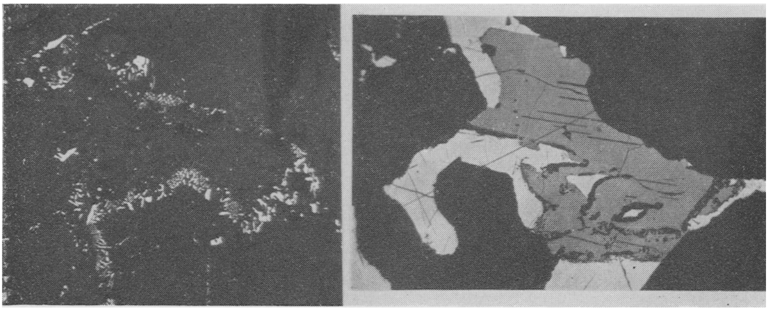
FIGS. 2 and 3: FIG. 2 (*left*). Biotite-diorite, Loch Bad nam Ban. Olivine, augite, biotite, iron ore, plagioclase. ×20. FIG. 3 (*right*). Biotite-diorite, Loch Bad nam Ban. Magnetite (light grey) with unmixing lamellae of ilmenite (medium to dark grey, reflection pleochroism) $\parallel$ (111) and small exsolution bodies of spinel $\parallel$ (100). Oil immersion, reflected light. ×250.

Patterns of spinel (mainly hercynite) exsolution are to be observed in many magnetites (fig. 3). A noteworthy feature of some grains of titanomagnetite is a distinct anomalous anisotropy under crossed nicols. In plain polarized light the reflectivity is normal. According to Ramdohr (1960), who was the first to observe this feature, it is due to formation of 'abnormal mixed crystals'.

Magnetite of later origin also occurs in rims around olivine. Hornblende has formed from olivine and contains magnetite in very fine-grained symplektic intergrowths (fig. 4). The structure of this intergrowth is often obscured in thin-section because of its extremely fine nature. The magnetite thus formed may in many cases continue into surrounding biotite.

Friedrich (1955) has described similar symplektic intergrowths from a gabbro–diorite in the Melibocus area, Odenwald, Germany. They have to be explained as synantetic rims in the sense of Sederholm (1916), not as eutectic, unmixing, or replacement structures. Similar intergrowths of magnetite with augite have been observed also.

Ilmenite is closely associated with magnetite and forms typical lamellae of varying widths parallel to {111} of the magnetite. Very small, partly rounded grains of spinel are frequently concentrated along bigger ilmenite lamellae. In smaller amounts, ilmenite occurs as independent grains or irregularly intergrown with magnetite. Subordinate amounts of ilmenite participate in the formation of oxide–silicate symplektites.



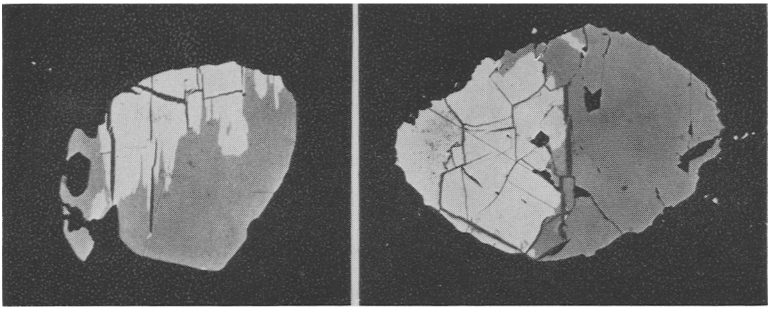
FIGS. 4 and 5: FIG. 4 (*left*). Biotite-diorite, Loch Bad nam Ban. Magnetite (white) forms graphic intergrowths with hornblende around olivine (dark grey). Reflected light, oil immersion. ×160. FIG. 5 (*right*). Biotite-diorite, Loch Bad nam Ban. Ilmenite (medium grey) forms graphic intergrowth with silicates (dark grey); magnetite (light grey) in irregular patches. Reflected light, oil immersion. ×140.

A rare, but interesting, feature is graphic intergrowths of ilmenite and silicate minerals, ilmenite constituting the host mineral (fig. 5). Newhouse (1936) records a similar observation from a diabase near Bechtoldsville, Pennsylvania.

The single grains of ilmenite seem to have formed shortly before the magnetite, as shown, for instance, in fig. 5. Similar age relations have been observed by Ramdohr (1940) in a great variety of coarse-grained igneous rocks. This statement does not, of course, apply to the unmixing lamellae of ilmenite. The general evidence that both ore minerals form after the main silicate crystallization is not affected by this observation.

Ilmenites that show unmixing of hematite parallel to {0001} are present in small amounts. The exsolution takes place in thin lamellae. In many coarse-grained igneous rocks this type is much more common.

Pyrrhotine is, after magnetite and ilmenite, the most widespread ore mineral. It mostly occurs in more or less rounded grains (globules) of up to 0·02 mm. diameter. Big grains, which contain other sulphides as well, may reach 1 mm. diameter. The appearance of pyrrhotine is distinctly different from that of the oxide ores. These globules represent original immiscible droplets of sulphide liquid as described by Newhouse (1936).



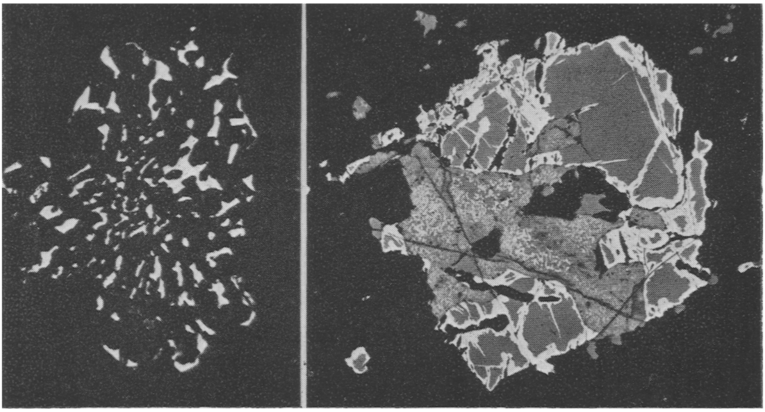
FIGS. 6 and 7: FIG. 6 (*left*). Biotite-diorite, Loch Bad nam Ban. Pyrrhotine (medium grey) and typical 'flame-like' bodies of pentlandite, which prefer basal directions of the pyrrhotine. Reflected light, oil immersion. ×230. FIG. 7 (*right*). Biotite-diorite, Loch Bad nam Ban. Pyrrhotine (medium grey), pentlandite (white, excellent cleavage) || (111), and chalcopyrite (light grey, soft). Reflected light, oil immersion. ×160.

Pentlandite occurs as typical 'flames' (fig. 6) in many pyrrhotines, or associated with pyrrhotine as relatively large grains with pronounced cleavage. A typical assemblage is illustrated in fig. 7.

Finally, chalcopyrite should be mentioned, which frequently is to be seen together with pyrrhotine–pentlandite intergrowths. Chalcopyrite is quantitatively insignificant.

The participation of both pyrrhotine and pentlandite in the formation of sulphide–silicate intergrowths, as shown in fig. 8, is most unusual. This type of pyrrhotine occurrence is not mentioned in the excellent account by Newhouse (1936), nor is the graphic intergrowth of pyrrhotine and pentlandite with silicates recorded by Ramdohr (1945) in his comprehensive survey of 'myrmekite'.

Cromaltite is a melanite pyroxenite of unusual character, which occurs as a small dyke in ledmorite (= melanite-malignite) near Bad na h'Achlaise, Ledmore, Assynt. Both the cromaltite and ledmorite are genetically related to the post-Cambrian Loch Borolan Alkaline Complex and were described by Shand (1930, 1939). Cromaltite occupies an important place in petrological literature because of controversy regarding limestone syntexis in relation to the origin of alkali rocks. In hand-specimen the rock is dark green, coarse-grained and cut by many carbonate veins. Pyroxene, melanite, and biotite are the main constituents, intergrown with one another and accompanied by ore and apatite as accessory minerals. Fig. 11 shows a typical section of cromaltite. An unusually high content of lime reported in old analyses is mainly to be related to the carbonates, which replace the silicates.

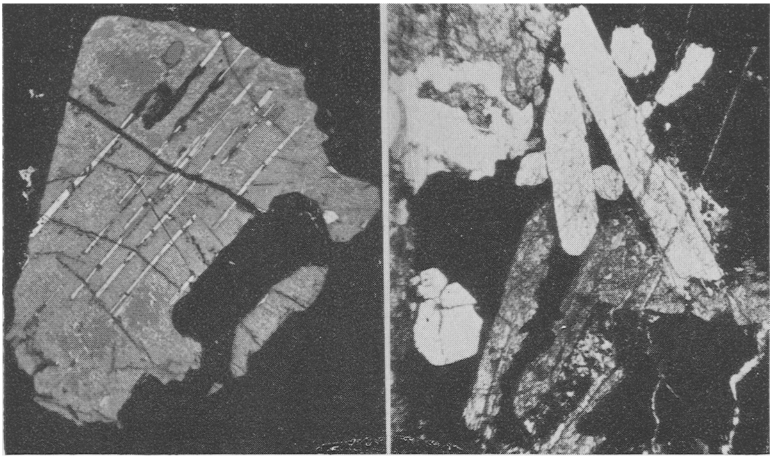


FIGS. 8 and 9: FIG. 8 (*left*). Biotite-diorite, Loch Bad nam Ban. Pyrrhotine (light grey) and pentlandite (white) in graphic intergrowth with silicate mineral. Reflected light, oil immersion. × 160. FIG. 9 (*right*). Epidiorite, Allt a Mhuilinn. Magnetite (medium grey) changed into hematite along cracks and grain boundaries; ilmenite has been decomposed to form a fine-grained graphic intergrowth of rutile and hematite. Reflected light, oil immersion. × 160.

Typical features of the ore paragenesis are the dominance of ilmenite-poor titanomagnetite, the widespread occurrence of pyrite and chalcopyrite, and the small amounts of bornite, covelline, and linnaeite.

Magnetite occurs in two generations: big grains with a diameter of about 1 mm., and smaller individuals of 0·1–0·5 mm. diameter. The latter are frequently completely decomposed to form leucoxene. The bigger magnetites are distinctly rounded and suggest the possibility of magmatic corrosion, and hence of the relatively early formation of magnetite. Exsolution of spinel (hercynite) is widespread, parallel to $\{111\}$ in typical patterns. Intense cataclasis that has affected the rock as a whole has resulted in fracturing many of the magnetite grains, thus providing channels for martitization.

Rutile is a further decomposition product of magnetite and often surrounds the latter in rings of well-developed crystals, as well as in irregular zones. This feature shows clearly in both thin and polished sections.



Figs. 10 and 11: Fig. 10 (*left*). Epidiorite, Allt a Mhuilinn. Ilmenite with (partly oxidized) unmixing lamellae of magnetite ∥ (0001) ('magnetoilmenite'). The ilmenite is, to a considerable extent, changed into a graphic intergrowth of rutile and hematite. Reflected light, oil immersion. ×160. Fig. 11 (*right*). Cromaltite, Bad na h'Achlaise. Typical section, melanite, augite, apatite, magnetite. ×30.

The amount of sulphides present is considerable. Pyrite sometimes replaces magnetite, but mostly it forms big crystals, which are frequently replaced in turn by chalcopyrite along fractures (fig. 12). To a small extent, chalcopyrite is also present as small grains amongst the silicates. The ore minerals have obviously recrystallized relatively easily after the deformation of the rock. This process is illustrated, for instance, by chalcopyrite grains that are composed of numerous small, intensely twin-lamellated crystals of different optical orientation.

Bornite is associated with chalcopyrite when the latter occurs in pyrite grains as well as inclusions in magnetite. It has formed at about the same time as chalcopyrite.

Small amounts of linnaeite join chalcopyrite in the replacement of pyrite. Its light-grey colour with violet tint in oil immersion and its isotropy are distinctive features. Phemister (1931) has shown that calcium and iron carbonates replace the silicates, and thus the original interpretation of Shand (1910) suggesting the assimilation of limestone by the cromaltite must be discounted. The views of Phemister are supported by ore-microscopic evidence. The oxide minerals, mainly represented by titanomagnetite, are typical constituents of the original ultrabasic rocks. The sulphides have been introduced later, most probably simultaneously with the carbonates. There are, of course, slight differences in age as far as the sulphides are concerned. Pyrite is the oldest, followed by chalcopyrite, bornite, and linnaeite. Thus the occurrence of linnaeite, which so far has not been recorded from igneous rocks, can be explained as a product of late hydrothermal activity. Finally, covelline may be mentioned, since it occurs very occasionally as an alteration product of chalcopyrite.

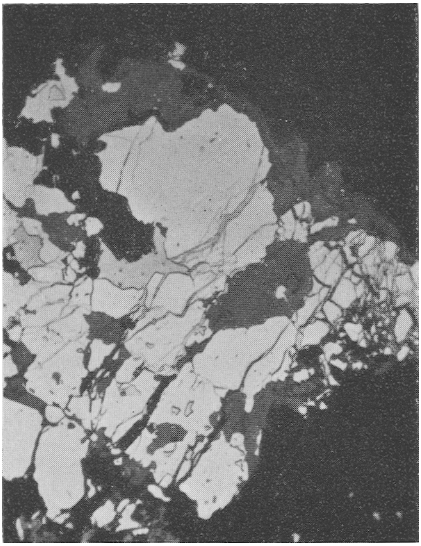


FIG. 12: Cromaltite, Bad na h'Achlaise. Magnetite (dark grey) is replaced by pyrite (white), which in turn is replaced by chalcopyrite (light grey). Reflected light, oil immersion. × 100.

Distribution of Co, Ni, *and* Cu.

Co, Ni, and Cu were determined using a Hilger large quartz spectrograph (E 742) and following the variable internal standard method with background correction recommended by Mitchell (1948). The Diabase W 1 was used as an external standard taken to contain 51 p.p.m. Co, 82 p.p.m. Ni, and 110 p.p.m. Cu (Ahrens and Fleischer, 1960). The results are shown in table I. The high Ni content of the biotite-diorite has to be ascribed to the considerable amount of pentlandite associated with pyrrhotine.

TABLE I. Distribution of Co, Ni, and Cu (in p.p.m.) in some Assynt rocks.

	Co	Ni	Cu
Epidiorite . .	57	27	206
Biotite-diorite . .	106	267	130
Cromaltite . .	54	9	420

The high value for Cu (420 p.p.m.) in cromaltite is obviously caused by the presence of chalcopyrite and bornite. No copper sulphides have been detected in polished sections of epidiorite. Nevertheless, the rock contains a considerable amount (206 p.p.m.) of Cu. Most probably, the original sulphides have been decomposed by slight weathering with retention of the copper. A similar case has been discussed by Wager, Vincent, and Smales (1957). The values for Co do not show any relation to the observed content of ore minerals in the rocks concerned.

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