Pseudomorphs of pyrrhotine after pyrite in the Ballachulish slates.

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THE Ballachulish slates,[1] exposed to the north and south of Loch Leven in Argyllshire, contain, in most places, cubes of pyrite up to half an inch in diameter. During a visit to the area in the spring of 1949 the writer's attention was attracted by the dark colour of the 'pyrite' cubes in the North Ballachulish slate quarry a little more than a mile east of Onich. On examination these proved to consist of a mass of haphazardly orientated crystals of pyrrhotine with irregular outlines. Slates collected from the main working quarry on the south shore of Loch Leven, on the other hand, contain cubes which are single crystals of unaltered pyrite.

This feature appeared to merit further investigation and in June 1949 the area[2] was revisited in order to ascertain the distribution of pyrite and pyrrhotine in relation to the geology of the region. As shown in fig. 1 the pyrite crystals are altered to pyrrhotine in a zone around the Ballachulish granite, while at greater distances from the contact the pyrite is unaltered. An intermediate zone can be recognized in which the pyrite crystals are either *partly* altered to pyrrhotine, or pseudomorphs of pyrrhotine after pyrite, and unaltered pyrite occur together in the same specimen. It is clear from this distribution that the pyrrhotine must have been formed by contact metamorphism of pre-existing pyrite in the slates. This is by no means an unusual phenomenon as the occurrence of pyrrhotine as a contact-metamorphic product of pyrite is known from a great number of other localities.[3]

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[1] For a further description of the Ballachulish slates see: Memoir of the Geological Survey, Scotland, no. 53, The Geology of Ben Nevis and Glen Coe (1916).

[2] During the field-work I was accompanied by O. v. Knorring, fil. lic., to whom thanks are due for help and discussions of the problems dealt with in this paper.

[3] It was originally thought that the existence of pyrrhotine might be dependent on the varying degree of regional metamorphism of the slates, and that the distribution of pyrite and pyrrhotine might give further clues to the tectonical architecture of the area. There is no evidence whatever for such an assumption. I am indebted to Professor W. Q. Kennedy for numerous discussions of the geology of the surroundings of Loch Leven, and for the keen interest he has taken in these investigations.

The alteration of pyrite to pyrrhotine is a very simple chemical process as follows: $FeS_2 \rightarrow FeS + S$. The sulphur formed by the dissociation of pyrite is probably reduced to sulphide ions or oxidized to sulphate ions and then removed as such from the place of formation.

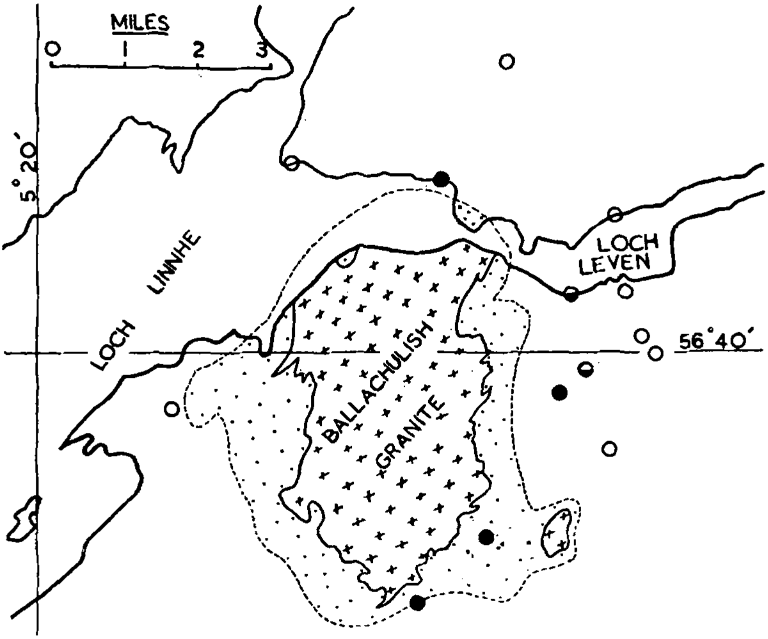

FIG. 1. Distribution of pyrite and pyrrhotine around the Ballachulish granite. Open circles indicate pyrite, filled circles pyrrhotine, and half-filled circles pyrite and pyrrhotine together. Crossed is Ballachulish granite, stippled the contact-metamorphic aureole according to Memoir of the Geological Survey, Scotland, no. 53.

The temperature at which this process has taken place is not easy to assess with any degree of accuracy. At atmospheric pressure pyrite dissociates to pyrrhotine and sulphur vapour at a temperature of 690° C. At this temperature the sulphur vapour-pressure of pyrrhotine is 1 atm. and decreases rapidly with decreasing temperature.[1] At 600° C. it is less than 20 mm., and will be very small indeed at 500° C. Above 690° C. no experiments have been carried out to determine the sulphur vapour-pressure of pyrite, but the shape of the vapour-pressure

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[1] R. Juza and W. Biltz, Zeits. Anorg. Chem., 1932, vol. 205, p. 273. [M.A. 5-138.]

curve indicates that it will increase very rapidly with increasing temperature.

The pressure on the pyrite cubes at the time of alteration was undoubtedly considerable, on account of the overlying rocks, and if the slates were impenetrable to sulphur vapour, it could be concluded that the pyrrhotine pseudomorphs were formed at a temperature considerably higher than 690° C. However, the sulphur vapour has probably been removed to some extent, either as such or by oxidation to SO_4^{2-} or reduction to S^{2-}. Either possibility means a transport of material to or from the site of reaction, and it can safely be assumed that a certain sulphur vapour-pressure must have been maintained around the pyrite cubes. Even if the most generous allowances are made for a removal of sulphur it seems highly improbable that the formation of pyrrhotine can have taken place at a temperature lower than 500–600° C. The curve of dissociation pressures of pyrite worked out in the Geophysical Laboratory[1] fully confirms this assumption.

These considerations throw an interesting sidelight on the genetical problems of the Ballachulish granite. Pyrrhotine is formed up to 1½ miles from the granite contact, which is considered to be nearly vertical. The temperature within the granite itself—whatever its mode of formation—must have been higher than in the surrounding rocks. It seems reasonable to assume a difference of at least 100° C. over a distance as great as 1½ miles. We are, therefore, led to postulate that the Ballachulish granite must have been formed at a temperature not lower than 600–700° C., a temperature of formation which might be expected in the case of a granite formed by solidification of a granitic magma.

It has long been recognized that nickel tends to be enriched in pyrrhotine and cobalt in pyrite. This is very clearly illustrated in the nickel deposit at Flåt in southern Norway.[2] The ore consists of pyrite, pyrrhotine, pentlandite, and chalcopyrite deposited in the order in which they are mentioned. The pyrite from Flåt contains 0·78 % Co (average of 13, ranging from 0·47–1·00 % Co) and less than 0·01 % Ni, giving a ratio Ni/Co less than 0·013 for pyrite, while the ratio Ni/Co for pyrrhotine from the same deposit is about 80. The Ni/Co ratio is, therefore, about 8000 times larger for pyrrhotine than for pyrite.

It is a matter of interest, therefore, to examine the behaviour of the Ni and Co content of the pyrite crystals in the Ballachulish slate during

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[1] H. E. Merwin and R. H. Lombard, Econ. Geol., 1937, vol. 32, p. 222. [M.A. 7-143.]

[2] H. Bjørlykke, Flåt nickel mine. Norges Geol. Undersøk., 1947, no. 168*b*. [M.A. 10-228.]

the alteration to pyrrhotine. Several determinations of Ni and Co have been carried out[1] and results are shown in table I. The Ni and Co contents of the pure pyrites and pyrrhotines from localities I–V clearly demonstrate that there is a systematic difference in the Ni/Co ratios for the two minerals. This difference can originate in one of two ways: (1) either by a decrease of the Co content during the alteration, or (2) by an increase of the Ni content. The first alternative seems the more probable, but the variation of the content of Ni and Co in the different crystals which have been analysed is too great to justify a definite conclusion. An analysis of the pyrite and pyrrhotine from a single, partly altered cube appeared to be the only method whereby the problem could be solved. A specimen from the easternmost of two slate quarries, west of West Laroch, contained a reasonably sized cube of pyrite partly altered to pyrrhotine. This crystal was crushed, and the pyrrhotine removed from the pyrite with a magnet. Because of the intimate intergrowth between the two minerals it was impossible to obtain pure samples. The pyrrhotine sample contained some pyrite and vice versa. The analyses of the impure samples (table I, pyrrhotine VI and pyrite VI) show, nevertheless, that the cobalt content has a pronounced tendency to decrease during the alteration of pyrite to pyrrhotine, whereas the nickel content remains nearly constant. It would appear, therefore, that when the Fe atoms in the pyrite lattice rearranged themselves to form a pyrrhotine lattice, any unsuitable atoms tend to be rejected.

TABLE I. Nickel and cobalt contents in pyrites and pyrrhotines from the following localities: I, easternmost of two slate quarries, west of West Laroch; II and III, western part of North Ballachulish slate quarry; IV, easternmost of three old slate quarries, SE. of Laroch; V, big slate quarry, Ballachulish (now worked); VI, easternmost of two slate quarries, west of West Laroch.

	% Ni by wt.	% Co by wt.	Ni atoms per 10,000 Fe atoms.	Co atoms per 10,000 Fe atoms.	Ni/Co atomic (& mean).	
Pyrrhotine I	0·076	0·042	11·70	6·47	1·81	(1·39)
„ II	0·012	0·014	1·84	2·08	0·88	
„ III	0·015	0·010	2·35	1·58	1·49	
Pyrite IV	0·012	0·033	2·47	6·63	0·37	(0·31)
„ V	0·005	0·019	0·95	3·79	0·25	
Pyrrhotine VI	0·013	0·022	2·00	3·41	0·59	
Pyrite VI	0·013	0·027	2·66	5·50	0·48	

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[1] The determinations were done by optical spectrographical methods, using the iron in pyrite and pyrrhotine as comparison substance. The intensities of the following lines were compared: Co 3453·5–Fe 3451·9 Å.; Ni 3050·8–Fe 3053·4 Å. The spectrographical work was done by L. Lund, mag. scient., and I offer my sincere thanks for his help and assistance.

Cobalt apparently does not fit the pyrrhotine lattice as well as does nickel, and has consequently been rejected more easily. The result is seen in the pronounced drop in the Ni/Co ratio demonstrated by the analyses given above.

A general rule may be formulated to the effect that when one mineral replaces another it does not, without modification, inherit the trace elements of the older mineral, but tends to readjust the trace-element content according to the properties of its own crystal lattice.