THE NAIRNE SULFIDE DEPOSIT

NAIRNE, SOUTH AUSTRALIA

Thesis submitted to the University of Adelaide
in partial fulfillment
of the requirements for the degree of
Master of Science in Geology

by

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April, 1959

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ABSTRACT

The sulfide deposit, which is the Nairne Pyritic Formation, contains at least five varieties of FeS_2, three of which are of secondary origin. The main bulk of the FeS_2 occurs as small grains distributed parallel with the bedding. Some of the FeS_2 occurs as pyrite in relatively large veins containing a suite of Ag-Sb minerals.

Two varieties of secondary FeS_2 are the result of pyrrhotite alteration. The concentric FeS_2 consists of pyrite, marcasite, or pyrite and marcasite. It is characterized by a porous concentric structure, and is extremely fine grained, thus presenting problems in flotation. The zoned pyrite may be either a direct replacement of the pyrrhotite, or a replacement of the concentric FeS_2. The third variety of secondary FeS_2 occurs with zeolite, siderite, and limonite and is definitely a product of weathering.

A detailed study of characteristics of syngenetic pyrite deposits shows that the Nairne formation is of sedimentary origin. The redeposition theory of Skinner (1958) and the hydrothermal theory of Edwards and Carlos (1954) are found untenable.

The sulfide veins containing the Ag-Sb minerals are described in detail. The observed relationships are compatible with either a magmatic or metamorphic origin.

A comparison of the Nairne deposit with similar deposits shows that it has all the characteristics of a syngenetic deposit. Ag-Sb veins in pyrite deposits are more ubiquitous than commonly thought, and in most instances these have been ascribed to metamorphic processes. The author feels that a metamorphic theory of origin for the Ag-Sb vein system at Nairne is the most realistic.

INTRODUCTION

In September, 1957, the author became interested in the sulfide mineralization at Nairne, South Australia, because of the poor recovery of pyrite in flotation during that period. The following analysis of flotation concentrate and tailing from Grassfire Hill ore clearly demonstrates that concentric pyrite is the non-floatable pyrite, and that it significantly affects the pyrite recovery:

	Flotation Concentrate	Flotation Tailing
% wt. superpanner con.	48	7
% vol. clear pyrite	85	16
% vol. concentric pyrite	13	74
% vol. pyrrhotite	2	trace
% vol. sphalerite	trace	trace
% vol. chalcopyrite	trace	-
% vol. limonite etc.	trace	10

Because of the economic significance of the concentric pyrite, an investigation was initiated to ascertain the nature of the material, and the depth to which it persists. The work of the past eighteen months has coped with this problem, and has led to a number of interesting discoveries pertaining to the mineralogy at Nairne. The author has made numerous visits to Nairne, and has examined in detail three drill cores from Grassfire Hill (D.D. 10, 14, 21) and two from an area south of Shephards Hill (D.D. 12, 13), as well as many surface specimens. The story of the Nairne sulfide deposit is not a simple one and a large part of this thesis has been devoted to a discussion relating to the significance of the observed information.

ACKNOWLEDGEMENTS

The work for this report was made possible by the South Australia Department of Mines, Research and Development Branch, Parkside, the United States Educational Foundation in Australia, and by the willing co-operation of Mr. J. Hammer, Mine Manager at Nairne. Also, the author is indebted to A. W. G. Whittle, Chief Mineralogist and Petrologist, S. A. Department of Mines, Profs. A. R. Alderman and E. A. Rudd of the University of Adelaide, Profs. A. N. Winchell and A. M. Bateman of Yale University, Prof. Paul Ramdohr of the University of Heidelberg, and Dr. Howard Worner, Director of the B. H. P. Research Labs, for their advice and encouragement, and to Douglas Luckett, for the preparation of polished sections.

GENERAL GEOLOGY

The pyrite deposits at Nairne are part of the Nairne Pyritic Formation, which is the basal formation of the Kanmantoo Group, 26,000 feet of fine-grained quartzites, siltstones, and graywackes. The Nairne Pyritic Formation (believed to be Cambro-Ordovician in age) has been traced for over 65 miles, and locally at Nairne it thickens and the beds dip approximately 70°E and strike essentially N-S (see cross-section). Open cut mining is being undertaken in three hills, which are part of the general ridge produced by the formation. The hills are, from S to N, Shephards Hill, Little Hill, and Grassfire Hill. A shear zone occurs just to the north of Grassfire Hill causing more fracturing in that hill than in the other two hills.

Skinner (1958) has made an extensive study of the general relationships of the Nairne formation, including a detailed study of the metamorphic assemblages involved; the reader is referred to this work for such details. The author will include these aspects, only when they are related to the particular problems affecting the sulfide mineralization.

GENERAL MINERALOGY

The Nairne pyrite deposit consists essentially of pyrite and pyrrhotite, with pyrrhotite being somewhat more predominant than pyrite; the deposit is worked for its sulfur content. Small amounts of sphalerite, galena, chalcopyrite, rutile, and arsenopyrite are also encountered. In general the sulfides are present as small grains distributed parallel with the bedding, and at Nairne they are concentrated into economic proportions in three parallel beds (see cross-sections). These beds are 50-100 feet thick and are separated by waste beds, approximately 20 feet thick.

In addition to the sulfide grains distributed parallel with the bedding, small veinlets of pyrite and pyrrhotite occur which cut the bedding. Larger veins are also present and these commonly contain, not only pyrite and pyrrhotite, but also an assemblage of Ag-Sb minerals.

The pyrrhotite is altered in a number of places to different varieties of iron sulfide. Investigation shows that the alteration is most intense near the surface outcrop and diminishes in intensity with depth. At the surface all pyrrhotite is altered, whereas at depth only certain narrow areas seem to have been affected. Among these areas are the larger veins, in which alteration has taken place to a depth of at least 450 feet (based on drill core examination). In the main rock mass at this depth, the pyrrhotite is for the most part unaltered,but where altered, the altering solutions have entered along the coarser-grained bands. Thus, it appears that surface alteration of pyrrhotite has been effected by weathering agencies. The deeper alteration is more of a problem, but it is not impossible that the effects of weathering continue down more than 400 feet (Ramdohr, 1955, p. 652).

Surface weathering has produced a gossan capping on the ore beds, the thickness of which varies from hill to hill. In the oxidized zone the rock has been completely altered to a mass of kaolin, basic iron sulfates, and residual quartz. The sulfides have also disappeared, leaving in their place limonite and jarosite. This zone trends downward into a zone of partial oxidation, in which the feldspars and pyrrhotite have been altered but the pyrite and quartz remain. The solutions liberated during weathering have carried dissolved material downward and have deposited it in cracks and fractures. This deposition has resulted in the formation of such minerals as zeolites, siderite, chalcedony, and limonite, in more or less concentric masses.

DETAILED MINERALOGY

RELATION BETWEEN SULFIDES AND COUNTRY ROCK

The most apparent relationship between the sulfides and the country rock is that the sulfides are distributed parallel with the bedding. The grain size of the sulfides generally reflects the grain size of the rock material surrounding them, the larger sulfide grains tending to occur with the larger rock grains. Skinner (1958) discovered graded bedding in approximately 5% of the sediments, and he noted that the sulfide grains were graded along with the rock minerals. I encountered no graded bedding, but instead numerous augen-like features. In their incipient stages of growth the augen appear as in Fig. 1. Here we see a central core of relatively fine-grained quartz and feldspar, surrounded by a sheath of muscovite laths, arranged parallel with the surface of the core, and tapering off at the ends, in the direction of the bedding. It is argued by some workers, that these features form by a shearing action, and that, in effect, the muscovite laths are "flowing" around a resistant core of quartz and feldspar, the direction of shearing being parallel with the bedding. Other workers, such as Ramberg (1952), point out that the core of quartz-feldspar may have started as a nucleus of growth during metamorphism. As it grew, it pushed aside the muscovite flakes, forming a football-shaped envelope. This concept is involved with such ideas as "form energy", force of crystallization, and migration of elements. As the nucleus starts to grow, it exerts pressure on the surrounding material. It may be that the interfacial tension between, say quartz and muscovite, is high, so that these two minerals tend not to intermix, and the force of crystallization of the quartz tends to push the muscovite aside, instead of incorporating it. At the same time there must be a give and take, as the nucleus cannot expand into "solid" rock. Instead, the mobile quartz and feldspar-forming material between the muscovite grains, migrates toward the nucleus, adding to its growth, and compensating for its expansion. This may explain why the mica surrounding the core is depleted of interstitial quartz and feldspar.

Further growth of the nucleus forms elongate areas, or lenticules, of relatively coarse-grained quartz, feldspar, and some muscovite. The size of the sulfide grains reflects this phenomenon, and we find relatively coarse grains of pyrite and pyrrhotite in the lenticules, whereas in the areas between these, only small grains of sulfides occur(Fig. 2). This relationship is a common feature at Nairne and is found throughout the rock mass. The pyrite tends to be concentrated in the coarse-grained areas, and the pyrrhotite in the fine-grained areas. The pyrrhotite commonly forms plates which are oriented parallel with the plates of mica.

The growth relationships between the sulfides and the rock minerals are those demonstrated by a compatible series of minerals. Instead of replacement, one finds the ore minerals enclosing uncorroded grains of gangue minerals, such as in Fig. 3. This indicates that the sulfides developed their present form under the influence of metamorphism, and were not emplaced by hydrothermal solutions or some such phenomenon.

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DESCRIPTIONS OF INDIVIDUAL MINERALS

Varieties of FeS_2

Investigations show that there are at least five varieties of FeS_2 present, three of which are of secondary origin.

Primary Pyrite

The term primary pyrite is here used to designate that variety of pyrite, which occurs as small (2 mm. and less) grains, distributed parallel with the bedding, and also that variety in small tension gashes. This pyrite is doubtless sygenetic, and its initial form was possibly as hydrous iron sulfides. The grains are idioblastic to anhedral. Pyrite in contact with pyrrhotite tends to exhibit good crystal outlines, whereas pyrite in contact with gangue tends to exhibit irregular outlines, as in Fig. 4.

The pyrite generally contains no inclusions. Rarely one finds a few grains which contain a number of minute unoriented inclusions of pyrrhotite and sphalerite. Some of the grains are anisotropic and not isotropic as should be expected from a cubic mineral. Anisotropism, however, could come about by distorting the crystal lattice; this could be caused by foreign elements in the pyrite. Some particularly anisotropic grains were separated and analyzed. The analysis showed 0.2% Ni, which might account for the anomalous anisotropism.

This variety of pyrite accounts for approximately 90% of the pyrite in the formation. It is resistant to weathering, and is commonly found unaltered, even where the feldspar and pyrrhotite have decomposed.

Vein Pyrite

This term designates pyrite found in the larger veins, along with the rare Ag-Sb minerals. It is coarser grained than the primary pyrite (grains up to 5 cm. across) and is more commonly euhedral. Inclusions are encountered in some of the grains,but they are by no means numerous. The pyrite is not uncommonly fractured, and the fractures filled with pyrrhotite, galena, and chalcopyrite. This variety of pyrite is rarely anisotropic.

Vein pyrite constitutes approximately 5% of the pyrite in the ore deposit. It is also resistant to alteration, and is commonly found enclosed by altered pyrrhotite.

At this point let us consider a partial spectrographic analysis of these two varieties of pyrite (analyses by A. B. Timms, S. A. Department of Mines):-

	Fe	S	Ni	Co	Mn	Ti
P.P.	46.3	52.5	.01	.02	.07	.05
V.P.	47.5	53.0	.01	.06	.005	.01

Pyrite is a non-stoichiometric compound and, according to Edwards (1954), may vary in composition from $FeS_{1.94}$ to $FeS_{2.05}$. By recalculating the above Fe-S ratios to 100% it is evident that primary pyrite has a composition of $FeS_{1.98}$ whereas vein pyrite has a composition of $FeS_{1.94}$. The samples were pure as far as could be ascertained, although a few impurities may have come in as inclusions. If we consider the material to be pure, however, then both pyrites do not have the same composition. Skinner has demonstrated to his satisfaction that the pyrite has a constant composition regardless of the other minerals present. If so, one would expect the composition of both varieties of pyrite to be the same. Since they do not appear to be, it may be that the vein pyrite was formed after the formation of the main body of sulfides. However, caution must be exercised in such deductions.

As regards the other elements, Co and Ni may enter into the pyrite lattice in substitution solid solution, and may be responsible for the anomalous anisotropism observed in some of the pyrite grains.

Secondary FeS_2

Three varieties of secondary iron sulfide are present; two of these are replacement products of pyrrhotite, and the third represents deposition from circulating ground water. The first two constitute approximately 5-10% of the pyrite in the ore deposit and are of definite economic significance; the third is a curiosity, representing less than 0.1% of the pyrite.

Replacement Products of Pyrrhotite

The replacement products of pyrrhotite are here referred to as concentric FeS_2 and zoned pyrite; they occur in roughly equal proportions.

Concentric FeS_2

This type of FeS_2 is responsible for the poor recovery of pyrite, especially in Grassfire Hill ore. In the typical example pyrrhotite is partially replaced by little olive-drab nodules, as much as 5 mm. in diameter; these tend to form masses suggestive of bunches of grapes. Under a binocular microscope these are found to consist of a number of concentric shells, composed of extremely fine-grained material; electron photomicrographs disclose that the grains are commonly less than 0.5 microns in diameter, although 2 microns is more the rule. In a number of instances the grains of one shell are markedly coarser than those in the adjacent shell. The shells commonly appear to be separated in places by a thin (approximately 3 microns in thickness) discontinuous void, paralleling the outline of the shell. These voids account for the concentric cracks observed in polished section (Fig. 5). In some specimens the material was rather porous, displaying numerous randomly-spaced voids less than 3 microns in diameter. Fig. 6 shows the nature of the concentric FeS_2. To be noted are the scalloped shells on some of the pieces, and the voids in the others. The porous nature of the material, and the fine grain size, are most probably the main factors hampering proper flotation. The voids probably absorb the reagents, and the rough irregular surface probably makes bubble attachment difficult; contrast the smooth shiny surface of the pyrrhotite with the rough dull surface of the concentric FeS_2!

Under the reflecting microscope the picture becomes more complex. I find that some of the nodules consist exclusively of pyrite, others of marcasite, and others of a mixture of pyrite and marcasite. The marcasite is typically bluish white in color whereas the pyrite is brownish yellow, slightly darker than ordinary pyrite. In some of the nodules the marcasite is disseminated throughout the pyrite (or vice versa) and in others the pyrite and marcasite form alternating bands. In those nodules composed of marcasite, a broad pattern of anisotropism is commonly encountered. This pattern passes over the concentric cracks, tending to indicate that the cracks were produced after the initial material had been formed and the texture developed.

Structurally there are two main types of material. In the first type the nodules are spherical. In Fig. 5 the nodules are composed entirely of pyrite. In Fig. 7 we see alternating bands of pyrite and marcasite; the marcasite is rather coarse-grained in this instance, as is betrayed by the anisotropism. In the other type the nodules tend to be elongate or cigar-shaped. In the example in Fig. 8 the marcasite has been etched black with 1:1 HNO_3. These two types are fairly distinct, and I do not think that type one is merely a circular cross section of type two.

More marcasite than pyrite appears to be present, although the relative amounts vary from specimen to specimen. The intimate mixture of pyrite and marcasite may be due to an oscillation of pH above and below 7 during formation.

Terminology for this variety of FeS_2 is somewhat confusing and it is time the problem was cleared up. The trouble seems to hinge on the question of what is melnikovite. Ramdohr (1955) defines melnikovite-pyrite or gelpyrite as a crystallized gel of FeS and $FeS_2 \pm As$ which now consists mainly of pyrite, but still contains small amounts of FeS, As and perhaps H_2O. He makes no distinctions as to place of formation. Also, he refers to the "birds-eye" structure formed by weathering of FeS and mentions that the products may be either marcasite or pyrite, but this still does not give us a proper terminology.

Uytenbogaardt (1951) defines melnikovite-pyrite as "concentric or radiated aggregates of a micro- or crypto-crystalline, may be partly amorphous, substance consisting of pyrite and marcasite, commonly also containing some As. The name should only be used when indicating such aggregates and not as a mineral name." Furthermore, he defines melnikovite as "black, finely divided pyrite, regarded as having been derived from iron sulphide gel."

Edwards (1954) also refers to melnikovite-pyrite and states that it is formed from melnikovite by alteration.

It is evident that no real unaminity exists. Furthermore, terms such as melnikovite-pyrite or melnikovite-marcasite are commonly used as more or less structural terms, alluding to the concentric nature of the aggregate. For example, Rechenberg (1950) reports melnikovite-marcasite from the Pb-Zn deposits in Recklinghausen. He records that marcasite alternates with "melnikovite-pyrite," both forming concentric layers. Hence he wishes to name the marcasite melnikovite-marcasite.

Melnikovite, the mineral in question, was publicly noted for the first time by Doss (1911) when he recorded the presence of the black, cryptocrystalline, gel-like iron sulfide in his description of the third bore for gas in Miocene clays, on the property of the brothers Melnikow, in the province of Samara.

- TABLE 1 -

Log for Bores II and III from Doss (1912a, p.664).

	Bore II		Bore III		Age
	Depth meters	Thickness	Depth meters	Thickness	
Brown surface clay	2.1 - 46.9	48.0	0.3 - 44.8	45.9	Recent
Yellow-brown clay-sand containing epsom salts	49.1-57.6	10.7	46.9 - 56.5	10.9	
Yellow-brown sandy clay	59.7	2.1	57.1	0.8	Miocene
Browner (Bore II), grayer (Bore III) iron sulfide free clay	61.9	2.1	58.1	0.8	
Orange-gray sandy clay containing iron sulfide in Bore II; none in Bore III	64.0 - 68.3	6.3	58.7 - 66.4	10.1	
Gray clay containing iron sulfide	70.4 - 93.9*	25.3	68.3 - 88.5*	20.0	
Bore II: Plates of iron sulfide; pyritic ss alternating with clay and sandy clay. Bore III: Grayer iron sulfide-bearing clay; sand cemented with clay and iron sulfide.	95.1	1.2	89.6*	2.2	
Light green-gray iron sulfide-bearing clay sand (contains gas)	96.3	0.8	91.7	2.1	
Light green-gray iron sulfide-bearing clay sand (proper gas stratum)	96.7	0.2	93.7	1.1	

*Areas from which Doss obtained sulfide material for examination.

Doss (1912a) later published a more detailed description of the bores and his experiments. Table 1 shows the log for bores II and III, from which the general stratigraphy is apparent. In his first attempts to derive a formula for the new mineral, Doss (1912b, p. 454) collected material from 93.9 meters depth in Bore II; from this he calculated the formula Fe_5S_7. For this purpose he had had only 0.043 gm. of the mineral, and there was none left for further work. To this end, 0.270 gm of the mineral was obtained from 74.7, 87.5, and 89.6 meters in Bore III; from this he calculated the formula FeS_2. The material was cryptocrystaline, formed colloform aggregates, had a black color, a hardness between 2 and 3, a specific gravity of 4.2-4.3, was strongly magnetic, and soluble in warm dil. HCl. Fracture was uneven to conchoidal, and the fractured surfaces had a steel-gray metallic shine.

The individual grains were not clearly visible with less than 260 power, and in polished section the material was seen to form a compact aggregate; a few tiny quartz and carbonate grains were also present. In a few places tiny pyrite crystals occur in the material, either alone or in groups. When in groups, there are spaces between the grains and a porous aggregate results (p. 458). Doss reckons that pyrite is the more stable variety of FeS_2 and that the new mineral is altering to pyrite. As evidence, he singles out the porosity of the pyrite aggregate. The pyrite is heavier than the new mineral (4.98 vs 4.2) and he infers a shrinkage to produce a unit weight of pyrite from the same weight of the new mineral.

Doss also believes that the material was precipitated in marine waters, the colloidal precipitate incorporating fine quartz particles on the sea floor (the tiny inclusions of carbonate indicate alkaline conditions of deposition, which agrees with a marine reducing environment). He further purports that sulfur-producing bacteria were active in the deposition of this material. Upon dissolving the FeS_2, Doss found tiny thread-like isotropic objects (amorphous quartz). He conjectured that these might be fossils of bacteria which were once active in producing H_2S and were trapped by, or settled into, the colloidal precipitate. He sent samples to Dr. B. Schorles in Dresden, a well-known specialist in iron bacteria; Schorles reckoned they were similar to _Gallionella ferruginea Ehrenbg_. Still others were similar to the iron bacteria _Spirophyllum ferrugineum Ellis_ (p. 472). If this is true, it seems very certain that this material was formed in a marine reducing environment, and not from any epigenetic solutions.

Doss (1912a, p. 683) named this new mineral "melnikowite": "Für das untersuchte Eisenbisulfid schlage ich den Namen _Melnikowit_ vor, in Anbetracht seiner erstmaligen Auffindung im Bereiche des Gutes der Gebrüder Melnikow." In English usage it has been rendered phonetically, so that we now have *melnikovite*, which preserves the Germanic pronounciation.

Lepp (1957) has produced melnikovite synthetically, and his experiments seem to re-establish melnikovite as a mineral in its own right. Lepp's melnikovite has the same formula and properties as does that of Doss, and in addition, Lepp has furnished x-ray data. Lepp also considers his mineral to form under marine reducing conditions.

Lepp may not have been the first to produce synthetic melnikovite. Prof. Gustav Bischof of Bonn (1829) performed a number of experiments with the Brohler mineral water which was notorious for precipitating 2/3 of its iron content within a few hours. The Professor attempted to prevent the iron precipitate by adding a deoxygenating agent, namely organic matter in the form of sugar. When he opened the sealed jugs and jars 13 months later, he found those with just enough sugar contained no precipitate, but in those which he had put too much sugar, there was a strong odor of H_2S and "In den Flaschen hatten sich grosse schwarze Flocken abgeschieden... (p. 32)." The Professor did not test the black precipitate, but it could have been melnikovite--the conditions were right.

Tarr (1927) claims a hydrothermal origin for melnikovite in the Cambrian dolemite in Missouri. He examined a few specimens which consist of alternate layers of pyrite and marcasite, commonly separated by "a thin band of a black powder-

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like material (p. 418)." The powder was not magnetic and contained many minute pyrite grains. He concludes that this black powder, was, in all probability, melnikovite, which has altered to pyrite. (Could not the material have been finely divided pyrite in the first place?) Furthermore, he uses the presence of marcasite to indicate that "the temperature of the solution during deposition was near 100° (p. 420)" and that this is a hydrothermal deposit, including the former melnikovite. Tarr would be hard put trying to explain the formation of marcasite from pyrrhotite at Nairne by weathering!

It is clear, then, that terms involving the name melnikovite should be applied only where melnikovite can be proved to be a forerunner of the pyrite or marcasite being considered; they are genetic terms and not structural terms, although structure of some sort may be implied. There is no evidence that the concentric FeS_2 at Nairne has been derived in any way from melnikovite; it is a secondary alteration product and should not be confused with the melnikovite of Doss and Lepp. Nairne is not the only such case of pyrite and marcasite formation--compare Foslie (1950), Newhouse (1925), Schwartz (1937a, 1937b), and Weston-Dunn (1922)--and, until a more appropriate term is proposed, it is the author's opinion that such aggregates should merely be referred to as concentric FeS_2, which is a structural, not a genetic term. Some degree of genesis may be indicated by employing such terms as primary concentric FeS_2 or secondary concentric FeS_2.

Zoned Pyrite

In a number of instances the pyrrhotite appears to be altered to a more or less rectangular boxwork, and from the walls of this boxwork project small crystals of pyrite. This phenomenon is found in all stages of development, and the crystals are not uncommonly 0.5 cm. across; the long dimension of a "box" may reach 1.5 cm. but 0.5 cm. is more the rule. It is common to find boxworks still containing remnants of pyrrhotite, as in Fig. 9. Also to be noted is the sharp contact between the zoned pyrite and the cube of vein pyrite. These boxworks are especially well developed in the large pyrrhotite masses in the larger veins, and have been found as deep as 450 feet below the surface.

In polished section the pyrite crystals are found to be isotropic and to consist of alternating zones of darker and lighter material (Fig. 10). The lighter material is slightly more brownish than regular pyrite and forms the thickest zones. The darker material is even more brownish and forms thin zones between the light zones. The outlines of the zones are essentially isometric, but need not necessarily follow the external outline of the crystal.

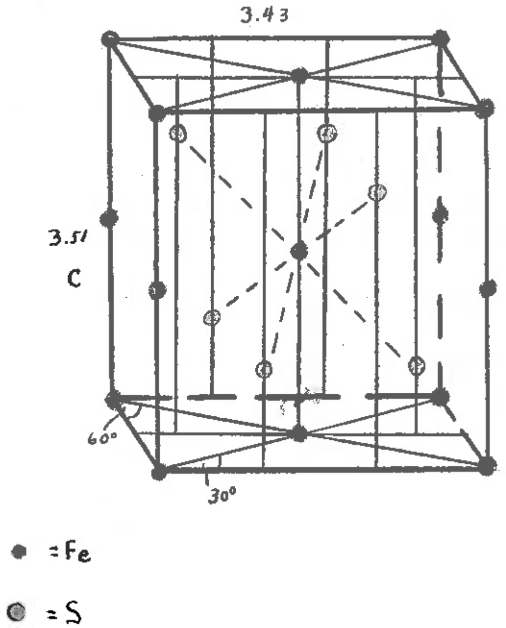
Not uncommonly the zoned pyrite will have as its "core" an area of concentric FeS_2 (Fig. 11). More recently examples have been encountered in which veinlets of zoned pyrite cut mass of concentric FeS_2 as in Fig. 12. These observations suggest that the zoned pyrite, at least in some instances, forms from the concentric FeS_2.

The analyses of these two forms of secondary FeS_2 show:

	Fe	S	Ni	Co	Mn	Ti
C. FeS_2	46.0	50.3	.15	.02	.07	.02
Z.P.	46.0	48.4	.13	.03	.05	.07

By recalculating the Fe-S ratios to 100% we get a formula of $FeS_{1.91}$ for the concentric FeS_2 and a formula of $FeS_{1.84}$ for the zoned pyrite. The composition of the zoned pyrite falls far below the accepted lower limit for pyrite ($FeS_{1.94}$). The reason for this is not understood at present; caution must be exercised in evaluating such a limited number of analyses. The Co and Ni may be responsible for the darker zones, as in bravoite.

At the suggestion of Dr. Worner, an attempt was made to learn why pyrite boxworks were produced by alteration of the pyrrhotite i.e. why is the replacement box-like instead of massive? A working hypothesis is that the boxworks are, in some way, related to the crystal structure of pyrrhotite. Cleavage might give a clue. Dana (1944, p. 232) reports only a basal parting (0001). Ramdohr (1954, p. 343) reports, in addition, a cleavage on $(11\bar{2}0)$. This, however, would not account for the observed boxworks. Moreover, the pyrrhotite at Nairne has very poor cleavage; uneven to sub-conchoidal fracture at best (Fig. 6). More insight into the crystal structure can be gained from x-ray studies. Alsén (1925) did extensive analytical and x-ray work on pyrrhotite. He deduced the arrangements of atoms to represent what is now known as the nickel arsenide structure, and gave pyrrhotite the highest hexagonal status (p. 38). In expressing the unit cell, Alsén realized that a hexagonal or an orthorhombic choice is possible, depending on how the points of the unit cell are selected. His orthorhombic interpretation (p. 39) is given below.



Orthorhombic unit cell of pyrrhotite

In it the S atoms form an almost regular octahedron around Fe. Winchell (per. comm.) is of the opinion that the orthorhombic unit cell is just as correct as the hexagonal, and perhaps easier to use. Alsén also noted that pyrrhotite was nonstoichiometric and that, as the S content increased, the c-axis decreased in length, whereas the length of the a-axis remained constant (p. 31). He concluded that S atoms must substitute for Fe atoms with increasing S content. If Alsén's suggestion is followed, the formula for pyrrhotite should be e.g. $Fe_{.473}S_{.527}$ which indicates that S substitutes for Fe. However, the formula may also be expressed $FeS_{1.054}$ which indicates a "stuffed" lattice, where S atoms occupy interatomic spaces. There is another way by which the formula of pyrrhotite may be expressed, namely, $Fe_{1-.053}S$ or $Fe_{.947}S$, which indicates that pyrrhotite has a defect structure, such that pyrrhotite becomes S-rich by vacating Fe sites in the lattice. That this latter formula expresses the correct interpretation of the pyrrhotite lattice, can be demonstrated graphically by plotting observed density changes vs calculated density changes for the "substitution" and "defect" theories. It is found that the "defect" curve most closely fits the "observed" curve. This has been executed in detail by Hägg and Sucksdorff (1933, p. 450) and amplified by Haraldsen (1941, p. 180).

A number of researchers have examined the composition range of pyrrhotite and its behavior at different temperatures. Treitschke and Tammann (1906) heated commercial ferrous sulfide and observed a volumetric modification at approximately 130°C. Rinne and Boeke (1907) repeated the experiment with pure ferrous sulfide and natural pyrrhotite. They found no modification and attributed this to the fact that commercial ferrous sulfide is 10% Fe and 80% FeS. Furthermore, they found that in mixtures containing less than 5% Fe, the heat absorption accompanying the inversion could not be detected, but that with 7% Fe or more, the transformation point was 138°C. Allen et. al. (1912, p. 207) also could not detect the change in pyrrhotite or pure troilite, although they assumed it still took place, but that the heat effects were too small to be measured by their methods. However, Roberts (1935) detected the heat change even in pure ferrous sulfide, by employing differential heating and cooling curves. Haraldsen (1937) confirmed the transition temperature using a sensitive electro-magnetic procedure.

More recently, Haraldsen (1941b) found that there are two different types of ferrous sulfide: paramagnetic troilite in the composition range FeS to $Fe_{.96}S$, and ferromagnetic pyrrhotite in the composition range $Fe_{.96}S$ to $Fe_{.92}S$. The pyrrhotite range is characterized by the nickel arsenide structure, whereas the troilite range is characterized by a superstructure from FeS to $Fe_{.98}S$ and a nickel arsenide structure from $Fe_{.98}S$ to $Fe_{.96}S$. Furthermore, the superstructure vanishes on heating above the critical temperature of 138°C, at which temperature a volumetric modification occurs. Hägg and Sucksdorff (1933) also reported a superstructure near the troilite region.

Their superstructure has six times the volume of the original NiAs type cell, but has the same type symmetry (p. 446). A few years later Sidhu and Hicks (1937) found evidence for a superlattice in both paramagnetic and ferromagnetic ferrous sulfide using synthetic and natural samples, analyzed by means of x-ray powder patterns. However, their x-ray diffraction studies on a ferromagnetic single crystal from Minas Geraes, Brazil, and on a paramagnetic single crystal from Maggiadone, Italy, failed to show a superlattice. Buerger (1947), on the other hand, has studied the cell and symmetry of ferromagnetic pyrrhotite crystals from Schneeberg, Saxony, and Morro Velho, Brazil and his results do not agree with those of previous workers. Buerger found a superstructure with sixteen times the volume of the simple NiAs cell, and this superstructure occurs, not in the paramagnetic troilite region, but in the ferromagnetic pyrrhotite region. Also, he has difficulty fitting his diffraction data into the assigned NiAs arrangement. The data do not show the translation periods of the assigned structure, so that, in Buerger's estimation, it is not unlikely that pyrrhotite belongs either to a lower hexagonal symmetry or to an orthorhombic or monoclinic symmetry. As concerns superstructures and supercells, Winchell (per. comm.) reckons that these would be expected in a defect structure such as this. If the omitted Fe^s occur in an ordered pattern, then these will form a larger superlattice. Although the NiAs structure is still the most probable for pyrrhotite, further investigations are needed to fully clarify the matter.

Having investigated the structure and behavior of pyrrhotite, it is possible to make a few generalizations concerning the formation of the pyrite boxworks. Pyrrhotite has a defect structure, and the superlattices are witness to that fact. Skinner (1958, p. 557) has detected weak superlattice lines in the Nairne pyrrhotite. Also, pyrrhotite may have orthorhombic symmetry, and at any rate the unit cell may reasonably be orthorhombic. It is therefore suggested the alteration of the pyrrhotite followed some type of mosaic block dislocation structure, the symmetry of which was influenced by the orthorhombic tendencies that pyrrhotite has been shown to display.

FeS_2 from Circulating Ground Water

In a few areas of the quarry, cracks have opened, and solutions formed during weathering have trickled down, altering the country rock and depositing various minerals. A common sequence of deposition is zeolite, siderite, limonite var. esmeraldite, and patches of FeS_2 in small (less than 0.15 mm. across) crystals (Fig. 13). Polished sections show a concentric structure and layers of intermixed pyrite and marcasite.

Pyrrhotite

Pyrrhotite is present throughout the ore and is somewhat more abundant than pyrite. The grain size of the pyrrhotite reflects the grain size of the enclosing rock grains, much the same as does primary pyrite. Unlike the pyrite, the pyrrhotite does not form crystals, but instead forms irregular masses which reflect the outlines of the enclosing gangue minerals. Commonly the pyrrhotite forms plates between laths of muscovite, and these, like the muscovite, are aligned parallel with the foliation. In some instances the pyrrhotite forms plates which grow in various orientation, as in Fig. 14, but these occurrences are rare. Where the pyrrhotite is in contact with pyrite, the pyrite is in most instances idioblastic into the pyrrhotite, showing that the pyrrhotite was mobile longer than the pyrite.

Internally the pyrrhotite shows no signs of stress. If pyrrhotite is stressed it tends to develop twinning lamellae and undulating extinction. These features are markedly absent from the main mass of pyrrhotite. These observations indicate that the pyrrhotite was mobile during metamorphism of the surrounding rock. The pyrrhotite contains no inclusions except for a few scattered crystals of arsenopyrite, although the large masses of pyrrhotite are notuncommonly cut by veinlets of chalcopyrite and sphalerite.

The following minerals are also found in the country rock:

Sphalerite ZnS

Sphalerite occurs as small rounded grains scattered throughout the ore and comprises less than 5% of the ore minerals. It is commonly found in the groundmass between the "augen" of pyrite + pyrrhotite and has no particular shape.

Internally the sphalerite contains no inclusions or exsolution bodies. In a few instances the sphalerite exhibited a marked anisotropism; this may have been caused by stress. Internal reflections are always present and are orange-red in color, indicating a fairly high iron content.

Chalcopyrite $CuFeS_2$

Chalcopyrite comprises less than 5% of the ore minerals and occurs essentially in pyrrhotite, commonly along pyrite-pyrrhotite grain boundaries. The chalcopyrite has no particular shape, although it commonly forms small veinlets which traverse the pyrrhotite or even fill cracks in pyrite.

Galena PbS

Galena is the least common of the lesser minerals and is, like chalcopyrite, commonly associated with the pyrrhotite. Fig. 14 shows such an association and in this case the galena is apparently younger than the pyrrhotite.

Rutile TiO_2

Rutile exhibits the same general relationships as does the sphalerite; it also represents less than 5% of the ore minerals.

Arsenopyrite FeAsS

A few crystals of arsenopyrite are scattered throughout the ore. Small crystals have been found in pyrrhotite and large crystals (as much as 2 cm. long) have been found in the groundmass. The larger crystals are commonly shattered and invaded by veinlets of galena, chalcopyrite, sphalerite, and pyrrhotite.

Graphite

Graphite is a ubiquitous, though easily overlooked component of the formation. It occurs as elongate grains in the gangue and is responsible, to some extent, for the gray color of the formation. The grains are very tiny, commonly less than one micron in length, thus going unnoticed under the microscope, unless high power is used. The largest grain of graphite observed was at a depth of 230 feet in bore 12; it was approximately 50 mm. long.

Minor Minerals

In addition to the above minerals, the main mass of sulfide ore is characterized by minute amounts of rounded grains of fahlerz $(Cu_2Ag_2)_3\ Sb_2S_6$ and bournonite $CuPbSbS_3$. These occur in association with the galena and are rarely encountered.

PARAGENESIS

The general paragenetic relationships are fairly simple. The main principle to be remembered is that the minerals crystallized under the influence of metamorphism and that the individual constituents were in equilibrium. The pyrite (and some arsenopyrite) crystallized first followed by pyrrhotite, sphalerite, chalcopyrite, and galena. The last four appear to be contemporaneous but occasionally cross-cutting relations are observed.

MINERALS COATING SMALL FRACTURES

Vivianite $Fe_3P_2O_8 \cdot 8H_2O$

Vivianite is a common constituent of the formation, but is recorded for the first time in this report. A. W. G. Whittle first brought it to my attention, and since then excellent examples have been encountered in both Grassfire and Shephards Hills. It typically coats fractures with a paper-thin layer of shiny, dirty-blue radiating laths. The fractures are generally but a few feet long and not uncommonly form an interlocking joint-like system; again, blasting makes overall field relations difficult. The fractures either parallel the foliation or cut across it. This fracturing is common throughout the quarry but is not of equal intensity throughout; it is most apparent in recent (October/58) quarrying on the 1290 level in Grassfire Hill. The vivianite is a surface coating only, and does not extend into the rock; it is commonly accompanied by smears of pyrite and pyrrhotite.

Chlorite

Chlorite occurs in much the same relationship as does vivianite. It similarly coats small fractures, although chlorite and vivianite need not occur together.

For reasons outlined later, it is believed that vivianite and chlorite were formed by metamorphism from elements already present in the country rock; Winchell (per. comm.) is also of this opinion.

THE LARGE SULFIDE VEINS

As mentioned before, veins containing a suite of Ag-Sb minerals cut the orebody. These veins are commonly rendered discontinuous by blasting. This confuses the issue somewhat, as is easily realized. On my last trips to the quarries, however, exposures were more advantageous and I have now arrived at the following conclusion: There are three types of veins or segregations present at Nairne. The most conspicuous are the large veins cutting across the formation as shown in Figs. 15 and 16. The vein is six to eight inches wide near the wheelbarrow and narrows upward; the upper regions are inaccessible. The vein makes a sharp contact with the country rock and nothing could be detected which might be ascribed to hydrothermal alteration. The vein is 50% gangue and 50% sulfides. The gangue is composed of coarse-grained quartz and feldspar (oligoclase) with lesser amounts of prehnite, muscovite, and clorite; accessory apatite is present. The quartz is strained so that it gives a biaxial negative figure. The sulfides are molded around the quartz and feldspar, intergrown with the mica, and enclosed (in some instances) by prehnite. Weathering has been very active, so that the oligoclase is starting to alter to a ? hydromica, and veinlets of siderite and limonite cut the vein. There is no pyrrhotite in the vein--it has been altered to secondary FeS_2, both zoned pyrite and concentric FeS_2. Approximately 35% of the sulfides is vein pyrite and 65% is secondary FeS_2. A few traces of chalcopyrite occur but no other sulfides were detected. Either they were not there in the first place, or they have succumbed to alteration (no alteration products were found). I noted three veins of this type in Grassfire Hill, the other two being similar, but smaller. In Shephards Hill I found something slightly different. Here blasting had exposed the same type of mineralization, but in this instance the veins contained angular fragments of the country rock; these appeared unaltered. The predominant gangue minerals were quartz and chlorite, with lesser plagioclase and no prehnite; the gangue accounted for 50% of the vein minerals. The sulfides were the same as in the other veins. The veins were as much as one foot wide, but blasting had rendered them discontinuous, so that their length could not be ascertained; they could not be found in the quarry face. It is my opinion that these veins represent a specific type which is rich in quartz, feldspar, pyrite and former pyrrhotite, but very poor in Ag-Sb minerals.

The second type of vein is illustrated in Fig. 17. Here the vein is only one to two inches wide, parallels the foliation, and has little "branches" which cut the rock. This type is also found, to a lesser extent, cutting the foliation. This vein could be traced for only four feet, the length of the block containing it; it tends to wedge out on the reverse side of the block. The main gangue mineral is quartz and the ore minerals are pyrite, pyrrhotite, sphalerite and galena; some secondary FeS_2 is also present. The material was not subjected to microscopic investigation but it is not unreasonable to assume that the galena contains a number of Ag-Sb minerals. Again the gangue-sulfide ratio is 50:50. Thus in the second type the veins are smaller but contain a greater variety of sulfides.

The third type is depicted in Fig. 18. This type is characterized by irregular areas which show little respect for the foliation. The length of these veins appears to be limited i.e. they seem to form elongate irregular "pockets" instead of clearly defined veins. The main gangue mineral is still quartz, but in addition there is abundant scapolite, chlorite and tremolite, the latter commonly occurring as elongate tan-colored crystals. The "vein" minerals commonly seem to merge with the country rock so that there are not the clear cut relationships displayed by the other two vein types. The gangue-sulfide ratio is approximately 40:60. Pyrite and pyrrhotite compose roughly 40% of the sulfides (pyrite 15% and pyrrhotite 25%) and the other 60% is composed of sphalerite, arsenopyrite, chalcopyrite, galena (40%) and the Ag-Sb minerals (20%). The pyrrhotite is commonly altered to secondary FeS_2, but this varies from exposure to exposure. Thus the third type of vein is characterized by irregular outlines, limited continuous length, and an even greater variety of gangue and sulfide minerals.

In this latter type of vein the mineralogy is complex, but extremely interesting. No fewer than eighteen ore minerals were encountered, a number of which are quite rare. It should be made clear, however, that these rare minerals compose less than 1% of the sulfides in the Nairne formation; this is doubtless why, previously, they have gone unnoticed. The minerals are, in order of decreasing abundance:

Ore Minerals:

Pyrrhotite	FeS	Bournonite	$CuPbSbS_3$
Pyrite	FeS_2	Pyrargyrite	Ag_3SbS_3
Galena	PbS	Ullmannite	$NiSbS$
Sphalerite	ZnS	Breithauptite	$NiSb$
Arsenopyrite	$FeAsS$	Gudmundite	$FeSbS$
Jamesonite	$Pb_4FeSb_5S_{14}$	Stibioluzonite	$Cu_3(Sb,As)S_4$
Chalcopyrite	$CuFeS_2$	Boulangerite	$Pb_5Sb_4S_{11}$
Fahlerz	$(Cu_2Ag_2)_3Sb_2S_6$		

As alteration products of FeS:

Concentric FeS_2

Zoned Pyrite

"Zwischenprodukt"

Gangue Minerals:

Quartz

Tremolite

Scapolite

Chlorite

Plagioclase

The identification of some of the rarer minerals caused many problems. Because of the small amounts and intimate intergrowths, it was not possible to check identifications by x-ray methods. Where there is doubt I have indicated this and listed the properties observed. A number of specimens were sent to Prof. Ramdohr at the University of Heidelberg for confirmation; his comments are given below.

The pyrite commonly forms idiomorphic crystals as much as 5 cm. across. In some instances these crystals are fractured and invaded by FeS, ZnS and PbS. Rounding of pyrite grains is also common as in Fig. 20; replacement may have been active in such cases. The pyrite grains are rarely anisotropic and rarely contain inclusions.

Arsenopyrite also tends to form idiomorphic grains; these vary greatly in size. Replacement of FeAsS by the later minerals is a common feature, as in Figs. 20 and 21. Where FeAsS is in contact with pyrite, mutual boundary relations occur; the two minerals may be veined by later minerals as in Fig. 19.

Two generations of pyrrhotite are present. The earliest formed shortly after the pyrite and FeAsS crystallized; it occurs as large anhedral grains as in Fig. 22, or as veins cutting pyrite and FeAsS. The later generation seems to have formed with the galena etc.; it occurs as small rod-shaped crystals with no apparent orientation, as in Figs. 21 and 22.

Sphalerite belongs to the general time of FeS formation; it occurs as rounded grains in FeS or PbS. Inclusions and exsolution bodies in ZnS are conspicuous by their absence. It is a rarity to find even a lath of FeS in ZnS, as in Fig. 22. However, a common feature is the presence of tiny droplets of $CuFeS_2$ on the ZnS-PbS grain boundary, as in Fig. 23. It is not unreasonable to consider these droplets as $CuFeS_2$ exsolutions bodies, which migrated to the ZnS-PbS grain boundary before they could solidify. Orange-red internal reflections are present in the ZnS, indicating a fairly high iron content.

Chalcopyrite began to form with the FeS and continued to form to the end of the mineralization. It occurs as irregular, commonly snake-like areas in FeS, as in Fig. 22; as tiny droplets on the ZnS-PbS grain boundary; and as elongate areas in jamesonite-PbS — pyrargyrite intergrowths, as in Fig. 24.

Galena started to form towards the end of the FeS formation; it commonly veins FeS. PbS tends to exhibit mutual boundary relations with sphalerite so that the two were formed more or less contemporaneously. The PbS is anhedral, filling spaces. It plays host to most of the rarer minerals.

Jamesonite is the most common sulfosalt present; it commonly forms intergrowths with PbS as in Figs. 20 and 21. That the intergrowths are oriented is not surprising; the jamesonite structure may be derived from the PbS type (Hellner, 1958).

Fahlerz and bournonite presented no problems in identification. The fahlerz is completely isotropic, and has a gray color with a blue-green tint, indicating a silver-bearing variety. Bournonite is darker green than fahlerz, is pleochroic, and is strongly anisotropic. Both commonly occur together, either as rounded grains in PbS, as in Fig. 22, or as elongate grains in jamesonite - PbS intergrowths, the grains being elongate parallel to the jamesonite laths, as in Figs. 24 and 25.

The identification of pyrargyrite was confirmed by Prof. Ramdohr. It is characteristically blue, and exhibits red internal reflections. Pyrargyrite is restricted to jamesonite - PbS intergrowths, as in Fig. 25; it tends to form elongate areas. $CuFeS_2$ is commonly associated with the pyrargyrite, as in Fig. 24.

Also associated with pyrargyrite is a brown-gray, strongly anisotropic mineral (Fig. 25). Its properties are:

Hardness: approx. that of pyrargyrite
Color: brown
Pleochroism: distinct, brown--brown with gray tint
x-Nicols: moderate to strong color effects

Because of the color and association with parargyrite I thought it might be sternbergite $AgFe_2S_3$. However, Prof. Ramdohr thinks it might be an unusual member of the stibioluzonite family $Cu_3(Sb,As)S_4$; the properties of both minerals can be very similar, especially in very small amounts.

Ullmannite, gudmundite, and breithauptite commonly occur together as in Fig. 26. The breithauptite was confirmed by Prof. Ramdohr; it is characterized by its strong pink-orangeviolet pleochroism. Prof. Ramdohr was not positive about the ullmannite, but could not think what else it might be. It has approximately the same hardness as gudmundite, breithauptite, and FeS; it is isotropic, and is somewhat lighter in color than PbS. The association with breithauptite, as in Fig. 26, is not uncommon; it is very likely that this mineral is ullmannite. Gudmundite was not in the specimens sent to Prof. Ramdohr. The mineral has a high reflectivity (higher than FeAsS) and is moderate to strongly anisotropic; the association is typical. All three minerals are not uncommonly late in forming, either by dissociation of pre-existing minerals, or by reaction caused by an influx of Sb and/or Ni (Ramdohr, 1955, p. 477 and 673). Such seems to be the case at Nairne. Note the relationships in Figs. 24, 26 and 27. Ragged borders against jamesonite, FeS, and PbS are common, as are remmants of jamesonite, FeS, and PbS in ullmannite. Nickeliferous FeS, PbS, and jamesonite could dissociate to yield these three minerals. With a small addition of Ni and Sb any or all of the three could be formed by a reaction with jamesonite; this might be the case in Fig. 27.

Boulangerite was observed but once--as a small rounded grain in PbS. It is a difficult mineral to distinguish by optical methods alone; its identification is, therefore, strictly tentative.

The peculiarities of con. FeS_2 and zoned pyrite have been explained elsewhere in this paper. Ramdohr's (1955, p. 463) "Zwischenprodukt" was encountered in one polished section. It replaces FeS and resembles con. FeS_2 but is grayer and strongly anisotropic without any color effects; the anisotropism is continuous across the concentric cracks. In some instances it exhibits a "seismogram-like" contact with the FeS. This has also been observed by Foslie (1950) at Ofoten, Norway. Frenzel (1957) considers this Zwischenprodukt to be a weakly reflecting variety of marcasite. His x-ray powder analysis agreed with that for marcasite.

Gangue mineral relationships are relatively simple. Tremolite tends to form crystals; quartz tends to form both crystals and massive aggregates; and plagioclase and scapolite are massive. The ore minerals are molded around these gangue minerals, although pyrite is commonly interleaved with chlorite. The gangue minerals do not always occur in the same proportions; it is not uncommon for any one to predominate over the others in one exposure and to be strictly subordinate in the next.

An attempt has been made to represent the paragenetic sequence in this type of vein diagrammatically; time of formation but not relative percentages is given (Table 2).

- TABLE 2 -

Paragenesis of minerals in the Ag-Sb veins. Lines indicate time of deposition, but not amount of material deposited.

MINERALS DEPOSITED IN FISSURES DURING WEATHERING

As mentioned, a few areas of the quarry contain deposits of secondary minerals which form crustiform masses in cracks and fissures. The filling of the fissures is from the sides inward and masses of radiating or colloform aggregates are common. These minerals are a function of weathering and represent less than 1% of the ore mass. The minerals encountered are zeolite, siderite, limonite, and pyrite with or without marcasite. The depositional sequence is not too consistent, although the most common order of deposition is zeolite-siderite-pyrite. The zeolite, siderite, and pyrite form radiating masses, commonly forming small hemispheres within one colloform crust. Commonly siderite and pyrite are found in the state of partial replacement by limonite as in Fig. 28. This variety of limonite forms radial masses, most of which are probably pseudomorphs after the siderite and pyrite.

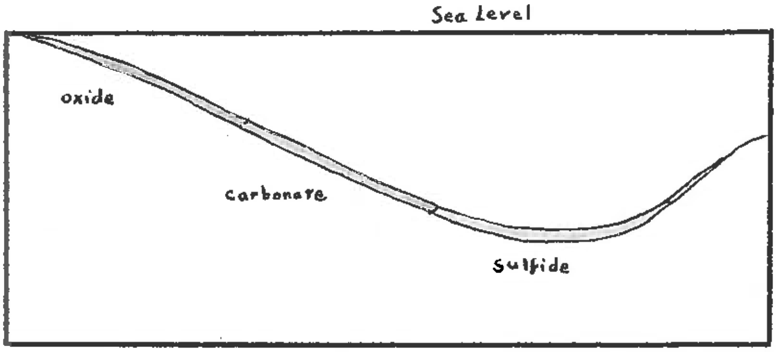
Another form of limonite is also present, and is found as pod-shaped masses, commonly surrounded by siderite. The properties appear to match those of esmeraldite, a rare variety of limonite described from limonitic rock in Esmeralda County, Nevada. It has a glassy lustre, conchoidal fracture, is very brittle, and has a hardness of 2 1/2. Under the microscope it appears as a eutectic-like intergrowth of a darker and lighter component with approximately the same hardness (Fig. 29). It is isotropic, is orange in thin section, and exhibits a few yellow-brown internal reflections under the reflecting microscope.

One commonly finds small radial areas of pyrite with or without marcasite on the outside of these masses; these have already been discussed.

ORIGIN OF THE NAIRNE PYRITIC FORMATION

The origin of the Nairne Pyritic Formation has been disputed for many years. Edwards and Skinner are the two main figures in this dispute. Edwards and Carlos (1954) maintain a hydrothermal origin based essentially on sulfur-selenium ratios. Skinner (1958), on the other hand, advocates a sedimentary origin because of the compatible relationships displayed between ore and gangue minerals, and the fact that this sulfide-bearing formation can be traced for more than sixty-five miles along its strike. I believe the results of my investigation may shed some light on this problem. However, it is first necessary to examine the methods by which a sedimentary iron sulfide deposit is formed.

James (1954) has produced the classic work on the sedimentary facies of iron-formation. In his paper he describes a hypothetical restricted basin and explains what would happen if sufficient iron were present in the water. On the wave and current-swept shelf area, oxygen is abundant and the iron would be precipitated as oxides, either hematite or magnetite, depending upon conditions. In the stagnant deepest part of the basin, little oxygen is present and organic matter yields H_2S by bacterial action. Under these reducing conditions



Hypothetical restricted basin (after James, 1954)

sulfides are precipitated. The intermediate zone is characterized by reducing conditions, but enough oxygen is present to remove organic matter, thus preventing formation of H_2S in important quantities; the product of deposition is iron carbonate.

Let us examine the area of sulfide deposition in greater detail. It is, first of all, an area of restricted circulation, characterized by an abundance of H_2S. Organic matter, settling to this bottom layer of water, is attacked by anaerobic bacteria which break up the organic proteins, thus yielding H_2S (James, 1954, p. 272). Also, sulfates, formed in higher, oxygen-rich layers of water, settle down and are attacked by sulfate-reducing anaerobic bacteria, thus yielding more H_2S (Galliher, 1933; Koyama and Sugawara, 1953). Because reducing conditions prevail, much organic material survives and is incorporated in the bottom sediments. A direct relationship is common between carbon and sulfide content. Hard (1931, p. 181) notes that, in the Upper Devonian bituminous, thinly-laminated shales of central New York State, the percentage of sulfur and iron sulfide is directly proportional to the amount of organic matter. What is the connection between organic matter and the precipitation of insoluble iron sulfide? It seems that the bacteria which thrive on the proteins in the organic matter are the important agents in iron sulfide precipitation, and not the organic matter itself. Harder (1919, p. 40-44) has shown that certain bacteria are some of the most efficient precipitating agents of iron sulfide. Gruner's (1922) experiments with the dissolving and precipitating of iron-bearing minerals show that, at low temperatures, organic matter alone does not reduce ferrous or ferric salts to iron sulfide; bacteria seem necessary. Huber and Garrels (1953, p. 352) demonstrate that, in an inorganic system, the rate of sulfide precipitation is very slow; it is apparently catalyzed in organic environments by biochemical agencies, such as bacteria. Thus it appears that organic matter favors bacterial activity which produces H_2S, and acts as a catalyst in the precipitation of iron sulfide. This combination is evidenced, not only by consolidated black sediments, but also by sediments forming today under reducing conditions, such as the sediments of the Black Sea which contain generally 2.5% pyrite and 3.0% organic substances (Wolansky, 1933, p. 400).

Phosphates are also a common feature of sediments formed under reducing conditions. Moore (1929-30) determined the P_2O_5 content in the dark muds in the locks of the Clyde Sea area and found 0.087 to 0.406% P_2O_5. Strøm (1936) has made a study of more than thirty Norwegian fjords; he finds the average P_2O_5 content of the bottom muds to be 0.22%.

Hydrogen ion concentration, and, more recently, oxidation-reduction potential, have also been studied with respect to this type of sedimentation. Galliher (1933, p. 58) calls attention to the alkaline conditions in the black calcareous muds from Monterey Bay, California; they have a pH of 8.1-8.6. Strøm (1936) found that, of twenty Norwegian fjords, eighteen had a pH between 7 and 8 in the bottom waters. Two had a pH below 7 (6.87 and 6.90), but these had a large influx of fresh water. Krumbein and Garrels (1952) have examined both pH and Eh controls in chemical sedimentation. Their diagram, Fig. 30, depicts marine reducing conditions in restricted basins as being in a pH range from 7-7.8, and below an Eh value of approximately -0.2.

In what sort of restricted basin do sediments of this nature form? There seems to be no set answer. The literature quotes marine reducing conditions and sulfide-bearing black

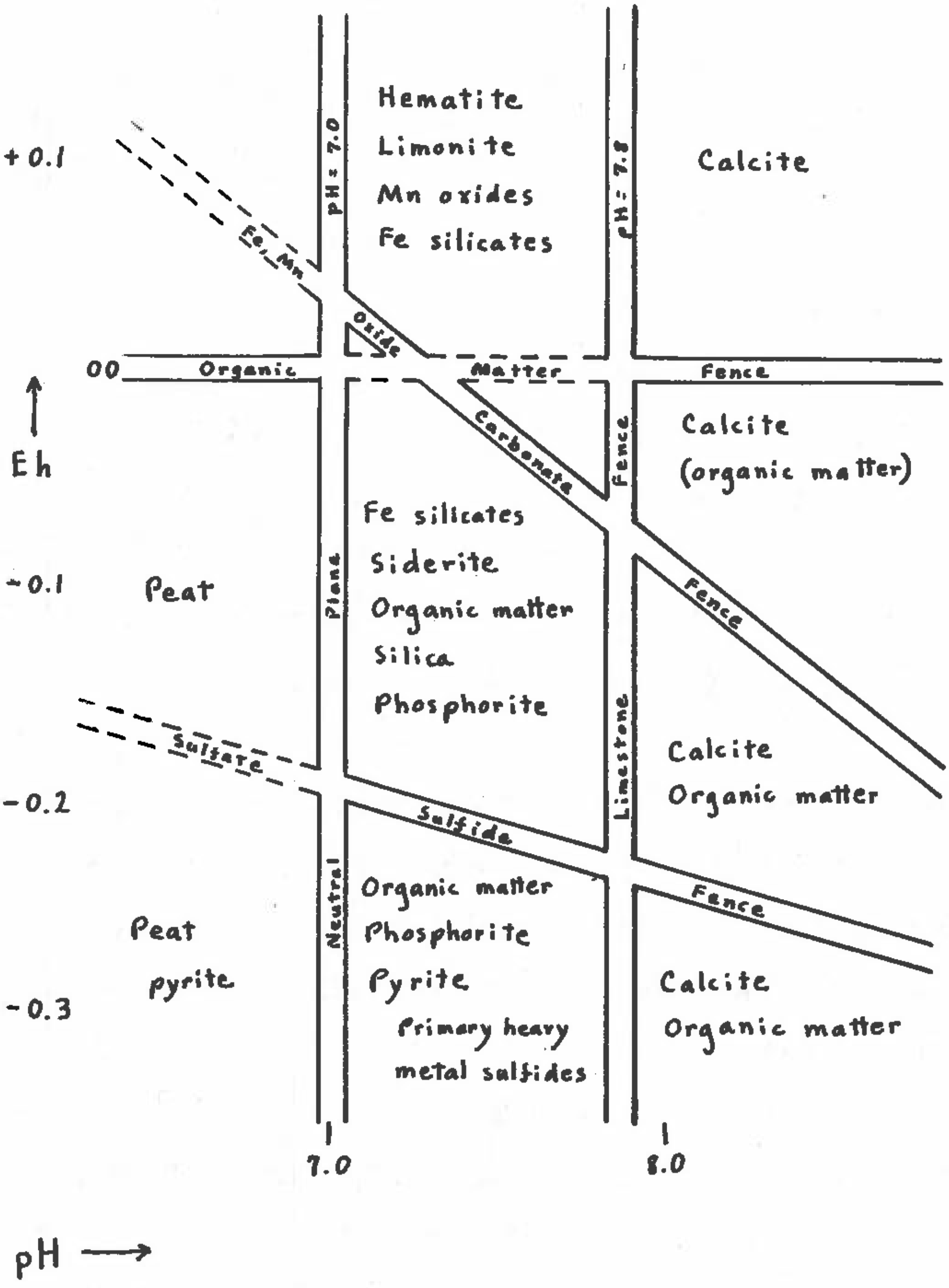


FIG. 30 Diagrammatic representation of sedimentary iron deposits based on Eh and pH. After Krumbein and Garrels (1952, p.26).

shale formation from such diverse areas as the shallow reed-filled bays along the shores of the Baltic (Twenhofel, 1915) and the considerably deeper fjords of Norway (Strøm, 1936). Twenhofel (1939, p. 118) states the problem rather well: "There are almost as many theories of the environments of origin of black shales as there are geologists who studied them." It seems all that is necessary is a basin with restricted circulation. He comments further that, in order to produce thick widespread deposits, it would be necessary to have a large basin, most probably land locked; it would not have to be very deep.

It might be well, at this point, to review the characteristics of the Nairne formation in the light of the foregoing discussion. It has been demonstrated that the characteristic assemblage for this type of sediment is organic matter, pyrite, and phosphate. The Nairne formation contains carbonaceous material, transformed during metamorphism into fine-grained graphite. That the formation contains iron sulfides, is evident. Locally the formation contains as much as 2.2% phosphates (unpublished S. A. Dept. Mines analyses) and attention is called to the vivianite which coats small fractures. Thus the Nairne Pyritic Formation falls very easily into the Krumbein-Garrels classification in Fig. 30. It occupies the area below the sulfate-sulfide fence, between pH 7 and 7.8. Although the Eh and pH conditions during the deposition of the Nairne formation cannot now be measured, nevertheless, by analogy, it seems very reasonable to conclude that the formation could have been formed by the normal processes of sedimentation in a marine reducing environment, which could have existed in the Kanmantoo trough (further geological interpretation is not to be warranted on the basis of this investigation).

Because the formation has undergone metamorphism, it is difficult to deduce the nature of the original sulfides (assuming, for argument's sake, a sedimentary origin). Melnikovite and/or hydrotroilite are possibilities. Pyrite has often been reported from such sediments currently forming (Wolansky, 1933; Sugawara et. al., 1954). Edwards and Baker (1951) have shown that, under anaerobic conditions, marcasite is limited to an acid fresh water environment, and pyrite is restricted to an alkaline marine environment. The fact that, at Nairne, pyrite and pyrrhotite are present in roughly equal proportions, may or may not be purely a function of metamorphism. Huber (1958) has calculated an "FeS" stability field below that of pyrite. Rosenthal (1956) has produced pyrrhotite synthetically at room temperatures with low sulfide ion concentration (sulfide ion concentration decreases with decreasing Eh), and Erd et. al. (1957) have discussed the low temperature origin of smythite (Fe_3S_4) and pyrrhotite in sedimentary rocks. If both "pyrite" and "pyrrhotite" did originally form, then, according to Huber's diagram (p. 131), the Eh value at the site of deposition may have been as low as Eh = -0.5. Although this is speculation, it is not beyond the realm of possibility, and must, therefore, be considered.

Thus far in our discussion, it is clear that mineralogical and chemical evidence supports a sedimentary origin for the Nairne formation. Let us now examine the various theories on the origin of the Nairne formation and its iron sulfides. The first to be considered is Skinner's theory of origin, as it is a variation of the sedimentary theory. Skinner (1958) believes that the sulfides were deposited in a shallow water environment, and then later redeposited in a deep water basin. His main arguments for this theory are that the grain size of the sulfides reflects the grain size of the enclosing rock minerals, and that he has found graded bedding, with similar size sorting. That the sulfides are not detrital is rather apparent--sulfides are not that resistant to weathering. Instead, as Skinner suggests, they were probably deposited by chemical precipitation, possibly as hydrous iron sulfides; these were subsequently recrystallized during metamorphism. However, that they were redeposited in a deep water environment, is not only difficult to believe, but also unnecessary. Skinner places great weight on the graded bedding he has found in the formation. Graded bedding, such as this, could have been caused, he argues, by turbidity currents (p. 561).

He next deduces that the Nairne formation was deposited by turbidity currents (p. 561). He has, however, found graded bedding in only 5% of the sediments, and these beds range from 1 cm. to 4 cm. in thickness (p. 549). Turbidity currents, such as those that flow out into the ocean deep, arise on the continental shelf. Loose mud etc., mixed with water, is shaken free by, say an earthquake, and rolls down into the basin, producing graded bedding (Dunbar and Rodgers, 1957, p. 202-208). If the entire Nairne formation had been deposited in this way, one would expect more than 5% of the sediments to display graded bedding. The 1-4 cm. thickness of each bed might also be open to question.

Skinner's other main argument is that the grain size of the sulfides reflects the grain size of the enclosing rock minerals. True as this may be, it need not be caused by turbidity currents. Seasonal fluctuations in sedimentation and precipitation might be the cause. Strøm (1936) found transitional layering between black muds, clay, and sand in the bottom muds of the Norwegian fjords; something similar might have occurred in the Nairne formation. Moreover, it could easily be a phenomenon dependent on metamorphism; the sulfide grain would tend to grow to the same size as the contiguous gangue minerals. Transitional grain sizes and segregations are commonly produced by metamorphism. Turner (1941) describes a not unsimilar phenomenon from South Island, New

Zealand.

Skinner also states that the sediments could not have been original black muds (p. 561). Why this is so is not clear. Black muds are black essentially because they contain carbonaceous material or finely-divided sulfides (Dunbar and Rodgers, 1957, p. 61). The Nairne formation contains both graphite and sulfides, hence they could have been original black sediments.[1]

Thus, from the above discussion, it is rather difficult to accept Skinner's theory of redeposition in a deep water environment. There is no evidence to show that the sediments were not deposited _in situ_. The estimated 5% of the sediments which contain graded bedding could easily be a minor and local feature, and sulfide-gangue grain size relationships may be ascribed to causes other than turbidity currents.

Edwards and Carlos (1954), on the other hand, advocate a hydrothermal origin for the sulfide deposit on the basis of S:Se ratios. They state that:

> Two handpicked samples of pyrite from different parts of the orebody, each obtained from several pounds weight of ore, and a super-panner concentrate of pyrite from coarsely crushed ore, all practically free from pyrrhotite, gave S:Se ratios of 9,950, 13,082 and 13,400. [p. 38]

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[1] Singewald and van Tuyl (1930) have found a black pigment, secreted as a result of metabolic processes of bacteria, and capable of producing dark color in sediments. However, its geological importance is yet to be ascertained.

This amounts to approximately 27-32g. Se/ton or 0.0027-0.0032% Se in pyrite. The ratios on which they bare their classification are: hydrothermal 10,000-20,000; sedimentary 38,000-480,000 and higher. Because the S:Se ratio is an inverse relationship, sedimentary pyrites will have the highest ratios but the smallest amounts of Se, whereas the hydrothermal pyrites will have the smallest ratios but the greatest Se content. In their classification Nairne would be listed as a hydrothermal deposit. How valid is this conclusion? Let us examine the problem in greater detail.

How does Se occur in pyrite? Goldschmidt (1937, p. 661) states that the radii, the charges, and the ionic type discern decide ? whether or not one element will substitute for another. Comparing Se and S we find:

	valence	ionic radius	covalent radius
Se	-2	1.98	1.17
S	-2	1.84	1.04

Rankama and Sahama (1950, p. 746) find the figures in good agreement so that Se can replace S diadochically in sulfide minerals. They also state that the replacement occurs more readily at elevated temperatures (p. 746), a point worth remembering. Moreover, it is possible for pyrite to absorb only as much Se as is present in the surrounding material. What in the geochemical abundance of Se, and where does it tend to concentrate itself? Coleman and Delevaux (1957, p. 525) give Goldschmidt's values for the average Se content of igneous rocks (0.00009%) and of sedimentary rocks (0.0001%). The analyses of Beath, Gilbert, and Eppson (1939) on the rocks of the Provo Canyon, Utah, as referred to by Rankama and Sahama (1950, p. 754), show that Se is concentrated chiefly in the carbonaceous shales, being as much as 0.00963% or 96.3g/ton.

Concerning the pyrite in various deposits, Carstens (1941b, p. 37) finds, that in the pyrite deposits of Norway, a division is possible. The "sedimentary" deposits he examined contained 1-2% graphite and had a Se content of 0-1 g/ton. The hydrothermal deposits contained no graphite and had a Se content of 20-30 g/ton. This is in accord with the ideas of Edwards and Carlos. However, the deposits are not described, and the field relationships are not stated. It should be remembered that the above discussion so far has shown that the amount of Se in pyrite depends on 1) the amount available, and 2) the temperature (and perhaps also pressure) at which the pyrite formed. The work of Coleman and Delevaux (1957) sheds much light on this subject. They have studied the Se content of sulfides in the Mesozoic rocks of the Colorado Plateau. They find two types of pyrite: 1) sedimentary and 2) hydrothermal. Their figures for the Se content of pyrite are:

Triassic	p. 514		Jurassic	p. 517	
Se	average	.17%	Se	average	.0015%
Se	hydrothermal	.20	Se	hydrothermal	.0019
Se	sedimentary	.14	Se	sedimentary	.0012

Their study shows that one of the most important factors regulating the amount of Se entering pyrite is the amount of Se available in the surrounding rock. The Se content of the formations is derived from volcanic emanations and reworking of volcanic debris during the time of deposition. They find that formations rich in Se contain sulfides rich in Se and vice versa. The Se content of the hydrothermal pyrite is slightly higher than the sedimentary pyrite. This is attributed to the mineralizing solutions traversing the formation and enriching themselves in Se to some extent.

Thus it is seen that Edwards and Carlos, in deducing a hydrothermal origin for the Nairne sulfide deposit on the basis of S:Se ratios, failed to take into account two essential variables: available Se and temperature of formation. In the vicinity of Nairne the formation has been raised to the andalusite-kyanite metamorphic facies, which indicates a fairly high temperature (this will be discussed in more detail later). In addition, the sediments are carbonaceous, and Se tends to be concentrated in carbon-bearing sediments. All in all, it seems that one would expect a fairly high content of

Se in pyrite at Nairne. On the basis of these arguments, I feel that the work of Edwards and Carlos does not prove a hydrothermal origin for the Nairne sulfide deposit.

Two miscellaneous comments on the origin of the Nairne sulfide deposit may also be examined at this time. Edwards (1956), in his paper on theories relating to ore genesis, takes a critical view of a sedimentary origin for Nairne. He states that: "The field evidence generally leans strongly towards a sedimentary origin, which is perhaps the simpler and more satisfying view to take, but the laboratory evidence is commonly conflicting with this simple view (p. 106)." However, he sights no references to this conflicting laboratory evidence. He then points out the regional scapolitization in the Cloncurry district, Queensland, which "must" be described as hydrothermal. He reckons this demonstrates that stratigraphically controlled deposits, such as Nairne, could be of hydrothermal origin. As further evidence of hydrothermal activity, he singles out the 800 known copper mineralizations in the Cloncurry district. However, these form "pockets" throughout the 3000 square mile area; there is no comparible phenomenon at Nairne. It is my personal feeling, that Edwards' proof by analogy, is based on a false premise that scapolitization in one district could prove hydrothermal pyritization in another; there is no evidence of replacement at Nairne.

Knight (1957) includes Nairne in his discussion of the "source bed concept." Knight's theory is that, in effect, all sulfide ore bodies are derived from sulfides that were deposited syngenetically at one particular sedimentary horizon, and then migrated under metamorphism. Knight purports to be the original proposer of the source bed concept. It is obvious, however, that his theory is merely a variation on the original lateral secretion hypothesis, formulated in the 1880's by Sandberger. He lists Nairne as supporting evidence for his theory. His knowledge is somewhat limited with respect to Nairne, however, as he claims it has been traced for <u>3</u> miles along its strike. Also he does not directly apply his theories of mobilization to Nairne. In short, he has not clearly defined his ideas concerning Nairne, so that his statements concerning that deposit are misleading. Objections to his theories are numerous (Chamberlain, 1958; Sullivan, 1958; Phillips, 1958; Kierans, 1958).

TEMPERATURE OF FORMATION

An application of the temperature of formation of the Nairne Pyritic Formation has just been mentioned, and its importance will be felt more and more as the discussion progresses. The two means of estimating the temperature of formation, used by Skinner (1958), are the pyrite-pyrrhotite and pyrrhotite-sphalerite geologic thermometers.

Pyrrhotite found in equilibrium with pyrite varies significantly in composition with temperature. Arnold (1957 and 1958) has examined these relationships in detail. He finds that Co and Ni will affect the FeS_2-FeS equilibrium, but that effects caused by Co and Ni not in excess of 0.15% are considered insignificant; the primary pyrite at Nairne contains less than 0.15% Co and Ni. Arnold (1957, p. 194) presents a phase relation curve, showing the affects of pressure and temperature on the composition of pyrrhotite coexisting in equilibrium with pyrite, from 325° to 785°C. In general, the greater the Fe content, the lower the temp of formation; below 400°C the curves are essentially the same for 1000 and 2000 bars. Skinner reads Arnold's graph and records a temperature of 275°C (Fe = 47.35 mol. %) for the temperature of formation at Nairne. My reading is 325°C.

The solubility of FeS in ZnS also varies directly with temperature. Kullerud (1953) has expressed the relationships graphically. The sphalerite at Nairne contains an average of 15.2 mol. % FeS and Skinner reads Kullerud's data to show a minimum temperature of formation of 500°C. The results of the two geologic thermometers do not agree. Kullerud states that MnS and CdS do not appreciably affect the solubility of FeS in ZnS, provided their concentration does not exceed 2.0 mil. %. The ZnS at Nairne contains 4.0 mol. % MnS, and Skinner thinks this might invalidate the FeS-ZnS thermometer;

he therefore favors the 275°C figure from the FeS_2-FeS thermometer. However, as Fleischer (1955, p. 993) notes, a high Mn content in garnet is itself an indication of high-temperature formation.

Bartels (in press) has critically examined Skinner's work and directs attention to the andalusite-kyanite stable pair at Nairne. His review of the pertinent literature shows that andalusite, and presumably kyanite, have a stability range, under hydrothermal synthesis, from 450° to approximately 650°C. He also notes that the plagioclase at Nairne ($Ab_{63}An_{33}Or_4$ by partial analysis) is in the andesine range, and "apparently is the plagioclase feldspar found at temperatures over 500°C during metamorphism when zoisite is not present." Thus a temperature of formation in the 500°C range seems more probable than a temperature in the 275°C range.

Co, Ni, and Mn in FeS and FeS_2

Within the last decade or so much attention has been given to the Co, Ni, and Mn content in pyrite and pyrrhotite, for use as a geologic thermometer, and as a method for distinguishing hydrothermal from sedimentary iron sulfide deposits. Before entering this discussion, a word of caution must be advanced. The amount of a minor element, such as Co or Ni, present in the deposit may not be sufficient to saturate the host. If not, as Fleischer (1955, p. 975) stresses, then it cannot be used as a geologic thermometer. Needless to say, it is not always known if there was sufficient Co and Ni present to saturate the pyrite and/or pyrrhotite.

How do Co, Ni, Mn and also Zn and Cu occur in pyrite and pyrrhotite? Hegemann (1941)has considered these relationships, and in addition has investigated spectrographic analyses of 450 pyrites and 110 pyrrhotites for information concerning Co, Ni, Mn, Zn and Cu. He finds that Mn and Zn are easily removed from FeS and FeS_2 by physical means, and that they do not form sulfides with bonding similar to that of FeS or FeS_2. Therefore, Mn and Zn, when in FeS or FeS_2, are mechanical impurities and not in the crystal lattice. Cu may be present only to a very limited extent. Co and Ni, on the other hand, form sulfides with similar bonding and lattice structure and therefore, he concludes, may be present in FeS and FeS_2 as an isomorphous mixture. Thus it would seem that Co and Ni would be the only trace elements of any use, as the others would not be expected to vary with temperature or pressure or mode of occurrence. However, Hegemann(1939) found, in analyses of pyrites from 50 deposits, that "sedimentary" deposits (Rammelsberg, Kupferberg etc.) contained MnO from 0.1% upwards and that "hydrothermal" deposits (Rio Tinto, Röros etc.) contained less than 0.1% MnO. Thus Mn rich pyrites are sedimentary but "Umgekehrt braucht aber nicht jedes sedimentäre Kieserzlager Mn-reichere Pyrite aufzuweisen (p. CXXVII)."

Carstens (1942a) has applied Hegemann's findings to the pyrite deposits of Norway. He finds that the Leksdal type (considered sedimentary) averaged 0.20% Mn and the Løkken type (considered hydrothermal) averaged 0.07% Mn content in pyrite. Auger (1941) found more Mn in pyrites from high temperature gold quartz deposits than in those of low temperature gold quartz deposits. Gavelin and Gabrielson (1947), on the other hand, found little variation in Swedish pyrite deposits, even though a systematic variation in Co and Ni was apparent.

With the above observations in mind, let us consider the Mn content of the pyrite at Nairne:

	Mn
p. p.	0.07%
v. p.	0.005
z. p.	0.05
con. FeS_2	0.07

It must be emphasized that these analyses, although made on hand picked, average material, are by no means extensive and must be treated with caution. Nevertheless they give some indication, and for this reason must be considered. All the analyses fit into the hydrothermal classification--that of the vein pyrite more than the others. Does this indicate a hydrothermal origin for the pyrite at Nairne? Not necessarily. There are three factors to be considered. The first is supply. Hegemann (1939) recognized this factor when he stated that all sedimentary pyrites need not be Mn-rich. Skinner (1958, p. 557) notes that the sediments at Nairne are very poor in Mn, although the sphalerites are considerably rich in Mn (average = 2.4%). However, ZnS is known to have a great affinity for Mn, especially in high temperature deposits, whereas there is little evidence for a similar relationship with respect to pyrite. The second aspect, then, is the temperature of formation. This has already been calculated at approximately ? 500°C, which is by no means a low temperature. The third consideration is the compatability of Mn (MnS_2) and FeS_2. Hegemann (1941) has shown that Mn occurs as a mechanical impurity in pyrite and also pyrrhotite. It is not unreasonable to suspect that, because with increasing temperature pyrite tends to produce more perfect crystals (Smith, 1947), a mechanical impurity would have a greater tendency to be expelled, the higher the temperature. Thus, one would expect a relatively low Mn content in the Nairne pyrite at a temperature of formation of approximately 500°C. Concerning the Mn content of the zoned pyrite and concentric FeS_2, which are low temperature alteration products of pyrrhotite, it can only be said that the secondary FeS_2 contains only that Mn supplied by the FeS as it altered, and that that supply was doubtless meager, as FeS has no particular affinity for Mn (MnS).

Information concerning Co and Ni in sulfides is more

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extensive. The results are, however, not uncommonly erratic. Frykland and Harner (1955) failed to get any systematic variation with depth, and consider this an indication that the Co and Ni contents did not reach equilibrium concentrations for the temperatures and pressures involved in the Coeur d'Alene district, Idaho. On the more positive side, Auger (1941) found that Co and Ni are more abundant in the pyrites of the high temperature gold quartz deposits, then in the low temperature gold quartz deposits studied. Bjørlykke (1945) observed similar relationship for Co in Norwegian nickel ores. Hawley (1952) analyzed more than 200 pyrite samples from what are considered epigenetic gold-bearing quartz veins and replacement deposits in Quebec and Ontario. The temperature of formation of the pyrite was measured with a pyrite geo-thermometer (see Smith, 1927) and he noted a variation in Co-Ni ratios for different temperatures of formation. He found that the low temperature pyrites contained more Ni than Co and the high temperature pyrites more Co than Ni. Carstens (1942b) examined the Co and Ni contents of Norwegian pyrite deposits and noted that the pyrites of the "sedimentary" deposits contain more Ni than Co (0.023% Ni; < 0.001% Co) and those of the "hydrothermal" deposits more Co than Ni (0.025% Co; 0.006% Ni). Gavelin and Gabrielson (1947) found roughly equal proportions of Co and Ni in pyrites of some Swedish phyllites and gneisses (0.01-0.09%), whereas pyrites in some Swedish hydrothermal deposits contained more Co than Ni (0.01-0.09% Co; < 0.001% Ni).

Comparisons have also been attempted between pyrite and pyrrhotite "in contact" in the same deposit. Rost (1939), in his work on ten sulfide deposits in the east Bavarian Grenzgebirge, found that Co was more abundant than Ni in FeS and FeS_2 where the two minerals did not occur together. Where together, FeS_2 still contained more Co but FeS contained more Ni than Co. Rost thinks that the Ni migrated to FeS from FeS_2. Gavelin and Gabrielson (1947) found slightly less Co than Ni in pyrrhotite (in contact with FeS_2?) from Swedish hydrothermal deposits. Bjørlykke and Jarp (1950) give results for Co in general agreement with these observations (Sulitjelma, Norway: pyrite flotation conc. 0.059% Co; pyrrhotite flotation conc. 0.030% Co).

Hegemann (1943) has performed a very comprehensive study of this subject and has produced results in general agreement with the above observations. For his work he evaluated 675 of his own spectrographic analyses and 90 from Rost. He found more Co and Ni in the pyrites of hydrothermal than those of sedimentary deposits, and that sedimentary pyrites contain more Ni than Co whereas hydrothermal pyrites contain more Co than Ni. Where pyrite occurred next to pyrrhotite, he found that Ni tended to concentrate itself in the FeS, whereas Co tended to concentrate itself in the FeS_2. Of particular interest are his observations regarding metamorphic deposits. He found that with increasing metamorphism the amount of Co and Ni in pyrite and pyrrhotite increased, but that in pyrite Co catches up to, and then passes, the Ni content. If FeS is present this may be explained by Ni going into FeS and perhaps some Co going into FeS_2 from FeS. However, if FeS is not present, this relationship is more difficult to explain; he considers the possibility of Co going into Mg silicates.

What do these observations mean in relation to Nairne? Consider the Co and Ni content of the pyrite at Nairne:

	Co	Ni
p. p.	0.02%	0.01%
v. p.	0.06	0.01
z. p.	0.03	0.13
con. FeS_2	0.02	0.15

Again caution is urged in evaluating such a limited number of analyses; nevertheless each analysis represents an average sampling. It is seen that in the primary and vein pyrite there is more Co than Ni, a characteristic of hydrothermal pyrite! But let us not forget Hegemann's (1943) observation that, with increasing metamorphism the Co content catches up to and overtakes the Ni content. The Formation at Nairne represents a fairly high degree of metamorphism (epidote-amphibolite to amphibolite facies) with a temperature of metamorphism of approximately 500°C. Thus the observed relationships are completely compatible with a sedimentary origin for the deposit.

Concerning the Co and Ni content of the zoned pyrite and concentric FeS_2, it is noted that Ni is greatly in excess of Co, which is a characteristic of low temperature, or sedimentary pyrite. However, low temperature pyrite contains less Co and Ni than high temperature pyrite; something seems to be wrong. The trouble is, of course, that the formation of the secondary FeS_2 must be related to the decomposition of the FeS. We have seen that Ni tends to concentrate itself in FeS with increasing metamorphism, where FeS and FeS_2 occur together, as they do at Nairne. Thus, it is not unreasonable to suppose that Nairne pyrrhotite is enriched in Ni, and that this enrichment was passed on to the secondary FeS_2. Bravoite, nickel-rich pyrite with some Co, is a low-temperature mineral which can form 'on its own', or by alteration of some pre-existing Ni-rich mineral, such as pentlandite. This it does in an analogous way to the formation of secondary FeS_2 from FeS (Bernard and Paděra, 1954, p. 167):

$$FeS + S \rightarrow FeS_2$$

$$(Fe, Ni)S + S \rightarrow (Fe, Ni)S_2$$

An addition of S is required, as is seen in the equations; this can be carried by low temperature solutions. An example of this type of mineral formation is described by Maucher (1937) from Turkey: the diabase in the Turkal area contains nickeliferous silicates and nickeliferous FeS which, in the process of weathering, yield garnierite, pyrite, marcasite, and bravoite. Kalb and Meyer (1926) examined bravoite from Mechernich, and managed to separate the light and dark zones. Analyses gave (p. 28):

	Co	Ni	Fe	Cu	S
light zones	trace	4.40%	38.02%	2.80%	50.77%
dark zones	3.32	24.28	17.44	0.23	51.00

They conclude that Co and Ni evidently replace Fe in the lattice, and are responsible for the darker zones. Frenzel (1957) notes that zoned pyrite with Ni-rich zones is a common product of alteration of nickeliferous pyrrhotite by weathering. The zoned pyrite at Nairne is not nickeliferous enough to be termed bravoite, but it is reasonable to suspect that the darker zones represent a concentration of Co and Ni.

ORIGIN OF THE LARGE SULFIDE VEINS

The veins containing the Ag-Sb minerals at Nairne are a recent discovery; they have caused much interest because of the implications involved, both economic and theoretical. If they represent hydrothermal (magmatic) activity, then it is possible they increase in magnitude with depth. If they are "metamorphic differentiates," then an increase with depth would not be expected, as the material for the veins would be derived from the formation itself. Also, up to this point, our discussion has shown that a sedimentary theory of origin is the most acceptable for the Nairne sulfide deposit, and that all the observed relationships can readily be explained using this premise. If these Ag-Sb veins were hydrothermal (magmatic), they might prove a serious obstacle to the complete acceptance of a sedimentary theory of origin for the Nairne deposit. To this end I shall discuss the possibilities of first, a magmatic hydrothermal origin, and second, a metamorphic origin.

HYDROTHERMAL (MAGMATIC) ORIGIN

Is there any reason to suspect a magmatic origin for these Ag-Sb veins? The answer is yes. Let us examine the geologic history of the area. Sedimentation in the Adelaide geosyncline continued uninterrupted from the Proterozoic into the Cambrian. After a small erosional period following the Archaeocyatha limestone of early Cambrian age, deposition of the Kanmantoo Group began in the newly-produced Kanmantoo trough, which was somewhat to the east of the Adelaide System geosyncline (Campana, 1958). Sedimentation in the trough and in the Adelaide geosynclinal area was terminated early in the Paleozoic (?Ordovician) by an orogeny, accompanied by widespread invasion of granites, such as those occurring at Mt. Kitchener, Palmer, Victor Harbour, Murray Bridge, and generally throughout the Upper South-East (Alderman and Parkin, 1958, p. 56; Campana, 1958, p. 16; Webb, 1958, p. 138). This profuse acid igneous activity could easily have given rise to mineralizing solutions.

Are there any ore deposits in the Kanmantoo System rocks which possibly bear witness to this igneous activity? There appear to be, and I am indebted to A. W. G. Whittle for the following list of mines and localities. The Callington-Kanmantoo district contains a number of ore deposits. These include the following mines: Adare, St. Ives, Wheal Margaret, Wheal Fortune, Paringa, Kanmantoo, Wheal Prosper, Callington, Bremer, Wheal Maria, and Wheal Friendship. The deposits represent mineralization along faults and fault intersections. The ore consists of pyrite, chalcopyrite, bornite, various Pb, Zn, Bi and As minerals, and quartz gangue. In addition there is the Wheal Ellen mine near Strathalbyn with PbS, ZnS, FeS_2 and some FeAsS. The Talisker Arsenic mine at Cape Jarvis, although occurring in a Marinoan inlier, probably belongs to this general period of mineralization. It is characterized by PbS, FeAsS, FeS_2, jamesonite, and fahlerz, accompanied by intense bleaching and sericitization of the enclosing argillaceous sediments. These deposits could easily represent mineralization from magmatic emmanations released by the cooling granite, during the final stages of the early Paleozoic orogeny. Such a sequence of events is not uncommon (Bateman, 1950, p. 303-304; Lindgren, 1933, p. 878-894). On this basis, one can postulate a possible magmatic origin for the Ag-Sb bearing veins at Nairne.

How do the Ag-Sb bearing veins at Nairne compare with other veins of this type? The Ag-Sb-Pb-Au-Zn-quartz veins of south Bolivia represent hydrothermal filling of cracks and fractures in sandstone and sandy slate; the veins have a direct relationship to intrusive igneous masses (Ahlfeld, 1952). Although massive ore is present, druses are a common feature. Sulfosalts occur in druses and as massive ore in quartzite at Park City, Utah (Van Horn and Hunt, 1915). At the Silver King mine, the association is galena, pyrite, sphalerite, jamesonite, and bournonite. At the Daly West mine it is pyrite, galena, bounonite, and tetrahedrite. In the Yellowknife area in Canada, hydrothermal solutions of magmatic origin have mineralized an extensive shear system (Coleman, 1957). There are three phases of mineral deposition:

1) pyrite, FeAsS
pyrite and FeAsS shattered
2) ZnS, $CuFeS_2$, FeS
(veined by sulfosalts)
3) PbS and sulfosalts

This is very similar to the paragenesis at Nairne (see Table 2). In addition, Coleman (p. 412) states that "well-developed crystals, especially of the acicular sulfosalts, are not uncommon."

In the Lindgren (1933) hypothermal-mesothermal-epithermal classification of hydrothermal deposits, veins of this type would most closely fit the mesothermal division. Such veins are formed at intermediate temperatures (175°-300°C) and depths (4,000-12,000 feet; 140-400 atm. pressure). These deposits are fissure veins with fairly regular strike and dip, having neither the extreme brecciated structure common to deposits formed close to the surface (epithermal), nor the lenticular form and irregular openings of the deep-seated deposits (hypothermal). Smooth walls and slickensides are abundant, and both massive ore and cavity fillings are common. The ore minerals characteristic of these veins are sulfides, arsenides, sulfantimonides, and sulfarsenides (p. 530). Oxides, such as hematite and magnetite, if present, occur in small amounts. The main gangue mineral is quartz, but carbonates and plagioclase are also common. As regards zoning, the ore is apt to become more pyritic and siliceous with depth (p. 531). The paragensis is: quartz, pyrite, FeAsS, FeS, ZnS, fahlerz, $CuFeS_2$, PbS followed by Ag_2S and the sulfosalts (p. 544). Replacement of the country rock is common in limestone, but is commonly absent in the more argillaceous rocks. Emmons (1940, p. 196) reconstructs the ideal vein system, from the surface downward. In general the sulfosalts belong to the upper half of the vein system i.e. a more or less mesothermal position.

The veins at Nairne exhibit a number of similarities with the hydrothermal veins described above. There are, however, no druses at Nairne. The veins might represent the lower portion of the mesothermal range. Or then again, one might envoke Graton's (1933, p. 545) concept of telescoping. Of more critical importance is the fact that there are three types of veins at Nairne viz. 1) the 6-8 inch wide veins containing essentially pyrite, former pyrrhotite, and silicates, 2) the 1-2 inch wide veins containing a somewhat greater variety of sulfides, and 3) the irregular pocket-like masses containing the main concentrations of Ag-Sb minerals. The first two form sharp contacts with the country rock, the third an irregular contact. Are these relationships compatible with a hydrothermal (magmatic) origin? Lindgren (1933, p. 531) noted that veins of this type became more pyritic and siliceous with depth; this might have a bearing on the subject. Also there is Neumann's (1948) theory of hydorthermal differentiation in the ore chamber or enroute, similar to magmatic differentiation; this might explain hydrothermal veins of different composition in the same area. However, what about the different vein forms? The two proper vein forms are not so difficult, but the irregular pockets present more than a few objections. Why the irregular pockets? Why the unsharp contact with the country rock? Could the mineralizing solutions have traversed "solid" rock to deposit a Ag-Sb rich paragenesis only in these pockets? It is possible to expect a variety of structural and mineralogical types in a single system? McKinstry (1955), in his discussion of the structure of hydrothermal ore deposits, finds that all this is possible. Thus, so far, there seems to be no reason why the veins could not have been emplaced by hydrothermal solutions of magmatic origin.

METAMORPHIC ORIGIN

We have seen in our discussion of trace elements in pyrite, that, although the Co-Ni relationships were characteristic of hydrothermal (magmatic) pyrite, nevertheless they were also the relationships to be expected in a sedimentary deposit, which had been affected by a fairly high degree of metamorphism. It was found that the relationships in the primary pyrite were essentially the same as those for the vein pyrite. However, the vein system is characterized by a Ag-Sb rich paragenesis. Ag-Sb minerals are very rarely encountered in the main mass of ore; they seem only to be found in the veins. Could these minerals have been derived, through metamorphism, from the formation itself? And if so what could be the original source of these rare elements? I shall attempt to answer these questions. It should first be noted, however, that all the minerals in the veins--Ag-Sb minerals excepted--could easily have been derived from the formation itself. The quartz, muscovite, plagioclase, scapolite, pyrite, pyrrhotite, sphalerite, galena, chalcopyrite, and arsenopyrite are all known in sufficient concentrations in the formation. Tremolite,and chlorite and vivianite on the fractures, are minerals whose constituents are certainly present in the formation. What is necessary, then, is to account for the rarer elements, and the mobilization of them and the more common constituents, into the veins.

Dilatancy is the expansion of granular masses when deformed, due to the rearrangement of the grains (Mead, 1925). That expansion occurs is demonstrated by deforming an enclosed rubber container filled with sand, and containing just enough fluid to fill the voids in a condition of maximum density packing. Water is made available by a tube thrust into the sand--similar to a barometer for measuring changes in pressure i.e. in volume. It is found that this sand-filled container cannot be bent, squeezed, or deformed in any manner, without lowering the level of the water in the vertical tube; thus regions of dilation have been formed, due to both rearrangement of sand grains and to fracture (p. 691). Solid rocks, however, are commonly deformed under high confining pressures and temperatures. In the ideal case the rocks will yield by plastic flow, with the development of a schistore texture. This is the case when the rate of deformation,under the existing P-T conditions, is slow enough to permit a rearrangement of the molecules, and hence plastic flow. If the rate of deformation is too great, fracturing will occur. If the rate of deformation is intermediate, then deformation will be by a combination of plastic flow and fracture. The dilated zone is, of course, a region of low fluid pressure, and any available fluids will move to fill these openings. Continued deformation would produce great drawing power in the dilated zones, and would give increased mobility to the fluid phase, so that the voids could be filled. Goodspeed (1940) also reviews this method of vein formation. Actual examples are probably more common than realized. Roberts (1953) discusses the formation of quartz pods and quartz veins in Precambrian schists in Idaho. Although in a general mining district, the closest ore deposit is more than a mile distant, and the pods and veins are devoid of economic minerals. The schists have been folded, and the quartz pods are commonly localized at, or near, the crests of anticlines or the troughs of synclines. The quartz veins cut the schist. The mineralogy of the pods and veins reflects the mineralogy of the enclosing schists, quartz being the predominant mineral. Chapman (1950) has studied quartz veins in a quartz-mica-feldspar-staurolite schist in western New Hampshire. The veins consist of quartz with lesser amounts of mica, feldspar and staurolite i.e. only those minerals already present in the schists. The veins are as much as two feet wide and many tens of feet long. Some are straight, whereas others are curved, folded, irregular, lenticular, or pod like. They follow the bedding, the schistority, or cut across both. No igneous activity has been noted in the district,and all factors seem to point to a metamorphic origin. Reed (1933a, 1933b) has investigated similar metamorphic segregations in the Shetland Islands at Nor Wick, Unst. They occur in kyanite schists and are of two different types: 1) veins with clear cut boundaries (concordant and crosscutting relationships), and 2) irregular masses with indeterminate margins (1933b, p. 319). The segregations consist of quartz and kyanite, as do the schists. Of particular importance are segregations in a nearby area of tectonic movement. A major thrust movement brought forward the Skaw Granite on to the kyanite schists. The passage of the granite stretched and sheared the schists, producing phyllite rocks consisting of chlorite, sericite, epidote, quartz, and iron ore (pyrite). A pre-thrusting igneous intrusion (now "spessartite") was caught up in the thrusting but, because it was harder and more brittle than the surrounding soft slippery phyllites, it yielded by fracture. "Into these fractures came metamorphic solutions active during the chloritic retrogression of the country rocks, and from these solutions quartz, chlorite, pyrite, and traces of copper minerals were deposited (1933a, p. 133)." The composition of the veins is essentially that of the surrounding rock, but copper minerals are not known in the country rock. Reed thinks that they have been concentrated in the segregations from tiny undetected amounts in the country rock. Breddin (1930) has studied the development of quartz veins in the Rhein Schiefergebirge. In the area of the Hunrückschiefer the veins range from a few mm. to 1.5 meters in thickness. They cut across the schists in all directions, and stop as suddenly as they start. Sandstone layers are commonly interlayered with the schists, and these are characteristically fractured, and the fractures filled with quartz-chlorite veins, the material being derived from the schists. The main component of the veins is quartz, with chlorite being next in abundance. Siderite and pyrite are also present, but to a lesser extent. An interesting feature is that the areas, in which metamorphism has been the greatest, contain the most quartz veins. The same is found true for the Siegen area, the heart of the Rhein Schiefergebirge. Similar relationships hold for the East Sauerland area. Here the veins contain a great deal of carbonate--as do the middle Devonian rocks in which they occur.

Thus, from the above examples, it is clear that metamorphic differentiates exist, and that the forms they assume through dilatancy, are commonly similar to the vein forms at Nairne.

It is one thing to observe the products of metamorphic differentiation and say it therefore exists; it is another to try to explain the mechanism by which it operates. In the many theories which have been proposed, diffusion is always an essential factor; the extent of diffusion is another matter. Rankama and Sahama (1950, p. 248-257) have discussed diffusion on the basis of kinetic energy. At a given temperature and pressure, the ions (atoms) of a structure are in a state of thermal vibration and each of the ions possesses a given amount of kinetic energy. It follows that different types of ions will have different KE values (even ions of the same type may show differences). With increasing temperature and pressure, some ions, especially those which are not strictly bound to a certain structure, may acquire enough KE to exceed the migration energy (that energy or force which tends to hold the structure together). When this happens, each ion with sufficient KE is liberated from its co-ordination and is free to seek a new one. These ions form a separate phase called the dispersed phase (p. 251). This dispersed phase may be a liquid or a gas, or it may consist of ions temporarily detached from their original places in mineral structures. Thus an ion is removed from its place in its crystal structure to another point in that structure, or to the grain boundary of the mineral. Temperature naturally aids this process. As Buerger (1948) points out, a temperature high enough to allow crystal growth maintains a high level of diffusion, because it has a tendency to disorder the structure of the mineral. Such "solid diffusion" is considered important in the growth of coronas and porphyroblasts, and for the production of Mn-rich garnet in schists (Turner, 1948). Turner feels that its importance is confined to transfer of matter through strictly limited distances. Bugge (1945), on the other hand, is a decidedly firmer devotee of the efficacy of diffusion. He states that, although in the upper parts of the earth's crust numerous cracks and pores in the rocks exist, so that material may be transported in a gaseous or liquid state, at greater depths the space problem is decidedly more involved. Here the intersticies between grains are very small; the dimensions in some instances approach inter-ionic distances (p. 8). He describes diffusion through crystal lattices and explains that matter will migrate from a zone of high chemical potential to a zone of low chemical potential, these potentials being created by differential thermo-dynamic processes operative in metamorphism. He argues that high pressure produces a better contact between mineral grains, and thus increases diffusibility in the solid state (p. 27). Should pressure give rise to fluid in the intersticies, it is thought that this would produce a good contact between the grains and thus facilitate exchange of ions between grains (p. 27). Bugge examines cases of diffusion in the Archean rocks of Norway and states that, during the formation of some arendalite rocks from a heterogeneous rock complex, ions probably migrated several thousand meters (p. 38).

Other workers are convinced of short distance diffusion, but for long distances, base their theories of transport on Eskola's (1932, p. 77) solution principle. Turner (1948) envisions transport by means of aqueous pore solutions which permeate the intergranular spaces in the rock. Temperature and pressure would be the essential factors in determining the rate of solution of different minerals. Material dissolved from one system would be redeposited in a second system, either as additional constituents of a stable series, or as an independent mineral assemblage (e.g. a vein), forming a metamorphic differentiate. McCallien (1934) has examined various writings on diffusion, and also concludes that solid diffusion is limited to short distances, whereas pore solutions can transport matter great distances, forming veins etc.

From whence comes the water for these pore solutions? Born (1929, p. 334) has demonstrated that, in the area of the Rhein Schiefergebirge, the water content of the rocks is inversely proportional to the degree of metamorphism; thus water is expelled during metamorphism. Dunn (1942, p. 233) states that "early sediments etc., where deep-folded, would come under the influence of high temperatures. In this environment chemically combined water in the sediments would be in increasingly unstable combination, and would migrate from the deepest zone, possibly taking with it certain other constituents." Correns (1943) has reached similar conclusions. On the more exact side, Goodspeed (1952, p. 151) notes that "during the granitization of argillaceous sediments, the transformation of kaolin to feldspar involves a liberation of 14 percent of combined water."

Thus, a 'middle of the road' theory of transport would go something like this: As metamorphism applied differential heat and pressure effects to the rock, ions would be freed from their enclosing matrix by the process of solid diffusion. At the same time water would be released. Solid diffusion would take place over a distance measured in centimeters, just the distance to reach the nearest intergranular pore space. The net end result would be the saturation of the country rock by what would be, in actuality, a hydrothermal solution (not to be confused with magmatic emmanations).

These solutions would migrate through the country rock to areas of lower chemical potential, and lower pressure generally, caused by dilation effects. Migration would be by means of intergranular pore spaces, fractures, joints, and foliation planes. In this manner the ions would reach the site of deposition. It seems reasonable that metamorphism, applied over a long duration of time, could easily produce large scale transport of sulfides.

Are all ions mobilized with equal ease? Korzhinsky (1950) has studied the mobility of elements and oxides and explains that mobility depends upon activity of solutions, temperature, and depth, and that by using the Gibbs' Phase Rule one can establish whether an element will be "perfectly mobile" or "inert." His conclusions seem to be more a matter of observations on actual rocks, rather than calculations applied to nature. At any rate, he has found a decreasing mobility series for high, medium, and low temperature metamorphism, although temperature limits are not defined. In all cases, water, CO_2 and S are the most mobile, with Fe and P_2O_5 being moderately mobile. SiO_2 is more mobile at lower than at higher temperatures. Aleksandrov and Zmeenkova (1958) studied the alteration of iron-rich and iron-poor argillaceous rocks of the Precambrian Krivoi Rog Series and found a differential migration of matter. Lapadu-Hargues (1945), in his study of seven classes of rocks representing the various stages of metamorphism, also found a differential migration of matter. For instance, Fe was most abundant in shales (3.6%) but decreased in amount with increasing metamorphism, so that it is almost absent in granulities (0.75%). He presents his findings diagrammatically (p. 300) which shows that the ions with smaller ionic radii tend to be dispersed with increasing metamorphism (are more mobile), whereas ions with larger ionic radii tend to be concentrated (are less mobile):

> ...les ions les plus petits émigreraient et se localiseraient dans les zones les plus corticales; les plus gros, au contraire, se disposeraient de préférence dans les zones plus profondes. [p. 301]

Thus mobility is a function of ionic radius:

8 fold	Fe	Mg	Na	Ca	K	Ba
coörd.	1.27	1.60	1.92	1.97	2.36	2.25

⟶ decreasing mobility

Ba is somewhat of an aberration, but data on Ba is scarce.

In the discussion of heavy metals to follow, the picture will become more complex, but for present purposes it is sufficient to realize that all elements do not have equal tendencies to migrateduring metamorphism. Having established this principle for the more common elements, it is now possible to examine the differential migration tendencies of the heavy metals and their relation to the mobility series for the rock-forming elements. However, if the Nairne formation possesses no heavy elements other than Fe, then a discussion of that nature might politely be termed useless. It is therefore necessary to establish the presence of the rarer metals in the Nairne formation, prior to the time of metamorphism. If this cannot be accomplished, then there is no case for a metamorphic origin for the Ag-Sb rich veins.

Source of the Rare Metals in the Formation

I suppose the problem of the rare metal content of the Nairne formation could readily be solved, if a set of total analyses existed for the rocks of the Nairne formation. Unfortunately, to my knowledge, such analyses are non-extant, most probably because of the prohibitive costs involved. I believe, however, that the use of analogy will serve just as well. To this end, let us first consider the source rocks for the Nairne Pyritic Formation. Campana (1958) states that the Adelaide geosyncline was supplied with sediments by two cratonic areas--the Gawler nucleus in the West, and the Willyama nucleus in the North. Also adding to the complexity of the sediments, was material derived from lava outpourings on the stable margins of the geosyncline; these occurred during epi-Torrensian and later times (Sprigg, 1952, p.158). However, as previously noted, deposition of the Kanmantoo Group began in early Cambrian time, in the newly produced Kanmantoo trough, located somewhat to the east of the Adelaide

System geosyncline (Campana, 1958, p. 18). The source of the sediments for this trough is still open to dispute.[1] Öpik (1956, p. 277), on palaeontological evidence suggests a land mass to the east, the "Meridional Divide." The most likely possibility, is that the sediments were derived from the Gawler nucleus to the west, and travelled across the area of the Adelaide System. The Gawler nucleus is essentially Eyre Peninsula and Yorke Peninsula. The Archean rocks of Eyre Peninsula are described by Johns (1958, p. 61-63) and those of Yorke Peninsula by Horwitz and Daily (1958, p. 47-49). In general, a great variety of rock types are present. The majority are slates, phyllites, schists, quartzites, graywackes, banded ferruginous rocks, gneissic rocks, and acid igneous intrusions. In addition there are numerous dikes and sills of both acid and basic types. Thus most of the rocks were of an acid character, although some basic rock types were also present; iron-bearing sediments and metasediments were common.

Goldschmidt (1932) points out that the trace element concentration of a sediment is a good indication of the nature of the rock from which it was derived. Conversely, knowing the rock type one should be able to predict, with reasonable accuracy, the relative amounts of various trace elements which

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[1] I am indebted to Dr. A. W. Kleemann of the University of Adelaide for his helpful notes on this topic.

should be found in the sediment. That igneous rocks and rock minerals contain rare metals, has been known for many years. Sandberger (1878) analyzed minerals from a number of different rocks. In two micas from volcanics he found Cu; in another mica Cu, Pb, Co, and Sb; in micas from gneiss Cu, Co, and Sb; and in basaltic hornblend Cu and Co. Becker (1888) had analyses performed on large quantities of fresh granite (in one case 15.5 pounds) in the Steamboat Springs area, California. The heavy metal examination showed As, Sb, Pb, Cu but no Au or Hg (Ag might have been present in the Pb). Rabbitt (Kaiser et. al., 1954) found distinct amounts of Co, Mo, Ni, Sn and V (Cu, Pb, Zn not tested) in kyanites from North Carolina. Clarke and Steiger (1914) found Ni, Cu, Zn, As, and Pb in a composite sample of 329 American igneous rocks, and Clarke (1924, p. 640-641) gives many references to base metals in silicates and igneous rocks.

Wager and Mitchell (1950) have studied the Skaergaard intrusion for the distribution of Cr, V, Ni, Co, and Cu. They found that, in general, Cr, Ni, and Co were concentrated in the more basic portions, V in the intermediate basic rocks, and Cu in the more acid portions. In contrasting siliceous (average 71.93% SiO_2) and sub-siliceous (average 51.67% SiO_2) rocks, Sandell and Goldich (1943) found that Ni, Co, Cu, and Zn favor basic rocks, and Pb and Mo favor acid rocks. Wilson (1953) found that metals with smaller ionic radii tend to be concentrated with basic rocks, and metals with progressively larger ionic radii with progressively more acidic rocks. Thus he found (p. 380):

Ion	ionic radius	peridotite	gabbro	diorite	granodiorite	granite
			Concentration g/ton (or ppm)			
Fe^3	.67	21500	22100	22100	12300	11000
Ti^3	.69	4200	5810	5040	3400	2300
Ni^2	.78	3160	158	40		2.4
Co^2	.82	237	79	32		8
Cu^2	.82		149	38		16
Fe^2	.83	58400	46300	34200	20600	13800
Zn^2	.83		90	120	200	30
Pb^2	1.32		5			30

Three elements in the Ag-Sb veins not considered by Wilson are As, Sb, and Ag. If his classification holds, we should find As^3 (.69) associated with basic rocks, Sb^3(.90) with slightly acid rocks, and Ag^1 (1.13) with acid rocks. Recent analyses by Onishi and Sandell (1955) show that Sb has no preference for acid or basic igneous rocks, which is approximately what would be expected. Thus at Nairne, on the basis of source rocks alone, we should expect to find abundant iron (concentration factor) and more Cu, Pb, Zn, Sb and Ag than Ni, Co and As.

Another possible source of heavy metals must be mentioned. The postulated source is underwater vulcanic exhalations.

Hegemann (1948a) supports such a theory, especially for deposits like Rammelsberg which are rich in base metals. Oftedahl (1958) extends this theory to include many "sedimentary" base metal deposits. His theories, however have not gone unchallenged (Kautsky, 1958; Landergren, 1958; Marmo, 1958). Although this may be a possible source for the heavy metals at Nairne, I know of no field evidence to support it.

It might be argued that the concentration of base metals in igneous rocks would hardly be great enough to have made any effect at Nairne. However, as Rankama and Sahama (1950) indicate by data they have collected, these elements tend to concentrate themselves in shales (p. 226):

g/ton or ppm

Element	Igneous	ss	shale	ls
S	520	2,800	2,600	1,100
Ti	4,400	960	4,300	
Mn	1,000	trace	620	385
Fe	50,000	9,900	47,300	4,000
As	5		5	
Ni	80	2-8	24	0
Co	23	0	8	0
Cu	70		192	20.2
Zn	132	20	200-1,000	≤ 50
Sb	1	1	3	
Ag	.10	.44	.05	.2
Pb	16	20	20	5-10

This is especially the case for carbonaceous sediments (Rankama and Sahama, 1950; Onishi and Sandell, 1955; Schneiderhöhn, 1955, p. 259). Schneiderhöhn (1949) analyzed a number of pyritiferous carbonaceous rocks from the upper Silurian in Thuringia and Saxony. He found the following concentrations (g/ton): Ti 860, V 900, Cr 52, Mo 156, Mn 70, Ni 63, Cu 66. Krauskopf (1955) made an extensive survey on the distribution of rare metals in various sediments. His data show that such elements as Fe, Pb, Zn, Cu, Se, Co, Ni, Ag, and Sb definitely tend to be concentrated in organic sediments. The process by which the rare metal sulfides would be precipitated, is essentially that already described for the precipitation of iron sulfide. In addition, concentration of rare metals in living organisms themselves, may be an important factor (p. 447).

Thus, by a study of rare metal content in source rocks, and the preferential concentration of the rarer metals in carbonaceous sediments, such as the Nairne formation, it is seen by analogy, that the Nairne Pyritic Formation must have contained at least small amounts of the rare metals before it was metamorphosed.

Relative Mobility of Sulfides

In speaking of the relative mobility of the sulfides, it should be understood that we are dealing with migrating ions, and not sulfides as such. Ramdohr (1953b) examined the sulfide relationships at Rammelsberg, the Witwatersrand, and Broken Hill. He notes that many of the sulfides have been recrystallized and pyrite has been cataclastically broken, but they have not wandered far from their sites. Schröke (1953) reports similar observations. This is not the problem at Nairne as I see it; what we have to contend with are migrating ions. It is obvious, that if the Ag-Sb minerals have been concentrated by metamorphism in the veins, it is because these elements are very mobile. Why are they more mobile, and what is the order of mobility? In dealing with the rock forming minerals we found that ionic radii were of practical value. However, in dealing with sulfides, it must be remembered that the structures deviate considerably from an ionic structure and there are numerous variations (Rankama and Sahama, 1950, p. 106). Szádeczky-Kardoss (1953-54) introduces a new concept--the ionic specific weight (Ionenwichte) which is a function of the ionic weight (A) and the ionic volume:

$$I = \frac{A}{4/3 \pi r^3} = \frac{3A}{4 \pi r^3}$$

This produces a series with little agreement as to ionic radius. Upon calculating a few values for heavy metal ions, I found no particular correlation with observed facts. Vinograd and McBain (1941) and Garrels et. al. (1949) have tried experiments employing diffusion of ions through pore solutions and in electrolytes. These experiments are conducted at room temperature without anything such as H_2S pressure being used. I feel their geologic application is somewhat limited. An interesting observation, however, is that in mixed salts, the general effect is to speed up fast ions and to retard slow ions. Also buffering action is very important. Sullivan (1957) suggests that paragenesis, and hence mobility, may reflect the thermal stability of minerals in the solid state. He deals with heat of formation, and to satisfy his conditions, he must transport his ores as vapors. Krauskopf (1957) on the other hand, has calculated the vapor pressures of the common metals and sulfides at 600°C and 1,000 atm pressure. Even at this P-T range it is apparent that "the low vapor pressures of most free metals, and the negligible decomposition of most metal sulfides at 600°C, indicate that transportation of metals as metal vapor cannot play a significant role in ore formation (p. 806)." Hence no mobility series based on vapor pressures, or even metallic melting points, seems possible (p. 806).

Let us turn to the "simpler" theory of solubility. Because the sulfides must dissolve before they can be transported, it follows that the most soluble will stay in solution the longest and thus be transported farthest. Weigel (1907) was the first to systematically determine the solubilities of the sulfides; this he did in pure water at 18°C. He used crystallized sulfides, both natural and artificial, and sulfides precipitated in the lab. He found the following order of decreasing solubility (p. 294):

Crystallized	Precipitated
MnS	MnS
FeS	ZnS
FeS_2	FeS
Wurtzite	CoS
NiS	NiS
CdS	CdS
Sphalerite	Sb_2S_3
Cu_2S	PbS
PbS	CuS
SnS_2	As_2S_3
Ag_2S	Ag_2S
SnS	Bi_2S_3
	HgS

Weigel notes the discrepancies between the two columns but cannot explain them. It will be noted that Weigel's order of decreasing solubility is approximately the order of crystallization in nature, although certainly not without exceptions. The only trouble is, that the most soluble are crystallized first! Bruner and Zawadzki (1910a, 1910b) discredit the work of Weigel on the basis of his calculations, and produce their own order of decreasing solubility which varies but slightly from that of Weigel. Kolthoff (1931) points out that Weigel did not carry out his experiments under oxygen-free conditions.

It is possible that Weigel measured, at least in part, the conductance of the metal hydroxides formed by oxidation of the sulfides. He also objects to Weigel's calculations of the solubility from his conductance measurements. Weigel assumed that, in his saturated solution, hydrolysis of the sulfide ion was complete, forming H_2S and OH^-. Kolthoff shows that it was mainly hydrolyzed to HS^-. Also the age of the precipitate is important. Freshly precipitated sulfides are, as a rule, not present in the stable form, and therefore exhibit a higher solubility. Weigel does not indicate the age of his precipitates, and neither do Bruner and Zawadzki. Kolthoff shows that the results of later workers clash because of this factor. Ravitz (1936) supports Kolthoff's attack on Weigel, and concludes that Weigel may really have measured the solubilities of the oxidation products on the surfaces of the sulfide minerals. He recalculates the solubilities and although they are slightly different numerically, the order is essentially the same. Verhoogen (1938) approaches the problem from a theoretical point of view, incorporating ideas concerning free energy of formation of sulfides, which varies with temperature considerations. Using Ravitz's values he calculates the solubilities to 400°C. He finds the sulfides more soluble, but in essentially the same order of solubility. As Verhoogen notes, there is still no explanation for the observed order in nature. In addition, solubilities have been so low (PbS:

3.62×10^{-11} at 25°C; Ravitz, 1936, p. 69) that it is indeed doubtful if enough material could be transported in this fashion. Garrels (1944) emphasized this point. His experiments showed that dilute and weakly acid and basic solutions are not capable of being effective metal carriers. Or, as Garrels put it more dramatically: "A volume of dilute solution equal to that of the Mediterranean Sea must have passed between the walls of every vein containing a few tons of copper ore (p. 480)." Hemley (1953) investigated a new angle, namely the solubility of PbS in H_2S saturated saline solutions at various pH values. He found that Pb was present to the extent of approximately 10^{-6} grams/liter at pH 1-8; this is in excess of the concentration predicted on the basis of the solubility product. His data indicate the existence of complexes such as $Pb(HS)_2$ and possibly $Pb(HS)_3^-$. The formation of these complexes is favored by increased S concentration (increased temperature) and acid to neutral pH conditions. Cu and Ag have also been reported to form sulfide or bisulfide complexes. He calculated the solubilities on that basis and found, in order of <u>increasing</u> solubility: Cu-Pb-Ag, the order of deposition observed in nature. However, the amount of material in solution was still rather small. Barton (1957) concludes, from experiments conducted at 25°C and 1 atm pressure, that the H_2S pressure would be too low to form heavy metal complexes of geologic proportions. More recently, however, Barnes (1958) has investigated the solubility of ZnS in H_2S saturated H_2O. The polarographically measured solubilities of ZnS exceed 10 mg/liter at 75°C and 300 psi; this is more than 10^6 times the calculated solubility product under these conditions. The solubility seems to be controlled by the formation of complex ions of the type (ZnS x H_2S). Even more recently Barnes (unpublished communication to Dr. M. L. Jensen, Yale) has achieved a solution of ZnS at 50°C and 300 psi containing 50 grams/liter!

It is evident from the above discussion that, although great advances are being made, at the present time our knowledge of sulfide solution and deposition is too meager to attempt a differential solubility classification. Worthy of note, however, is the importance of H_2S which has recently been demonstrated. During metamorphism of the Nairne formation, material for forming sulfide ion complexes would have been abundant, thus facilitating transport of heavy metals.

Although theoretically and experimentally we cannot yet predict sulfide mobilities, we can take recourse to observed relationships in nature. Taupitz (1954) has produced a painstaking work on the behavior of ore minerals during metamorphism. In addition to published material, he has made use of the extensive collections at the Clausthal mining school and also much unpublished material. He starts his discussion with sedimentation and notes that under mildly reducing conditions FeS_2 precipitates; under stronger, ZnS and then PbS with As and Sb; very strong, Cu, Ni, Co, Ag, Au; and finally, V, Mo, U and Cr (p. 108). Simple diagenesis, without particular temperature or pressure, merely consolidates the sediments, and the ore minerals develop in place. With slight differential stress some ore minerals, quartz, and chlorite may begin to migrate to fractures as at Ergani-Maden in Turkey. With increasing metamorphism and tectonic stress, the ore minerals wander farther, and fill larger low pressure zones in the rocks, as at Rammelsberg, where fractures in the country rock are filled with quartz and calcite, but fractures in the ore body zone also contain ore minerals. As a more detailed example, he refers to the sulfide deposits at Klingenthal-Graslitz in the Erzgebirge, which are ore pockets in quartz phyllites. Where the phyllites have been tectonically stressed, openings have formed and filled with the more mobile elements, with quartz, chlorite and feldspar as gangue. The ore in the country rock and in the pockets was analyzed; the most mobile of the ore elements had enriched themselves in the ore pockets (p. 313):

	Ore in country rock	Ore in pockets and veinlets
Cu	1.01 - 1.95%	7.87%
S	35 - 46	23.81
Fe	46.3 - 52.9	35.28
Co	-	.20
Ni	.1	.1
Sb	-	.08
Sn	-	-
Bi	-	.27
As	.06 - .30	.18
Ag	trace	70 g/ton
Au	trace	2 g/ton

He lists a number of other examples, and from his observations on different deposits, he has deduced the behavior of the ore minerals during metamorphism (Table 3). A careful study of his chart, coupled with a consideration of the foregoing discussions on metamorphism, definitely indicates that the Ag-Sb rich veins at Nairne could have been formed by metamorphic processes. In the veins at Nairne, silicates, pyrite, and pyrrhotite predominate; this is a concentration phenomenon. That the rarer metals are also represented is a function of their great mobility under metamorphic conditions. As concerns differences in mineralogy in the veins, one could postulate that the large veins formed swiftly,being filled with readily

- TABLE 3 -

Behavior of the ore minerals by epi to mesozonal metamorphism. After Taupitz (1954, p. 135).

Behavior	Mineral	Tendency for idioblastic formation in original environment	Tendency for enrichment in mobilized material as opposed to original ore	Migration Distance
Very Mobile	Siderite Magnesite	often noteworthy	moderate to very great	very far: as much as Kms.
Relatively Mobile	Co-Ni arsenides Bi, Ag, Au Spiesglanz Quartz	little	often amazingly great	often relatively far: mostly less than 100 m
	FeAsS (Fe,Co)AsS	noticeable		
	$CuFeS_2$, PbS	small	moderate	
	Chlorite	noteworthy		
Moderately Mobile	Fahlerz	very small	great	small? possibly noteworthy
	ZnS, FeS	very small	moderate to small	mostly not far
	Feldspar Calcite	commonly noteworthy		
Rather Stable	Pyrite Hematite	great	little	mostly small
Stable	Magnetite	great	very small	almost nil

available material (quartz, feldspar, FeS, FeS_2); the narrower veins formed less swiftly, and incorporated also some of the rarer metals; the discontinuous, irregular pockets took the longest time to form, and as dilatancy separated the rock grains, the mobile rarer metals migrated to this area of low pressure, perhaps even displacing silicates to some extent. This is, of course, speculation, but not without evidence.

COMPARISON WITH SIMILAR DEPOSITS

We have seen in the foregoing discussion, that the Nairne Pyritic Formation, as a whole, can most logically be accounted for on the basis of sedimentary and subsequent metamorphic processes. The Ag-Sb vein system presents a few more problems and it is seen that, although the veins could have a magmatic origin, all the observed relationships may be ascribed to metamorphic phenomena. To attempt to discern between the two origins is difficult because of the relatively high degree of metamorphism, experienced by the Nairne formation at the site of the quarry, the only place where sufficient unweathered material is available. Prof. Rudd suggested to me that a comparison of the Nairne deposit with similar deposits might be of useful consequence. To this end I have examined, by means of the literature, every pyrite deposit to which I could find reference; a complete bibliography is appended. Needless to say, sufficient information on each deposit was not always available, and in many instances similarities were not great enough to cause the deposit to be mentioned in this report. Caution must be exercised. It usually follows that that which is mentioned is there, but not that that which is not mentioned is not present. An obvious example is that Skinner (1958) makes no mention of the Ag-Sb veins. Or further, Ward stated in 1927 that some boring had been done at Nairne, and that the concentrates from the cores consisted of approximately 50% pyrite, 30% pyrrhotite, and 20% insoluble matter; the concentrates were free from Pb, Cu, As, and Ag!

Lake Superior Region

One of the major occurrences of pyritic carbonaceous slate is in the Iron River-Crystal Falls district of Michigan, just south of Lake Superior. Here the productive iron formation is underlain by these black slates, having an average thickness of 50 feet (James, 1954, James and Dutton, 1951; Pettijohn, 1952). The slate is typically thin banded, with enough carbon to yield a distinctly graphitic streak. The pyrite content varies from layer to layer, ranging from a few percent in some, to approximately 75% in others. For the most part the pyrite is not visible, even where it composes 40% of the rock. Locally, where the rock is slightly metamorphosed, the pyrite grains have grown larger and are quite visible. Analyses of the graphitic slate show, in addition to FeS_2 and C, as much as 0.20% P_2O_5 (James, 1951, p. 255, Nanz, 1953); no reference is made to rare metals. These pyritic slates are of Huronian age and are considered sedimentary, essentially because it is hard to imagine hydrothermal solutions depositing three different types of iron-bearing units (pyrite, siderite, magnetite) in the same series of rocks with no overlapping.

Certain similarities with Nairne are noticed. Although more FeS_2 is present in these rocks then at Nairne, the mineral assemblage is essentially the same and some layers are more pyritic than others. Nairne represents a much higher grade of metamorphism.

Pettijohn (1943) describes the Archean sediments of the southern Canadian shield. A large portion of these are graywackes and associated slates which are noteworthy for two features--their pyrite and their carbon content. The pyrite is scattered throughout the graywackes and slates and tends to form cubes which attain a larger size in the graywackes than in the slates. Pettijohn interprets this as a function of primary sedimentation i.e. the permeability and grain size of the sediments governed the migration and growing ability of the FeS_2 deposited concurrently with the sediment. Thus the more permeable and large-grained graywackes made for larger and fewer pyrite crystals, whereas the less permeable and finer-grained slates produced smaller and more abundant crystals (p. 948). At Nairne the sulfides also tend to grow to the same size as the contiguous rock grains.

The pyrite is commonly concentrated along certain layers or along the bedding planes, similar to Nairne. In addition, carbon is scattered throughout the rocks and imparts to them their gray color. The carbon tends to be concentrated in pyrite rich zones, and a common origin is therefore thought very probable.

The graywackes display graded bedding and minor slump structures. The graded bedding occurs on a much larger scale than at Nairne and the beds range from one inch to thirteen inches in thickness. After a careful resume of such features in other deposits, he concludes (p. 950-956) that the graded bedding observed in the graywackes was caused by annual fluctuations in conditions of deposition!

The deposits are considered sedimentary and lie in the metamorphic series between those described above by James, and those at Nairne. No mention was made of the rare metals.

Newfoundland

The Wabana iron ore forms part of a series of Ordovician sediments, which are exposed on Bell Island in the south central portion of Conception Bay (Hayes, 1915). The beds, although tilted, are not metamorphosed to any extent. The ore zone is approximately eighty-three feet thick, and iron-rich beds alternate with iron-free sandstone and shale layers. Most of the beds are oölitic hematite, but pyritiferous beds also occur. The pyrite oölites have a concentric structure, and incorporate fragments of shells and graptolite fossils. The oölites are rich in phosphate and the shale matrix is black with abundant fossil remains. Although of limited applicability to Nairne, nevertheless, these pyrite beds are of marine origin and FeS_2, phosphate, and carbon are present.

St. Lawrence and Jefferson Counties, N. Y.

The pyrite deposits of St. Lawrence and Jefferson Counties occur in distinctive rusty-weathering pyritic gneisses, belonging to the Precambrian Grenville Series of metasedimentary and mixed-rock formations (Smyth, 1912; Miller, 1926; Prucha, 1956). The gneisses are essentially chloritic and graphitic quartz-feldspar-mica gneisses, containing disseminated pyrite with or without pyrrhotite. The belt can be traced for tens of miles and the total thickness of the Grenville Series in this region is 15,000-16,000 feet. The gneisses represent a higher degree of metamorphism than found at Nairne, but the mineral relationships are essentially the same. As at Nairne, the pyrite tends to have crystal outlines and the pyrrhotite tends to be anhedral. The pyrite occurs as "disseminated grains, coarse knots, reticulating stringers, and cross-cutting dikelets in rusty gneiss gangue (Prucha, 1956, p. 343)." Traces of $CuFeS_2$ and ZnS were noted in the polished sections examined by Prucha; Ag-Sb minerals were not detected. Graphite is widespread in the gneisses; it commonly occurs without pyrite but pyrite never occurs without it (Smyth, 1912, p. 167). The deposit is considered of sedimentary origin, essentially because the pyrite is confined to the carbonaceous gneisses. Another reason is that at Balmat and Edwards the pyrite deposits lie within a few thousand feet stratigraphically of the magmatic Pb-Zn belt, but do not contain any significant amounts of these sulfides (Smyth, 1917; Brown, 1936 and 1947).

At Balmat and Edwards the main band of gneiss is two hundred feet thick. The ore deposits occur in limestone as replacement phenomena. Pyrite, ZnS, PbS, FeS, hematite, and magnetite are the characteristic ore minerals. The hydrothermal mineralization evidently affected the limestone because they had the greatest porosity, but did not touch the gneisses, because they had the lowest porosity (Brown, 1948).

Thus far we have examined sedimentary pyrite deposits which, although apparently containing no Ag-Sb minerals, show many similarities with the Nairne deposit. Let us now turn our attention to deposits in which the rarer metals have been noted.

Poland

The Szipot Series in the Carpathians represents Flysch type sediments and extends through Poland. It is seven hundred and fifty meters thick and is divided into five units. Sedimentation is depicted as occurring in a basin or trough. At the time the third unit was deposited the basin was deepest. In this unit Ni-bearing shales were discovered by Z. Sujkowski (1936 and 1938) in 1935. The shales are black, gray, green and red, and are lower Cretaceous in age. The rarer metals are concentrated in the black and gray carbonaceous, Mn-rich shales. These shales contain different kinds of nodules, such as small concretions of pyrite, millerite and arsenopyrite, rather large bulks of Mn, carbonates, and cayeuxite nodules. The cayeuxite nodules (named for Prof. L. Cayeux) are dark black, have a hardness of 7, Sp.G of 3.15-3.20, and look homogeneous. A typical analysis gave (1936, p. 139):

SiO_2	15.36%	Al_2O_3	1.22%
S	10.17	MoO	1.20
As	13.42	ZnO	.40
Sb	21.61	Cr_2O_3	.18
Fe	16.76	MnO	.08
Ge	5.85	CoO	traces
MgO	1.95	CaO	traces
P_2O_5	1.60	NiO	.87
CO_2	1.60		

The most numerous type of nodule is the pyrite-marcasite nodule which contains substantial amounts of Sb, As, Se, Pb, Zn, Ni, and Co. It is of interest to note that Cu was never found. The assemblage of rare metals is in general agreement with the average composition of the shales.

It seems that the mineralization is contemporaneous with the deposition of the shales, as it is confined to them exclusively. Also, igneous rocks are unknown in the region.

Here is a remarkable concentration of rare metals. These sediments are unmetamorphosed but it is not hard to see that we have a potential Rammelsberg--only the metamorphism is needed. Nairne is, of course, not anywhere as rich in rare metals as these shales, but it is evident that heavy metals can be concentrated through chemical sedimentation.

Germany

No discussion on sedimentary sulfide deposits would be complete without reference to the Mansfeld Kupferschiefer and also to Rammelsberg. The literature on both is very extensive. However, because the origin of both is still undecided, a short commentary will suffice.

Kupferschiefer

The Kupferschiefer stretches for many kilometers. Carbonaceous matter and pyrite are ubiquitous and an average of 3% Cu is present. Also represented are economic amounts of Ag, Mo, Pb, Zn and V, with traces of Ni, Au, Pt and others (Schneiderhöhn, 1955, p. 264-266). Schneiderhöhn (1955) interprets the Kupferschiefer to be of sedimentary origin. Shouten (1946b) declares the Cu-Pb-Zn mineralization epigenetic because of replacement textures, but maintains a syngenetic origin for the pyrite and carbonates, as they are the minerals most commonly replaced. However, he comments that "The origin of the solutions containing copper, lead, and zinc, and the path followed by them, were omitted from the discussion (p.538)."

Rammelsberg

Rammelsberg is characterized by a concordant "banderz" texture, and the ore consists of pyrite, FeS, PbS, ZnS and $CuFeS_2$, but with economic amounts of Sb, As, Cd, Ag, Co, Bi, Sn, Ni, Hg, Au and others. Berg (1933) and Schmidt (1933) advocate a sedimentary origin, with subsequent tectonics moving the ore into the neighboring country rock. Kraume (1954), who has spent many years at the mine, visualizes a series of submarine exhalations on the floor of the middle Devonian sea, with quiet periods during which normal sedimentation occurred--thus the banded structure. During metamorphism of the Variscan period, the ore was recrystallized and a small part remobilized, this wandering into the neighboring areas. Schouten (1946a) proposes an epigenetic origin on the basis of "replacement" textures. Ramdohr (1953a), however, retaliates, demonstrating that many of Schouten's replacement textures are products of chemical sedimentation.

Pfaffenreuth

A more productive deposit, from the standpoint of similarities with Nairne, is that at Bayerland (Pfaffenreuth) described by Maucher (1939). The ore occurs as a series of small ore lenses, which are concordant with the enclosing Ordovician phyllites and garnet-mica schists. The area has been stressed and metamorphosed. Post-Ordovician igneous activity (acid and basic) is present. The main ore minerals are FeS_2, FeS, ZnS, $CuFeS_2$ and PbS, with a little FeAsS.

In addition, a number of Ag-Sb veins cut the main ore. Their width is commonly measured in centimeters, but veins as much as one foot in width have been noted. The veins consist essentially of quartz plus the rare minerals; some veins are essentially rare minerals with a little quartz. PbS is the most common and forms intergrowths with jamesonite. FeAsS forms crystals very similar to those in the galena at Nairne. Also present are FeS, FeS_2, ZnS, $CuFeS_2$, bournonite and other sulfosalts. Maucher contemplates the origin of these veins. The veins could be magmatic or metamorphic; he reckons they are probably metamorphic and that they represent concentrations of the more mobile elements.

Finland

Ylöjärvi

The general rock types of the Ylöjärvi area are basic tuffitic schists, acid volcanics, and phyllites derived from the volcanics by weathering (Simonen and Neuvonen, 1947). There appear to be no pyritic carbonaceous sediments. Metamorphism varies from the greenschist to the amphibolite facies. The areas containing the sulfides are quartz-sericite masses, derived from the enclosing volcanics by an addition of Ca and SiO_2 (Saksela, 1947). These masses were impregnated with pyrite crystals and numerous pyrite veins (usually 1 cm. wide) parallel to the schistocity. The pyrite is fractured and intruded by FeS, ZnS and $CuFeS_2$. Ag-Sb rich quartz veins formed next. These tend to follow the schistocity but also cut across it along fractures. In these veins pyrite and FeAsS were the first to form, followed by FeS, PbS and the various sulfosalts. The deposit is held to be hydrothermal, essentially because of the quartz-sericite metasomatism. The origin of the solutions is not known for sure, but it is suspected they arose through granitization north of the area. Thus a pyrite deposit with late Ag-Sb veins which does not appear to have a sedimentary origin. Because the deposits are in volcanics, and the area has locally experienced strong metamorphism, one could postulate a lateral secretion theory, the ore constituents having been derived through metamorphism from the surrounding volcanics;

a somewhat similar theory has been proposed by Stanton (1955) for the lower Paleozoic mineralization near Bathurst, New South Wales. However, this must remain speculation.

Lake Pyhöjärvi

Marmo and Mikkola (1951) have investigated the graphitic sulfide-bearing schists of Finland. They have come to the conclusion that the greater part of the sulfides are syngenetic and were mobilized during the folding and metamorphism. Concentrations of FeS, ZnS and $CuFeS_2$ are always connected with points corresponding to minimum pressure (p. 10). At Lake Pyhöjärvi, FeS is intergrown with graphite demonstrating a contemporaneous origin. They consider the first stage of mineralization to have been the formation of FeS and lesser amounts of ZnS and $CuFeS_2$ parallel to the bedding. The second stage consisted of pyrite veinlets which cut the rock, and are concentrated in areas of negative pressure, much the same as the pyrite veinlets at Nairne. No Ag-Sb minerals were noted.

Outokumpu

The Outokumpu ore deposit has long been one of the strongholds of the magmatists(Väyrynen, 1935 and 1939; Vähätalo, 1953; Schneiderhöhn, 1955, p. 326-327). The rocks of the Outokumpu complex include quartzites, black phyllitic schist, mica schist, and skarn rock; the skarn rocks are considered a product os regional metamorphism. The schists are graphitic and contain sulfides. The ore itself contains 27.5% Fe, 27.0% S, 40.0% SiO_2, 4.5% Cu, 1.0% Zn and 0.2% Co, 0.1% Ni, 1 g Au/ton, 12 g Ag/ton (Väyrynen, 1939, p. 85). Recently Saksela (1957) described, in great detail, the relationships in the Outokumpu ore district. The ore deposit is in quartzite but is closely related to the contiguous graphitic schists. In the schists can be found, in varying amounts, all the metals in the ore; pyrite and pyrrhotite are abundant in the schist. The ore fills fractures and brecciated areas as well as intergranular spaces in the quartzite--replacement is not the ore-building mechanism (p. 298). Saksela reasons that the graphitic schists were the source of the sulfides in the quartzites. During metamorphism the schists behaved plastically but the more brittle quartzites fractured, producing open spaces. The ore then migrated, under temperature and pressure, to these more structurally favorable places. No Ag-Sb veins were noted. Concerning a hydrothermal origin, he comments that the "parent" granite has not yet been found.

Sweden

Skellefte District

The Skellefte ore deposits, until recently, have been viewed as being hydrothermal (Schneiduhöhn, 1950, p. 324-355). Gavelin (1955) has taken a new approach. He notes that many of the deposits are situated in volcanics (with inliers of sediments) not far below the graphite-bearing phyllites and schists; these graphitic rocks are sulfide-bearing. On the basis of field evidence, Gavelin concludes that the vast granite and gneiss areas to the south of the Skellefte district were formed by metamorphism. This granitization led to mobilization of the granitic masses which finally pushed toward the north i.e. the Skellefte district. Large amount of graphitic schist were doubtless subjected to this regional metamorphism, and the mobile ore minerals migrated as a consequence. During the metamorphism, the graphitic sediments deformed plastically but the volcanics tended to deform by fracturing, producing areas of low pressure into which the ore constituents migrated.

Lindsköld

The Lindsköld ore belongs to a group of Cu-bearing iron sulfide deposits occurring within the altered Archean volcanics in the NW part of the Skellefte district in northern Sweden. Gavelin (1945) encountered two small veins in the ore deposit, each averaging 1-2 cm. wide, with pinching and swelling. Although small differences in composition occur in the veinlets, in general they are characterized by an assemblage of As-Co-Ni-Ag sulfides with lesser amounts of Sb, Zn, Pb, and Cu sulfides. In addition, quartz, calcite, and zeolites are present. Druses are not uncommon. Gavelin (p. 15) entertains the idea that these veins may represent selective remobilization of the primary ore.

Laver

Ödman (1945) has discovered a similar pargenesis from the Laver mine in the same district. In this case Ni-Co-Ag sulfides occur along a 5-15 cm. wide brecciated fault zone. Also, $CuFeS_2$, Fe, ZnS, FeS_2 and quartz, calcite and zeolites are present.

Eastern Högkulla and Bjurliden

Eastern Högkulla and Bjurliden are sulfide deposits occurring in siliceous rocks with interbedded tuffitic leptites and amphibolites. As is common in the Skellefte field, sulfide-bearing graphitic phyllites are in the intermediate area (Högbom, 1935). According to Gavelin and Gabrielson (1947) Bjurliden has been strongly metamorphosed and Högkulla less intensely. Gavelin (1936) describes a number of veins which cut the banded ore. These contain Pb-Cu-Ag-Sb sulfides and quartz. It is also noted that these elements are found in sulfides scattered throughout the main ore consisting essentially of FeS_2, FeS, and ZnS. The paragenetic relationships are essentially those found in the veins at Nairne.

Norway

As mentioned in the discussion of Co, Ni and Mn in pyrite, two classes of pyrite deposits are recognized in Norway--the Lökken type (hydrothermal, strongly metamorphosed) and the Leksdal type (sedimentary, weakly metamorphosed). One of the general ways of distinguishing a hydrothermal from a sedimentary deposit in Norway, has been by the size of the pyrite crystals. The sedimentary pyrite crystals are commonly less than 5μ whereas the hydrothermal are commonly 50-200μ in diameter (Carstens, 1941a).

Sulitjelma District

The deposits at Sulitjelma have always been somewhat of an enigma. Most workers have considered these deposits to be hydrothermal because of the large crystals of pyrite. Carstens, however, finds that the crystals enclose fragments of quartz, mica, ZnS, $CuFeS_2$, etc.; they are porphyroblasts, a product of metamorphism. Locally, the deposits have been intensely metamorphosed (amphibolite facies) and FeS, ZnS, $CuFeS_2$ and PbS are developed. Krause (1956) has executed detailed field work at the Sulitjelma deposits. The ore bodies occur in carbonaceous Silurian sediments. In actuality, pyrite occurs throughout the formation, but is found in workable amounts at only a few places e.g. Jakobsbakken. The pyritiferous sediments can be followed for more than 30 km.

They have been folded into broad anticlines and synclines, and have been metamorphosed to biotite schist in the vicinity of Jakobsbakken, but the degree of metamorphism varies from mine to mine. The ore follows the bedding so that Krause must conclude (p. 142): "...dass es sich hier um eine einzige grosse Lagerstätte handelt, die lediglich in mehrere bauwürdige Abschnitte aufgeteilt ist." For these reasons he regards Sulitjelma as a syngenetic, metamorphosed ore deposit; the similarities with Nairne are apparent.

Jakobsbakken

Jakobsbakken has been studied by many workers, but it was not until 1937 that the Ag-Sb veins were discovered, by Ramdohr (1938) on a visit to the mine. Ramdohr points out that veins of this nature in pyrite deposits are more ubiquitous than is commonly thought. As in the veins already described from other Scandinavian deposits, these contain a paragenesis very similar to that at Nairne. Brethauptite and ullmannite are missing from Jakobsbakken, but all the other minerals are represented, plus a number of rare sulfosalts. FeAsS "skeletons" occur as they do at Nairne (Fig. 20) and gudmundite appears to have arisen in FeS by an addition of Sb (p. 286), not unlike Nairne. Krause (1956) has also examined the Ag-Sb rich veins and he considers them a product of metamorphism: "Die antimonreichen Paragenesen dürfen wahrscheinlich metamorphe Mobilisate gedeutet werden (p. 146)."

Thus, from our discussion of pyrite deposits which show similarities to Nairne, we find that the relationships at Nairne are typically syngenetic. No one deposit described had all the characteristics displayed at Nairne, but the essential similarities were there. Metamorphism has complicated the issue to some extent. In the case of the Ag-Sb rich veins, it is seen that such an occurrence in pyrite deposits is not as rare as is commonly thought. In most every instance the vein minerals represent an enrichment of elements which are already present in the main sulfide mass, and this phenomenon may, in most instances, be ascribed to metamorphic processes. These Ag-Sb veins are not recorded for every syngenetic or mobilized pyrite deposit. It is possible that these elements were not present in the first place; it is also possible that they have gone unnoticed.

SUMMARY AND CONCLUSIONS

A study of the sulfide mineralogy at Nairne shows that there are present at least five varieties of FeS_2. The main bulk of the FeS_2 occurs as small grains of pyrite distributed parallel with the bedding. Some of the FeS_2 occurs as larger grains of pyrite in a vein system containing a suite of Ag-Sb minerals. Three varieties of secondary FeS_2 are present. Two of these, concentric FeS_2 and zoned pyrite, are the result of pyrrhotite alteration. The concentric FeS_2 consists of pyrite, marcasite, or pyrite and marcasite. It is characterized by a porous concentric structure and is extremely fine grained, thus presenting problems in flotation. The zoned pyrite is characterized by a zoned texture, most probably occasioned by concentrations of Co and Ni forming darker zones. It may be either a direct replacement of the pyrrhotite or a replacement of the concentric FeS_2. The boxwork structure, commonly formed by the zoned pyrite, is probably related to orthorhombic tendencies in the pyrrhotite crystal structure. The third variety of secondary FeS_2 occurs with zeolite, siderite, and limonite and is a product of weathering.

In addition to pyrite, pyrrhotite is a main constituent of the ore; there are lesser amounts of sphalerite, chalcopyrite, galena, rutile, and arsenopyrite. Graphite is a ubiquitous constituent of the formation and is responsible, to some extent, for its gray color. Vivianite and chlorite are found coating small fractures, and are believed to have been formed during metamorphism.

The large sulfide veins cut the formation, and contain no less than eighteen ore minerals, some of which are quite rare. Three types of veins are present: 1) 6-8 inch wide veins consisting essentially of pyrite, former pyrrhotite, and gangue, 2) 1-2 inch wide veins which contain a greater variety of ore minerals, and 3) discontinuous irregular pockets containing the main mass of the Ag-Sb minerals.

The origin of the Nairne Pyritic Formation has been studied from a theoretical point of view. It is found that the formation has all the characteristics of a sediment deposited under marine reducing conditions. The three important features--carbon, pyrite, and phosphate--are all present, and sulfide-gangue relationships are those developed between compatible minerals; there is no evidence of replacement. Skinner's (1958) theory of deposition in a shallow environment, and then later redeposition in a deep water basin, is found to lack sufficient support. All his criteria may be accounted for without envoking redeposition in a deep water basin. Edwards and Carlos' (1954) theory of hydrothermal origin, based on S:Se ratios for pyrite, is also found untenable. By evaluating two essential factors--available Se and temperature of formation--which Edwards and Carlos did not consider, it is found that their S:Se ratios for Nairne pyrite are completely compatible with a sedimentary and subsequent metamorphic origin for the sulfide deposit.

The criteria of geothermometry are applied to the deposit, and it is found that a temperature of formation (metamorphism) in the 500°C range seems more probable than Skinner's 275°C selection.

A study of Co, Ni, and Mn in pyrite shows that the observed relationships in the primary pyrite (and also the vein pyrite), are those which would be expected in a sedimentary pyrite deposit, which had been subjected to a fairly high degree of metamorphism.

Thus, as concerns the origin of the Nairne Pyritic Formation, there are no known features at Nairne which definitely point to a hydrothermal (magmatic) origin. Conversely, all observed relationships are those which would be expected in a sedimentary pyrite deposit which had, during metamorphism, attained a temperature of 500°C, and had reached the amphibolite facies.

The Ag-Sb rich vein system presents a greater variety of problems. There are other ore deposits of magmatic derivation in the Kanmantoo, so that to claim a magmatic origin for the veins would set no precedent. In addition, the mineralogy, and physical relationships between veins and country rock, are compatible with a hydrothermal (magmatic) origin.

The idea was entertained that these veins might be metamorphic differentiates, the vein material having been derived from the surrounding country rock. A survey of the literature established the reality of metamorphic differentiates, and showed that the forms they assume, through dilatancy, are commonly similar to the vein forms at Nairne. Furthermore, a theoretical discussion of ion transport during metamorphism, clarifies the processes by which ions may travel to areas of low pressure, and also shows that all ions do not have the same degree of mobility. Thus, it is possible that the Ag-Sb mineral constituents might be more mobile than the other constituents in the rock, and would therefore tend to concentrate themselves in areas of low pressure. By analogy, it was shown that at least small amounts of the rarer metals existed in the Nairne formation before metamorphism, but an attempt to deduce the relative mobility of the elements, based on experimental and theoretical data, was fruitless, because of the present limitations of scientific knowledge. However, an extensive study by Taupitz (1954) of observed metamorphic relationships in nature, demonstrates that a theory of metamorphic origin for the Ag-Sb vein system is completely tenable.

Thus, the origin of the Ag-Sb vein system at Nairne cannot readily be determined. The observed relationships seem compatible with either a magmatic or metamorphic theory of origin.

A comparison of the Nairne Pyritic Formation with similar deposits, demonstrates that the relationships observed at Nairne are typically syngenetic. Ag-Sb veins in pyrite deposits appear more ubiquitous than is commonly thought. The literature lists numerous examples, and after a careful study of field relationships, most authors have reached the conclusion that these veins represent an enrichment of elements already present in the main sulfide mass, effected by metamorphic processes.

The Ag-Sb vein system at Nairne contains elements present in the surrounding rock. Because it would be natural to expect metamorphic differentiates at Nairne (based on theoretical grounds, and recorded instances in similar deposits) the author feels that, although a magmatic origin is possible, a metamorphic origin for the veins at Nairne is the most realistic.

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FIG. 1 Incipient growth of lenticule in country rock. Thin section. x 150

FIG. 2 Portion of developed lenticule surrounded by finer-grained area. Thin section. x 45

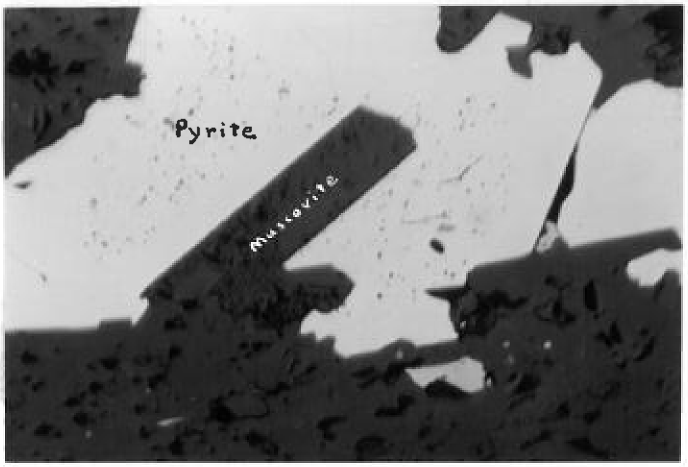


FIG. 3 Pyrite partially enclosing uncorroded muscovite lath. Polished section. x 84

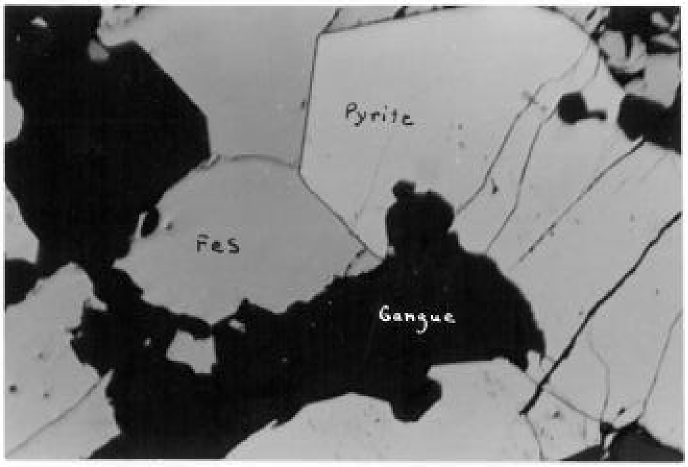


FIG. 4 x 84 Pyrite in contact with FeS and gangue.

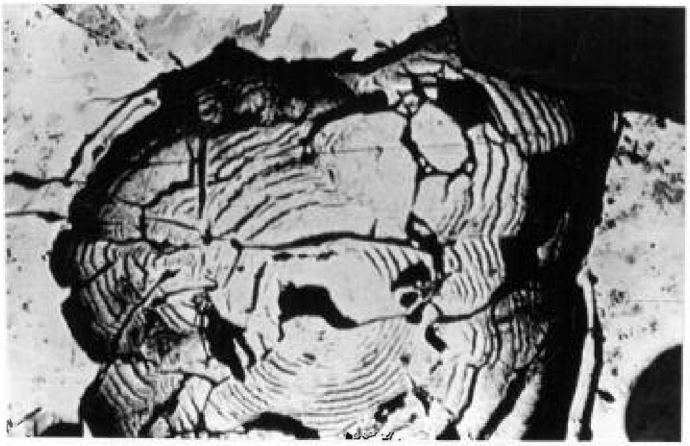


FIG. 5 Concentric FeS_2 in pyrrhotite. Note concentric cracks. x 84

FIG. 6 Fragments of FeS and con. FeS_2. Contrast smooth, shiny surface of the FeS with the rough, irregular surface of the con. FeS_2. x 30

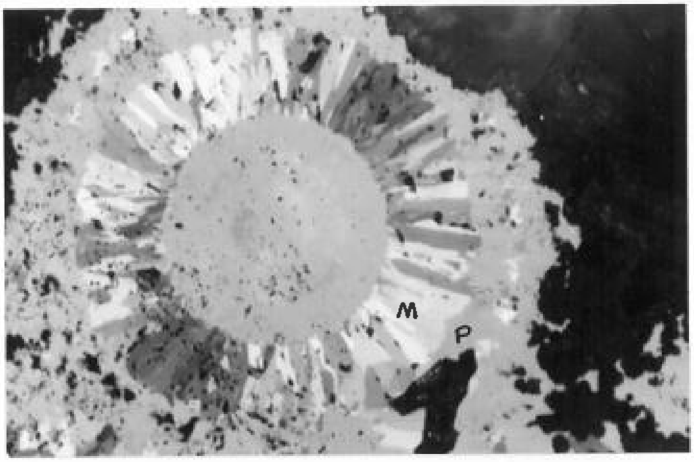


FIG. 7 Nodule of secondary pyrite and marcasite. Marcasite is betrayed by its anisotropism. x 250 crossed Nicols

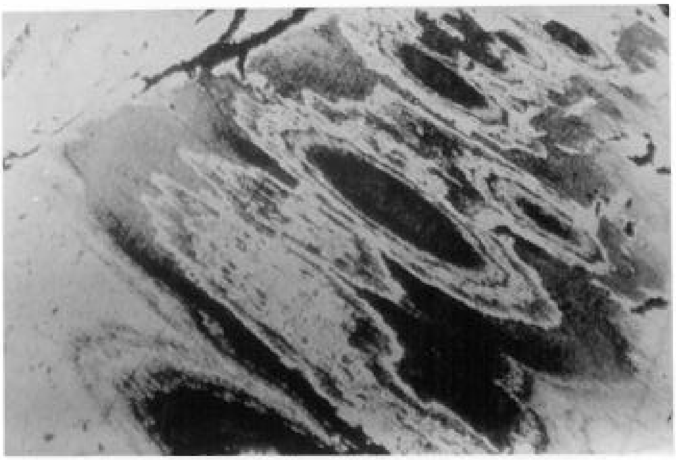


FIG. 8 Cigar-shaped areas of con. FeS_2 in zoned pyrite. Marcasite is etched black with 1:1 HNO_3. x 84

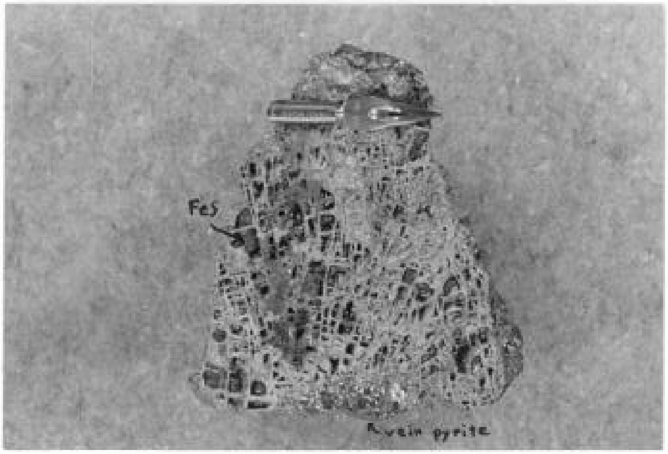


FIG. 9 Secondary FeS_2 boxwork containing remnants of FeS. Note shiny cube of unaltered vein pyrite. x $\frac{1}{2}$

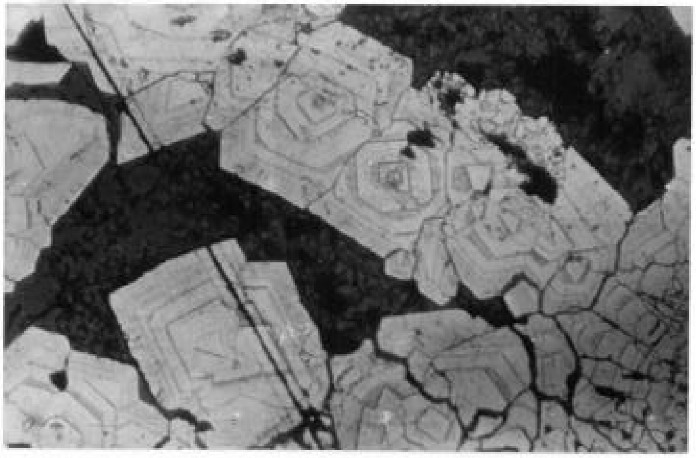


FIG. 10 Zoned pyrite. Etched. x 84

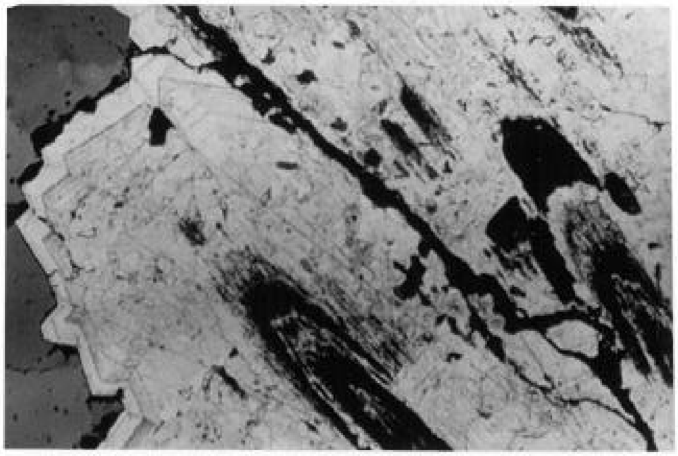


FIG. 11 Zoned pyrite with core of con. FeS_2.
Etched. x 84

FIG. 12 Zoned pyrite cutting con. FeS_2.
Etched. x 84

FIG. 13 Cavity containing patches of FeS_2 on limonite on siderite. x 3/4

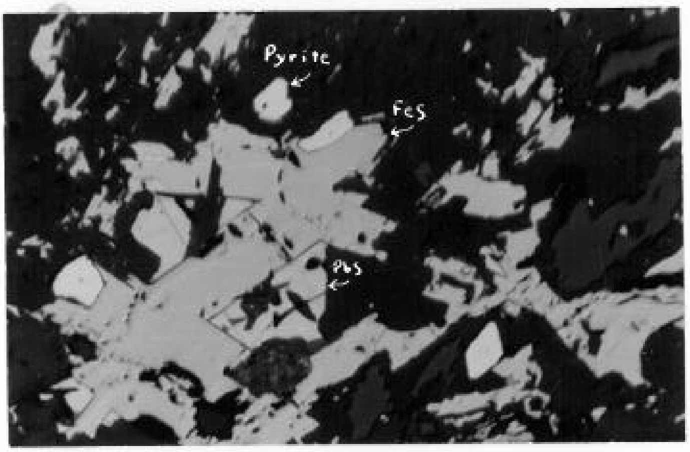


FIG. 14 Pyrrhotite laths with interstitial galena. x 84

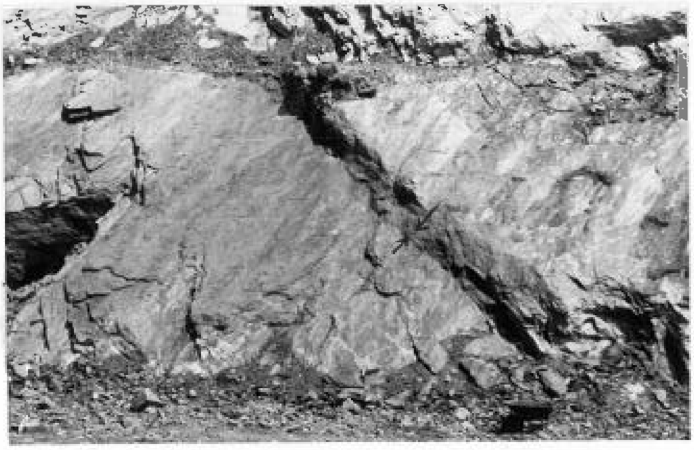


FIG. 15 Grassfire Hill; 1320 level. Quarry face showing 6-8 inch wide vein. Wheelbarrow for scale.

FIG. 16 Grassfire Hill. Vein trace on quarry face.

FIG. 17 Shephards Hill. Block containing 1-2 inch wide vein.

FIG. 18 Shephards Hill. Block containing irregular veins rich in Ag-Sb minerals.

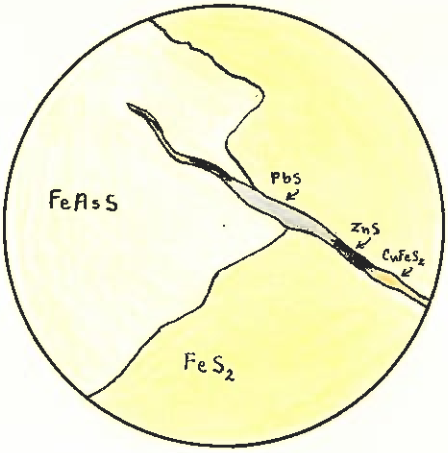


FIG. 19 Pyrite and FeAsS exhibiting mutual boundaries texture, and cut by veinlet containing PbS, ZnS and $CuFeS_2$. x 100

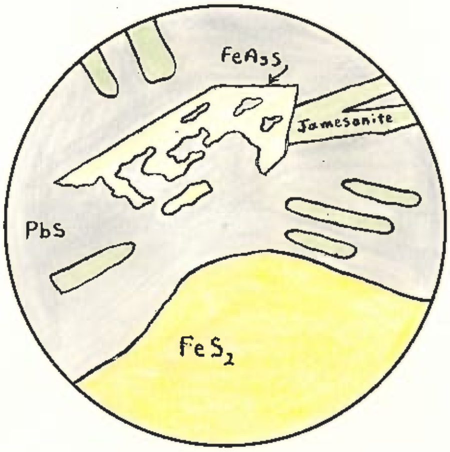


FIG. 20 PbS replacing FeAsS. Also, laths of jamesonite in PbS. x 100

FIG. 21 Jamesonite-galena intergrowth, with laths of FeS and corroded grains of FeAsS. x 84 crossed Nicols

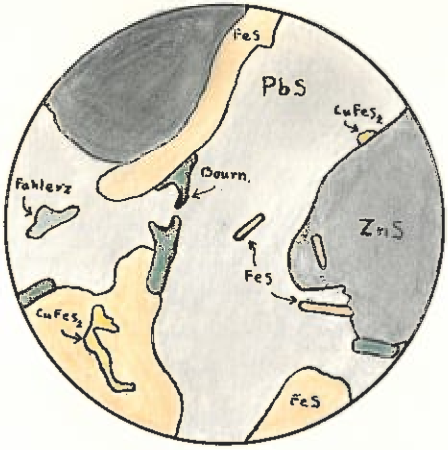


FIG. 22 FeS as anhedral grains and small laths. Note sinuous area of $CuFeS_2$ in FeS. Black is gangue. x 100

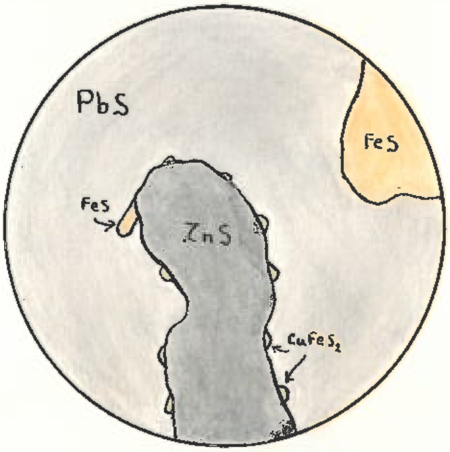


FIG. 23 Droplets of $CuFeS_2$ on ZnS-PbS grain boundary. x 100

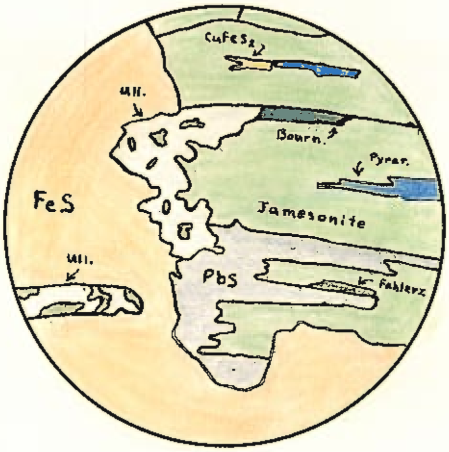


FIG. 24 Intergrowth of PbS, fahlerz, $CuFeS_2$, jamesonite, bournonite and pyrargyrite. Note ullmannite containing ?remnants of FeS and jamesonite. x 200

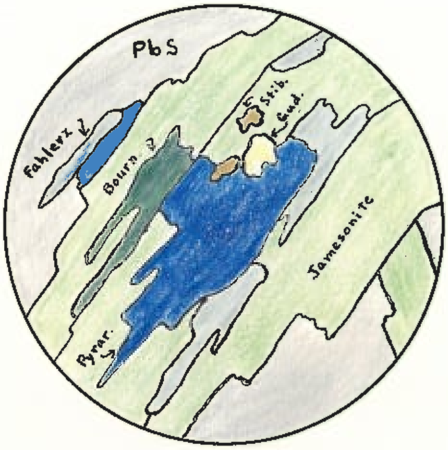


FIG. 25 Intergrowth of jamesonite, fahlerz, PbS, bournonite, and pyrargyrite. Note occurrence of ?stibioluzonite and gudmundite. x 200

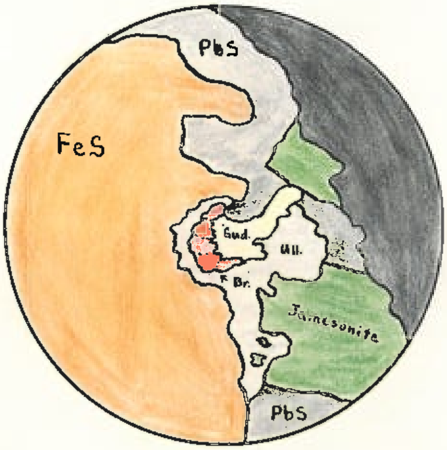


FIG. 26 Ullmannite, gudmundite, and breithauptite occurring together. Note ragged border against FeS, PbS, and jamesonite. Black is gangue. x 200

FIG. 27 Breithauptite and ullmannite. Note ragged boundary against galena and jamesonite. x 250

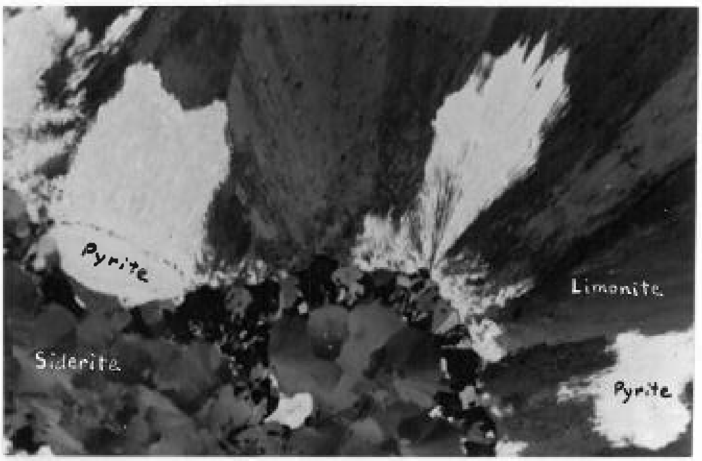


FIG. 28 Limonite replacing secondary pyrite. x 84 crossed Nicols

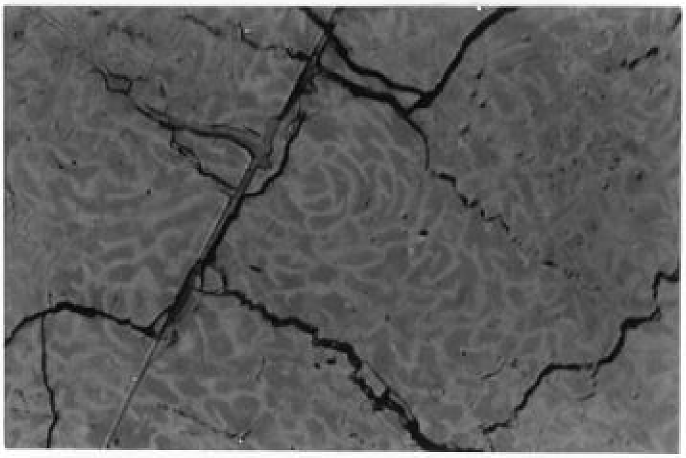
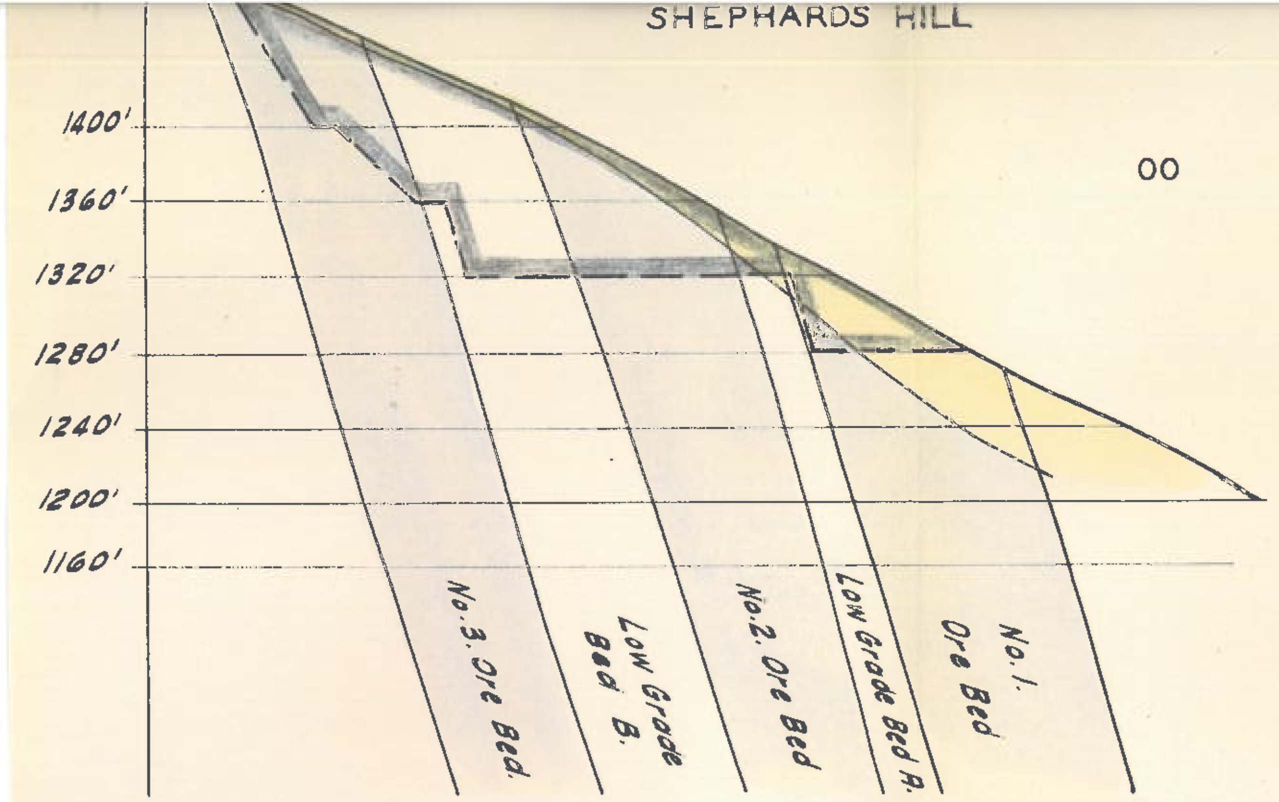


FIG. 29 Esmeraldite. Note eutectic-like intergrowth of lighter and darker component. x 84

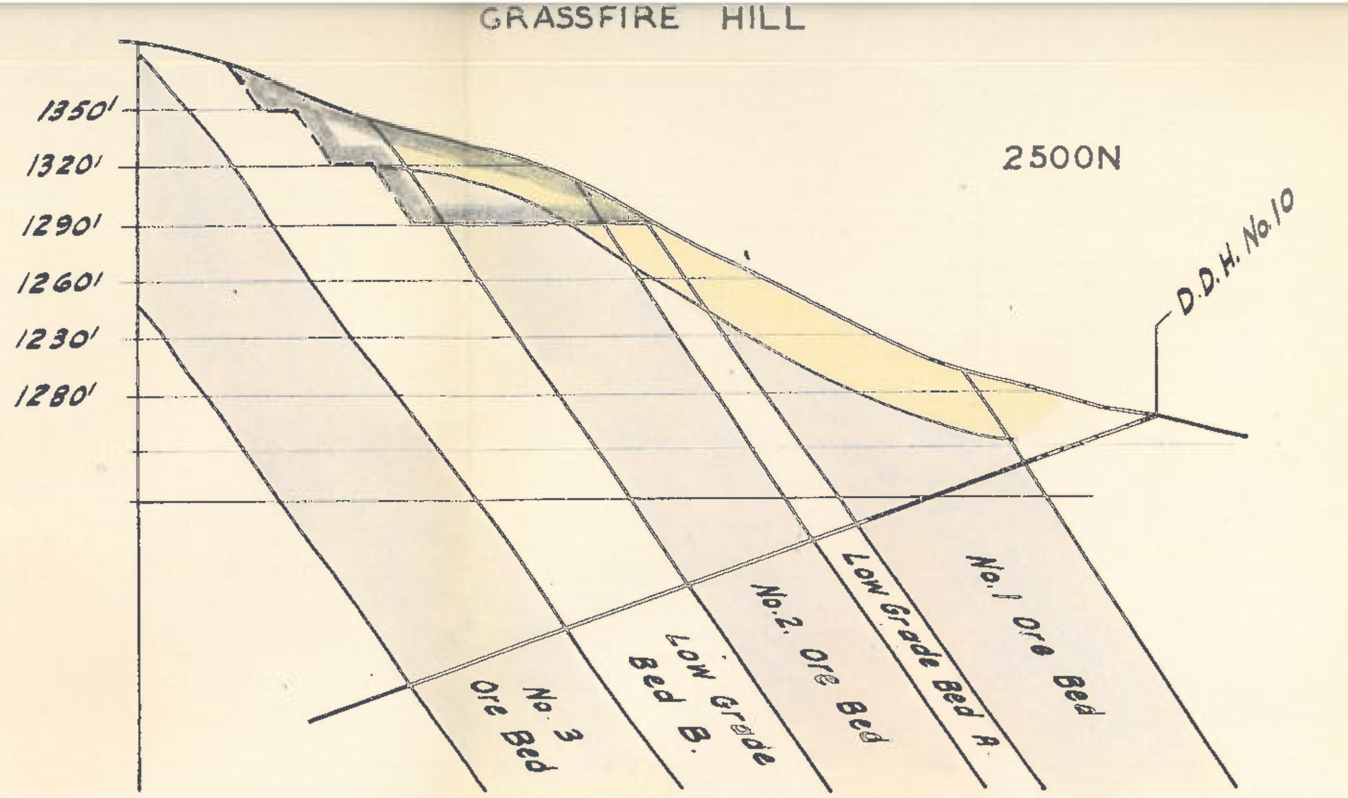
SHEPHARDS HILL

00



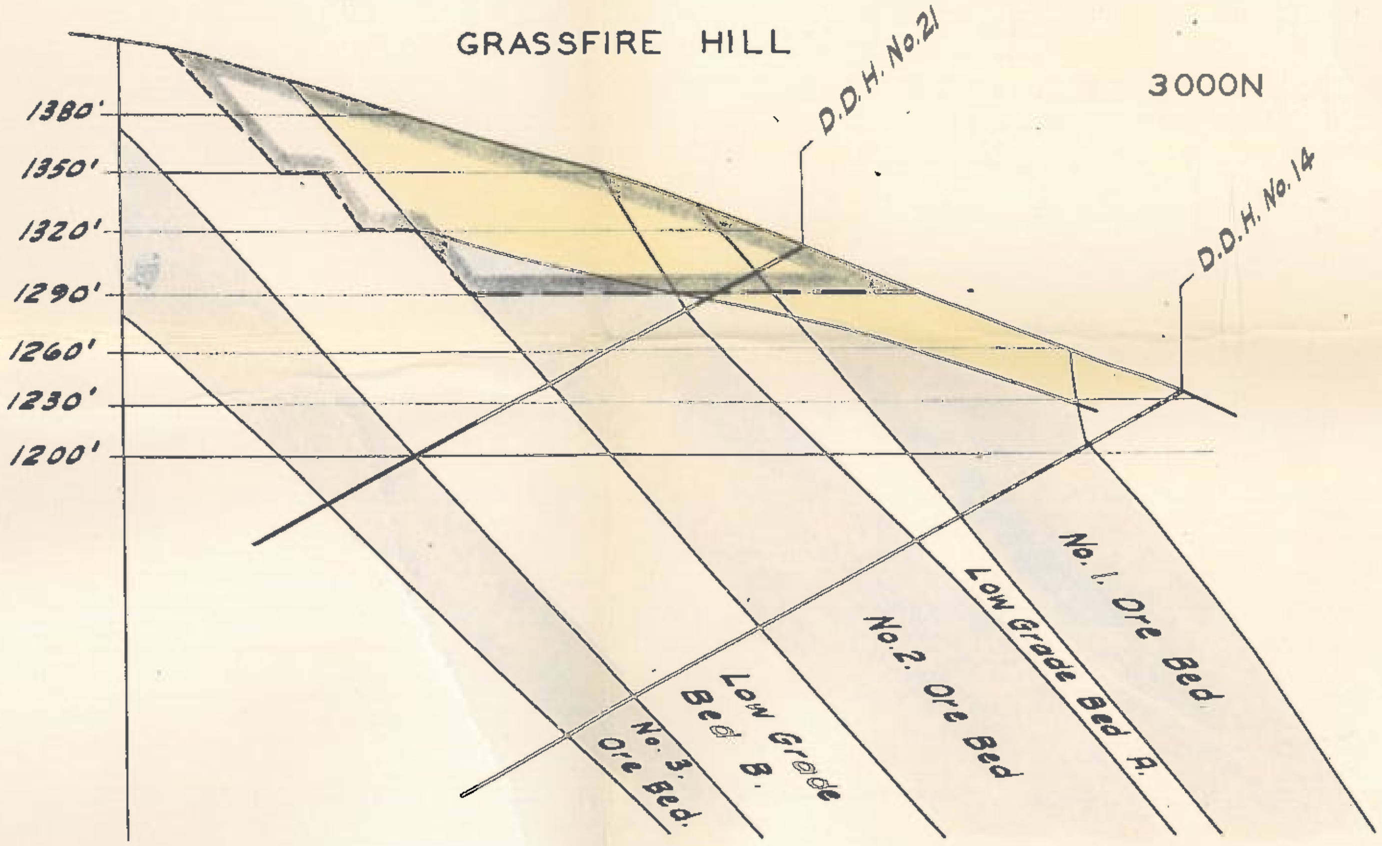
GRASSFIRE HILL

2500N



GRASSFIRE HILL

3000N



Excavation .... ▨

Overburden .... 🟨

SCALE:- 100 FEET TO 1 INCH

S.A. DEPARTMENT OF MINES

NAIRNE PYRITE DEPOSIT

Approved	Passed	Drn.	Scale : 100' = 1"
			58 - 197