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CONTACT METASOMATISM AND ORE DEPOSITION:
TEM PIUTE, NEVADA

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Reprinted from ECONOMIC GEOLOGY, Vol. 62, No. 3, May, 1967

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ABSTRACT

Ore at Tem Piute occurs in a thermally zoned, contact-metasomatic garnet-pyroxene skarn zone separating barren limestone and hornfels from unmineralized quartz monzonite. The scheelite is more abundant in garnet areas and the sulfides in the diopsidic bands.

Two unusual features are the number of different ore minerals and the thermally controlled mineralogical zoning across the aureole. Pyrrhotite (and associated marcasite), magnetite and, locally, molybdenite and ilvaite are concentrated close to the quartz monzonite in the "inner" portion of the contact aureole. Sphalerite together with lesser amounts of galena, bismuthinite, cosalite, galenobismutite and native bismuth, occur close to the limestone contact in the "outer" portion of the skarn aureole. tungsten-copper-silver deposit. The ore minerals¹ occur in a banded

¹ Used in the same sense as in the standard texts on ore mineralogy and ore microscopy, i.e., there is no implication of commercial value.

Here fluorite is the characteristic gangue. This partitioning of the minerals is in response to thermal differences across the aureole. Certain minerals such as pyrite, chalcopyrite, and scheelite, are uniformly distributed throughout the aureole.

All available pyrrhotite is at least in part monoclinic and thus not directly suitable for geothermometry; there are indications, however, that some annealed monoclinic pyrrhotites may yield valid crystallization temperatures. Annealed samples indicate an apparent temperature of deposition in the "inner" part of the aureole of between approximately 455° C and 510° C. Such temperatures are reasonable but, in view of the possibility of compositional changes having occurred during the initial change from the hexagonal state, the values must be viewed with caution. Some of the sulfo-salts in the "outer" portion of the aureole, based on thermochemical calculations, formed below $235^{\circ} \pm 25^{\circ}$ C. Thus, the indication is that the ore minerals were deposited at rather low temperatures for a contact-metasomatic ore deposit and that there was a surprisingly high-temperature gradient across this narrow contact zone.

INTRODUCTION

CONTACT-METASOMATIC ore deposits are of unique interest because of their singular occurrence within the metamorphic aureoles at the edges of igneous intrusions. Being unquestionably related to the igneous activity, they are exempt from the growing syngenetic-epigenetic controversy which is currently throwing doubt on the hypothesized origins of many "hydrothermal" ore deposits. On the other hand, there is disagreement regarding the genetic relation between contact-metasomatic and hydrothermal deposits. Consequently a comparative study of several contact-metasomatic deposits was initiated. The author, in a previous paper (9), discussed a major Mexican contact-metasomatic copper deposit and concluded that this type of deposit is properly considered as a subtype within the larger genetic group of high-temperature hydrothermal deposits.

Tem Piute was another district studied in the course of this investigation. It was chosen because of a) its isolation from igneous and metamorphic activity other than that directly related to the igneous intrusives and ore deposits, b) its excellent geologic accessibility, and c) its limited size and thus ease of thorough investigation. The deposits, as examples of contact-metasomatic mineralization, are of particular interest because of their thermally controlled mineralogical zoning and the genetic relationship exhibited within a remarkably varied and complex suite of ore minerals. The purpose of the study was to investigate the origin and environment of deposition of these minerals and, as the deposits have not previously been studied in detail, to describe those features of particular geologic interest.

Permission to study Tem Piute was given by the Wah Chang Mining Corporation and Mr. Merle Schofield, President of the North Tem Piute Mining & Development Company. Mr. Wesley Koyen showed the writer around in the field, and Mr. Jeff Wiegand helped as a field assistant. Dr. Paul Ramdohr helped interpret some of the more complex polished sections. The guidance of Dr. Chas. H. Behre, Jr., is greatly appreciated. The manu-

script was critically read by Drs. Behre and Brian Skinner and Mr. George Boyd, all of whom provided helpful comments.

LOCATION AND HISTORY OF MINING

The town and mining district of Tem Piute (also called Tempiute) in Lincoln County, Nevada, are located toward the north end of the Timpahute Mountains, a short but rugged range rising out of the broad and flat intermontane valleys of the Great Basin. It lies 160 miles north of Las Vegas.

The first mining operations in the Tem Piute district, for silver, were in 1868 (21). Although the production figures to the present are incomplete, it is unlikely that the district produced great quantities of ore. Mining activity was expanded in the years immediately preceding World War II and for a number of years thereafter mining increased, with tungsten being the primary metal of interest. The underground and open pit workings were most recently mined on a large scale by the Black Rock Mining Corporation, subsidiary of the Wah Chang Corporation. Since cessation of that operation, in 1957, only minor base metal and Ag production has occurred, mainly by independent operators.

The Wah Chang operations, centered at the Lincoln mine, produced most of the ore, but its workings were inaccessible at the time of this study. However, the North Tem Piute Mining & Development Company also has claims along the contact zone. Although reported production from its properties is small, the mine workings are accessible and have exposed the contact zone and mineralization in a number of places.

PREVIOUS STUDY

Published geologic reports on Tem Piute are rare. The earliest reference to the regional setting of the Timpahute range is given by Gilbert (16). A Bureau of Mines report (7) provides a terse summary of the geology and the mining and extraction of the ore, as well as a brief discussion of the exploration work done by the U. S. Bureau of Mines. A short but more detailed report on the geology of the tungsten deposits is by Wyant and Lemmon (28). Aspects of the mineralogy were discussed by Buseck (11).

GENERAL GEOLOGY

This section is partly based on the report by Wyant and Lemmon (28). Over 7,000 feet of Paleozoic sediments exist in the northern end of the Timpahute Range. Ordovician sediments are exposed on the west side of the range. Toward the east, almost a mile of Silurian and Devonian dolomite and limestone with minor quartzite and shale occur. The easternmost exposures consist of Carboniferous limestone, shale and sandstone.

The structure is that of a northward trending monocline dipping steeply to the east, thereby exposing the oldest beds on the western side of the range. A hypothesized overthrust from the southwest may have been the cause of the

steepening and local overturning of the beds in the northern part of the range (28). Anomalous stratigraphic relations also argue in favor of this overthrust.

Two quartz monzonite stocks transect this thrust plate and have been emplaced approximately along the Devonian-Carboniferous contact (Fig. 1). The intrusions are locally concordant with the sediments; the beds dip radially away from the intrusion at angles of 40° to 85°. The igneous bodies have been instrumental in forming the contact-metasomatic aureoles. The skarn is best developed along the southern stock and the ore deposits also occur along this body. The two small stocks, each less than one mile across, are separated by only 600 feet of limestone on the surface. The southern and larger stock consists of roughly equigranular, medium grained quartz monzonite containing sparse phenocrysts of feldspar. The elongated biotite provides a weak lineation, especially near the contacts. Plagioclase composition, determined from maximum extinction angles, ranges between Ab_{58} and Ab_{68} .

TABLE 1
MODAL COMPOSITION OF TEM PIUTE QUARTZ MONZONITE

	No. 1	No. 2	No. 3	No. 4
Quartz	26.3	29.5	36.5	31.1
Orthoclase	32.4	28.6	29.7	21.5
Plagioclase	35.3	33.3	26.6	38.4
Biotite	3.1	6.2	4.4	6.4
Chlorite ¹	1.5	1.0	1.5	1.1
Magnetite	1.1	1.0	0.8	1.1
Muscovite	0.1	0.2	0.4	0.2
Sphene ₁	0.1	—	Tr	0.1
Apatite	0.1	0.2	0.1	0.1
Zircon	Tr	Tr	Tr	Tr
Pyroxene	Tr	Tr	Tr	Tr

The modal composition, based on a minimum of 1,600 points per sample, is indicated in Table 1. Sample 1 was collected adjacent to the skarn contact; samples 2, 3 and 4 at distances of 140, 300 and 500 feet from the contact, respectively. Towards the contact the modal quartz content decreases and the orthoclase and possibly plagioclase contents increase.

THE CONTACT-METASOMATIC AUREOLE

The effect of the quartz monzonite intrusion is evident in the sediments surrounding the southernmost stock; alteration, mainly local bleaching and marmorization, extends up to 700 feet from the contact, with a skarn and hornfels zone developed adjacent to the stock (Fig. 2). This zone extends over 6,000 feet along the western edge of the stock. Ore mineralization in the district occurs almost exclusively within the skarn and is relatively uniform over a vertical range of at least 1,300 feet (28).

The main adit level of the North Tem Piute Mining & Development Company, connecting with the 200 South Callahan Drift of the Lincoln mine, has

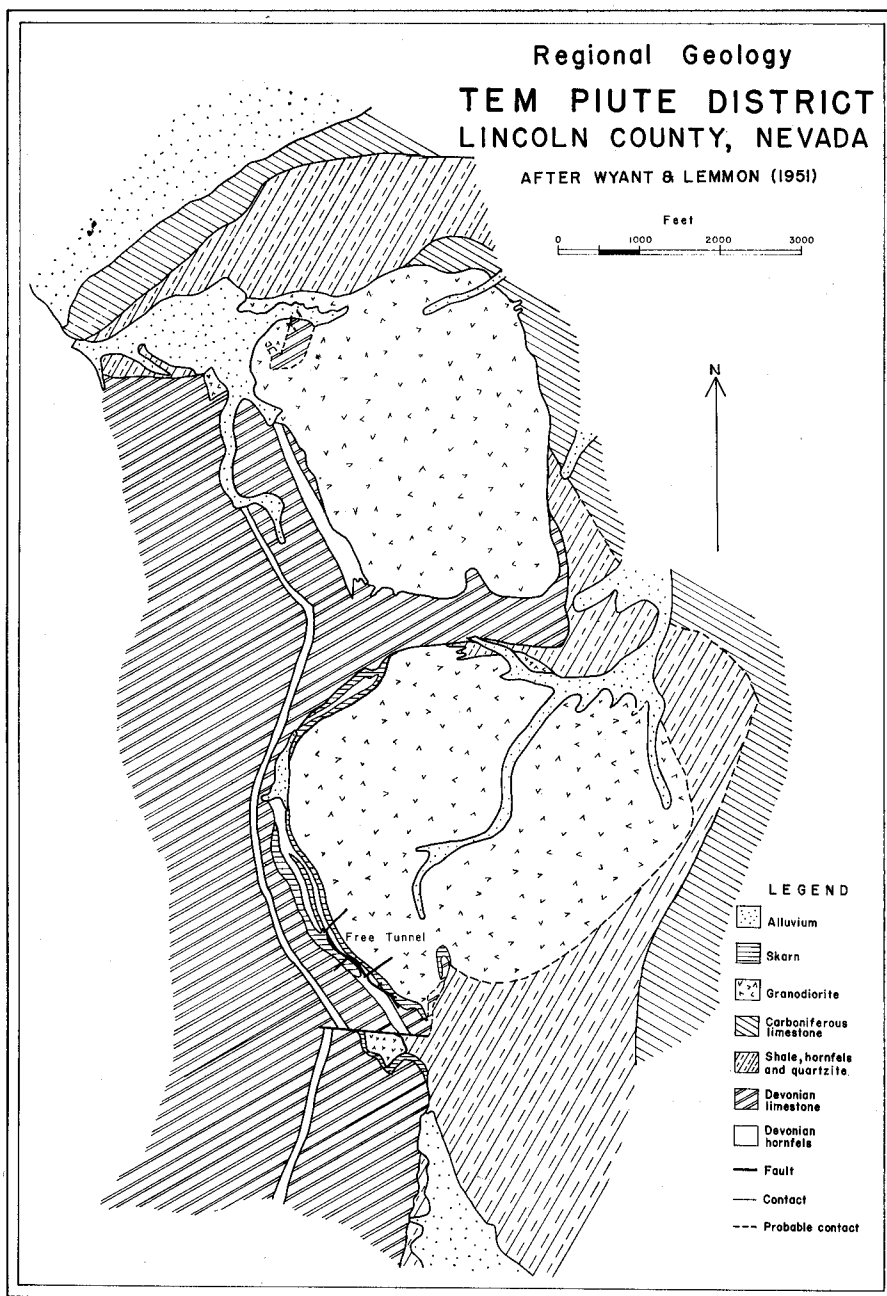


FIG. 1. Map of the regional geology of the Tem Piute district.
(Note: Granodiorite should read Quartz monzonite.)

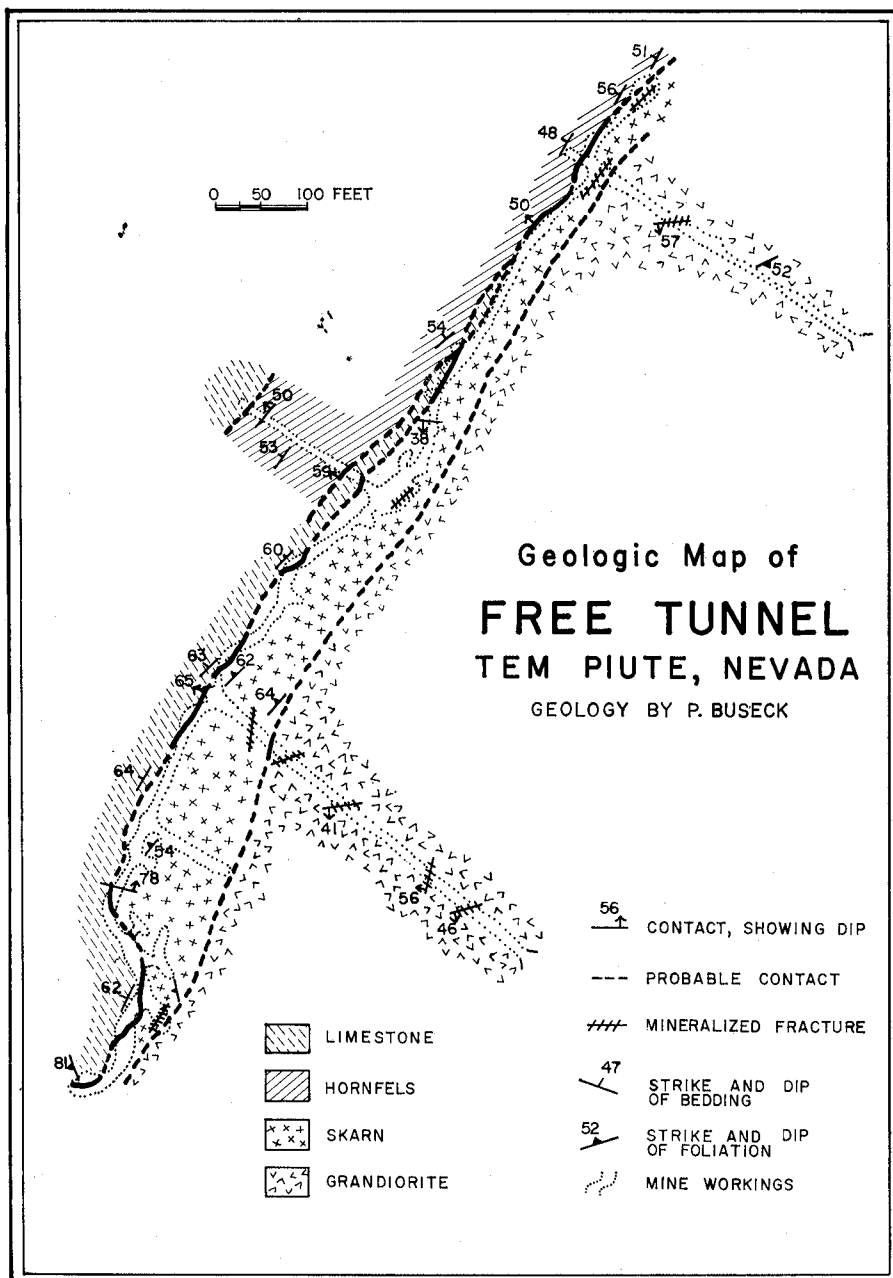


FIG. 2. Geologic map of the Free Tunnel, Tem Piute, Nevada.
(Note: Granodiorite should read Quartz monzonite.)

been variously named the Schofield, DMEA and Free Tunnel; the latter name is used in this paper. It extends along the contact for over 1,400 feet and cuts completely across the contact in several places (Fig. 2), making it ideal for a study of the contact aureole. Although not abundant, ore mineralization is widespread. The following description applies to the Free Tunnel.

Skarn.—Four rock types are exposed in the Free Tunnel: quartz monzonite, skarn, hornfels, and limestone. Skarn, the most pronounced product of the metasomatism, is present in a band between 25 and 120 feet wide between the quartz monzonite and fresh limestone. The skarn contains residual bedding, parallel to that in the adjacent limestones, indicating that the skarn is a metasedimentary rock. Microscopically, the fresh limestones contain calcite with local sandy horizons, whereas the skarn consists almost entirely of Ca, Fe, Mg, and Al silicates. Clearly, except for Ca, these elements plus Si must have been introduced into the limestones in large quantities to form the skarn. The restriction of the skarn silicates to the quartz monzonite contact, and the lack of other igneous activity in the immediate vicinity suggests that the quartz monzonite produced the metasomatism.

In some areas the skarn consists mainly of friable, coarse, granular red garnets; elsewhere the garnet skarn contains green bands, microscopically identifiable as pyroxene with minor sericite. The bands, as well as the skarn-limestone contact, locally parallel the limestone bedding, indicating the control exerted by the sediments on the formation of the calc-silicates.

The most abundant mineral in the skarn is garnet, subhedral to euhedral, complexly twinned, and zoned. Almost all the garnet is anisotropic but the birefringence is generally low, averaging approximately 0.004. Garnet with isotropic zones occurs near the igneous and sedimentary contacts and wherever considerable amounts of pyroxene are present. As seen in thin section, all of the garnet is colored faint red or yellow, with the former predominating.

Indices of refraction and unit cell edges show the garnets to be grossularite-andradites in the range of 60–95 weight percent andradite. Compositional zoning is pronounced and leads in some cases to preferential replacement (Fig. 3). The spread in composition within single garnet crystals indicates a lack of bulk equilibrium.

Clinopyroxene occurs throughout the skarn. It is weakly colored and pleochroic, from reddish (X) to greenish or grayish green (Y). The beta index of refraction is 1.715 ± 0.005 suggesting a composition between diopside and aegirine-augite. Its length is greatest—up to 5 mm—where it occurs along the skarn contacts. In such places it is anhedral. Where interstitial to garnet it is generally smaller; still smaller subhedral to euhedral grains, averaging a few tenths of a millimeter long, are commonly enclosed by calcite, quartz and especially poikiloblastic garnet. In some cases the pyroxene grains are in bands cutting across large, euhedral garnet crystals. The bands reflect original compositional differences in the metasomatised sediments.

Fibrous actinolite and some tremolite has replaced pyroxene and, to a lesser extent, garnet and calcite. It is also intergrown with the opaque minerals, but in such cases its color and pleochroism are less pronounced. A minor yellow mineral rarely replacing the pyroxene is urallite.

In places an unusual silicate is associated with the sulfide minerals. It is in radiating fibrous crystals that are locally isotropic but elsewhere have a low birefringence displayed in a brilliant anomalous blue. Optically it shows parallel extinction, is length slow, pleochroic from green parallel to its length to colorless or pale brown perpendicular to its length, has a refractive index of 1.631 ± 0.005 , and is possibly optically negative. Winchell and Winchell (27) call such a chlorite aphrosiderite whereas Tröger (25) refers to it as prochlorite. Tröger notes it may occur as an alteration product of garnet. Another phyllosilicate, probably phlogopite, is also restricted to areas of sulfide mineralization. It occurs in subhedral crystals and is commonly altered to a green chlorite exhibiting none of the anomalous interference colors of the prochlorite.

Limestone.—A thin band of bleached limestone separates skarn from fresh black limestone. It is the only contact effect macroscopically visible in the limestone. Otherwise the contact is sharp, with massive skarn separated from fresh limestone by less than 5 cm.

The limestone, now partly marmorized, consists of interlocking grains of calcite and minor quartz. All the bands contain carbonaceous matter, the only exception being narrow zones of coarse, clear calcite that cut across the bedding. The zones are probably old conduits and the fluids that passed through them produced calcite recrystallization and also removed the carbonaceous material.

Pyroxene, muscovite and garnet are sparsely disseminated within the limestone. Radiate acicular actinolite-tremolite occurs along the contacts between the siliceous and calcareous beds.

Hornfels.—Although less widespread than limestone, beds of hornfels consisting mainly of pyroxene and quartz, also occur along the skarn contacts in the northwestern part of the Free Tunnel (Fig. 2). Away from the skarn the hornfels is white and contains long, thin, grayish lenses parallel to the bedding. Near the limestone, but more markedly near the skarn, its color is green, apparently having been more profoundly affected by the metasomatising fluids. The contact between it and the skarn parallels the bedding just as does the limestone-skarn contact. In one place where the contact between hornfels and limestone is exposed, there is a 4-inch band of skarn between them. Toward the limestone this skarn consists mainly of garnet, whereas closer to the hornfels it contains mostly pyroxene, clearly reflecting the compositions of the original host rocks.

Quartz Monzonite.—The effects of the metasomatism are not as profound in the quartz monzonite as in the sediments, but it is clear that changes have occurred there also. As in many contact-metasomatic tungsten deposits, the most pronounced alteration immediately next to the contact is silicification so intense that macroscopically the former quartz monzonite resembles quartzite. With magnification it is apparent that many of the minerals originally in the fresh quartz monzonite are still present after metasomatism, but in smaller amounts. Both the potash and plagioclase feldspars have been partly altered to sericite. Biotite is sparse, most of it having been altered

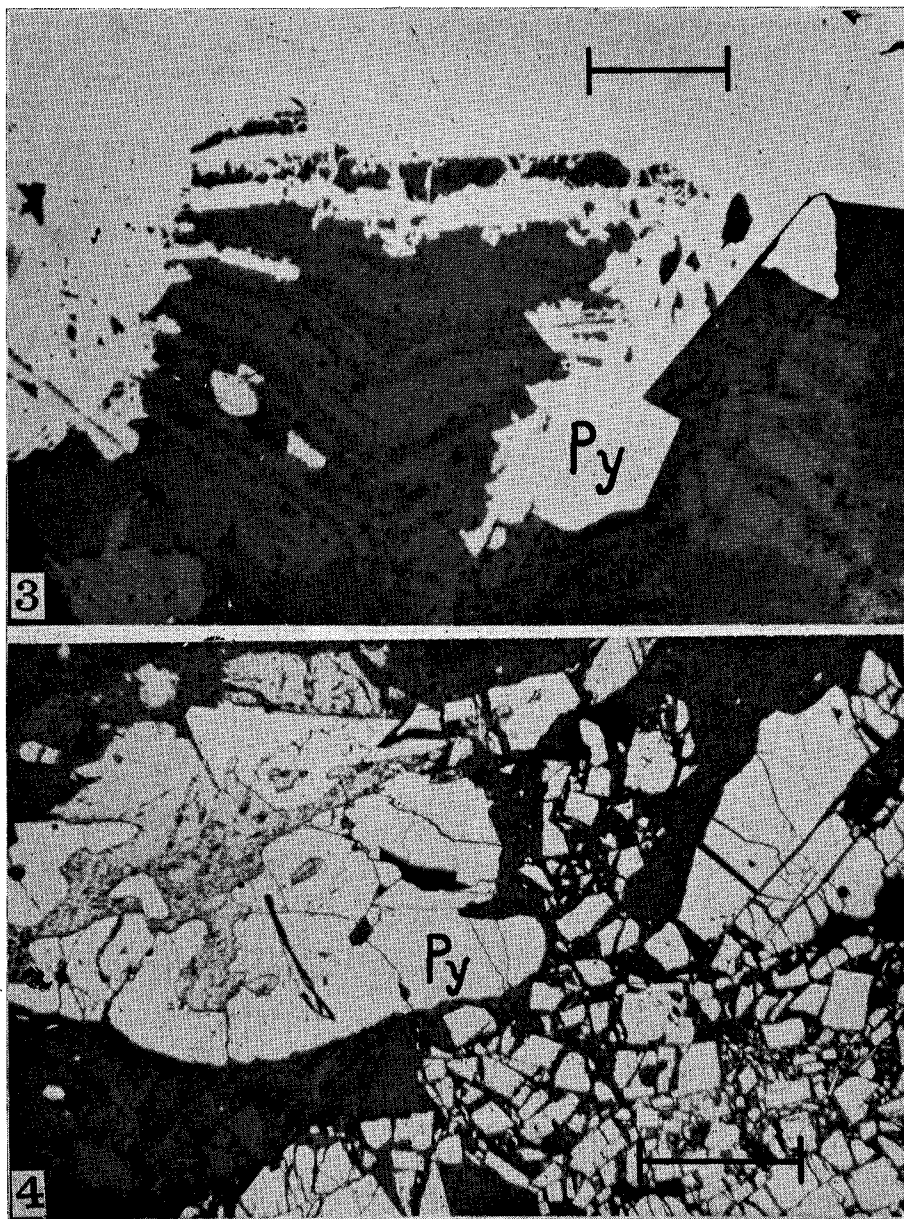


FIG. 3. Zoned garnet with preferential pyrite (py) replacement of certain zones; this is an example of compositional variation within a single garnet crystal and also of the sensitivity of the replacing mineral to the composition of the host. Scale bar = 100 μ .

FIG. 4. Pyrite (py) being replaced by bismuth minerals; note shattered pyrite exhibiting cubic cleavage. Scale bar = 1 mm.

also. Besides the quartz and crosscutting veinlets of clear, anhedral calcite, muscovite is the main "new" mineral within the igneous rock, comprising from 5 to 10 percent of the total volume. In the center of the stock, muscovite is in much smaller amounts. Pyrite, associated with muscovite, is disseminated in the quartz monzonite near its contacts.

The skarn silicates are rare within the quartz monzonite. Insofar as the skarn banding indicates that the skarn host was sedimentary and the quartz monzonite itself contains no garnet or pyroxene, this area differs markedly from Concepcion del Oro where skarn formed within the igneous rock (9). The only silicates so observed at Tem Piute are subhedral, poikiloblastic epidote crystals and minor amounts of prochlorite in the silicified border areas of the quartz monzonite.

ORE MINERALIZATION

The ore mineralogy of the Free Tunnel is complex, but only a few minerals are widespread and they occur almost exclusively in the skarn. No ore minerals were observed in the limestone; the hornfels contains minor pyrite, mainly on joint surfaces. Molybdenite occurs along the contact between hornfels and skarn, and the quartz monzonite is essentially unmineralized. The skarn, by contrast, contains pyrite, chalcopyrite, pyrrhotite, magnetite, marcasite, sphalerite, scheelite, molybdenite, traces of galena, hematite, galenobismutite, cosalite, bismuthinite and native bismuth. In view of the simple mineralogy of many contact-metasomatic deposits, this complex suite is remarkable. Generally, the pyrite and other sulfides are concentrated in the green (pyroxene and quartz) zones whereas the scheelite is more common in the red (garnet) bands within the skarn.

Pyrite.—Pyrite, the most common and widespread ore mineral within the skarn, was one of the earliest ore minerals to crystallize. It is locally in massive concentrations the size of a clenched fist. In shattered zones the pyrite has broken into well-developed rectangular fragments exhibiting a good {100} cleavage (Fig. 4).

Inclusions of pyrrhotite and chalcopyrite are characteristically within the pyrite, even though in many cases these minerals were not observed externally adjacent to the pyrite. Commonly both minerals occur within the same inclusions; pyrrhotite predominates except where the minerals are also present in fractures cutting pyrite. Small, sparse prismatic crystals with a very high index of refraction, possibly rutile, are also locally enclosed by pyrite.

Experimental work in the system Cu-Fe-S, summarized by Barton and Skinner (5) and Yund and Kullerud (29), has shown that there is a tie-line switch at $330 \pm 5^\circ \text{C}$. Above this temperature pyrrhotite plus chalcopyrite react to form cubanite plus pyrite. Thus, the observed Tem Piute assemblage of pyrite, pyrrhotite and chalcopyrite may indicate a temperature of stability below $330 \pm 5^\circ \text{C}$. It is also true, however, that chalcopyrite solid solution may again coexist with pyrrhotite at elevated temperatures such as 700°C —thus the observed assemblage could instead represent a frozen high-temperature suite. In view of the rapid reaction rates demonstrated by Brett (8), it

is possible that the observed minerals are the result of reëquilibration either from such an initial high-temperature chalcopyrite-bearing assemblage or from a moderate-temperature cubanite-bearing assemblage. The textural relations do not permit a unique discrimination between the alternatives.

Pyrrhotite.—Pyrrhotite is a common constituent of the skarn but is not as widely distributed as pyrite. It occurs in massive bodies as well as in small grains associated with chalcopyrite and sphalerite. In contrast to pyrite, the pyrrhotite is not generally in discrete grains disseminated throughout the skarn. Most pyrrhotite is in granular aggregates, the grains being irregular, interlocking, anhedral and up to a few millimeters across. The pyrrhotite is most abundant in the inner portions of the aureole, close to the formerly hot quartz monzonite and in places it is in fairly pure masses two or more meters across. In one place several bands of pyrrhotite roughly parallel the skarn banding and may indicate preferential replacement of certain silicate beds. However, at least minor amounts of pyrrhotite occur throughout the skarn. The pyrrhotite is generally associated with pyrite.

Pyrrhotite is younger than pyrite, commonly surrounding euhedral crystals and locally veining the pyrite. In a few places the euhedral pyrite faces in contact with pyrrhotite show evidence of reaction. It is probable, judging from the results of the compositional measurements described below, that the two minerals did equilibrate. The pyrrhotite d_{102} has roughly the same value wherever pyrite is present while this spacing is consistently larger, indicating a lower activity of sulfur, where pyrite is absent.

Pyrrhotite Alteration; Marcasite.—Along the peripheries of the pyrrhotite grains and along fractures it commonly is altered to pyrite, magnetite and/or marcasite (Fig. 5). The most common alteration products are pyrite with minor magnetite. This pyrite is fine-grained, in places less than $1\ \mu$ in diameter, although locally the individual pyrite grains have coalesced. The pyrite is sharply angular to rectangular and even as an alteration product it tends to be euhedral. The magnetite is in tiny rounded grains within the pyrite masses and both are in irregular bodies with well-defined contacts toward the pyrrhotite (Fig. 5).

Locally the pyrrhotite breaks down to form "bird's eye" structures containing bands 5 to $10\ \mu$ wide and separated by concentric fractures. Elsewhere material intermediate in appearance between pyrrhotite and pyrite is common. This has been termed "Zwischenprodukt" (inbetween product) by Ramdohr (22, p. 463). It is probably a fine-grained, intimate mixture of both iron sulfides, thereby producing properties that are seemingly intermediate to the two.

Marcasite lamellae, twinned perpendicular to their length, also occur as an alteration product of the pyrrhotite. Where the marcasite is not associated with pyrite, no magnetite is present either. Apparently the reaction by which pyrrhotite is altered to marcasite does not require the introduction of oxygen. Allen, Crenshaw and Merwin (1) showed that marcasite inverts to pyrite above 450°C and more recent evidence presented by Kullerud (19) suggests that it is unstable above 300°C . In the present instance there is no evidence

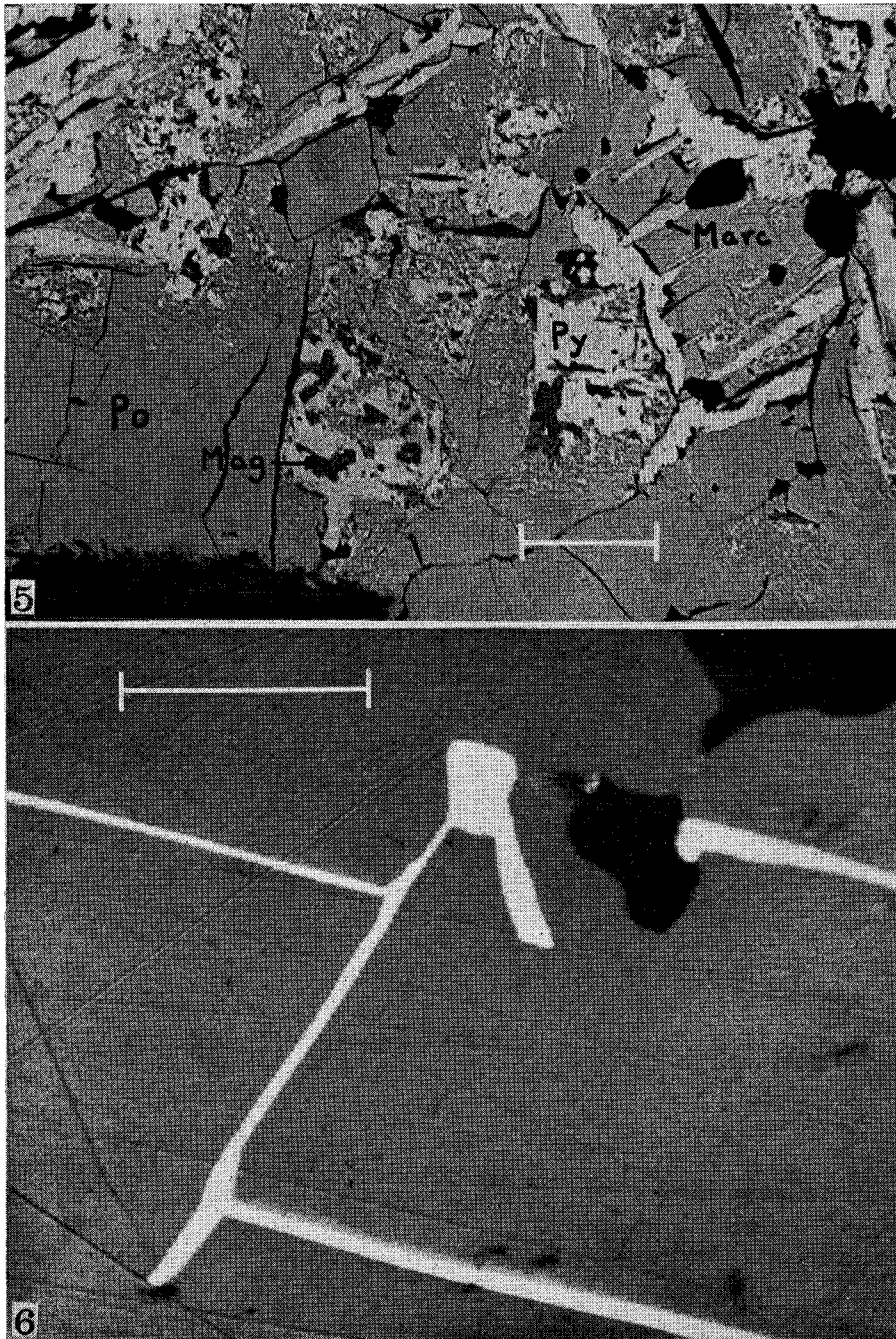


FIG. 5. Pyrrhotite (po) altered to irregular masses of pyrite (py) and magnetite (mag) and also to lamellar marcasite (marc). Scale bar = 100 μ .

FIG. 6. Pyrrhotite (white) lamellae within sphalerite; note flaring where the lamellae intersect, suggesting that they may be the result of replacement. (Oil immersion.) Scale bar = 50 μ .

for such an inversion and so the marcasite must have formed at lower temperatures, perhaps as a result of normal near-surface alteration. However, some chalcopyrite is younger than marcasite, thereby suggesting that the marcasite may not have resulted from supergene alteration, but may have formed during the later stages of mineralization. Much of the pyrrhotite from Tem Piute has been altered in a similar fashion to that at Concepcion del Oro (9).

Chalcopyrite.—Chalcopyrite is widespread but less abundant than either pyrite or pyrrhotite. It is generally associated with the other sulfides and is almost invariably present with pyrrhotite as small inclusions within pyrite. It is also locally within fractures cutting the pyrite, whereas the associated pyrrhotite is only rarely in similar fractures. Chalcopyrite locally veins and rims the pyrrhotite, as well as surrounding pyrite crystals. In other places it is intergrown with the "Zwischenprodukt" and yet elsewhere it truncates some of the long marcasite lamellae within pyrrhotite. It is clear that chalcopyrite formed throughout much of the period of mineralization at Tem Piute.

Sphalerite.—Sphalerite is another abundant sulfide, but only in certain parts of the aureole. It is uncommon close to the igneous contact, but a thin streak is concentrated 1 or 2 cm from the limestone contact and parallel to it. It was not seen with magnetite or molybdenite and it is only rarely associated with pyrrhotite. Sphalerite occurs in the skarn in crosscutting veinlets up to 2 cm wide as well as in discrete, irregular, anhedral grains following particular silicate bands, indicating local selective replacement of certain zones in the skarn.

Inclusions of either chalcopyrite or pyrrhotite are characteristic features of the sphalerite, even where these minerals do not occur externally to the zinc mineral. In only one instance were pyrrhotite and chalcopyrite seen together within sphalerite. The specimens containing pyrrhotite are located farther from the sedimentary contact than those containing chalcopyrite. The pyrrhotite occurs in oriented lamellae or in rounded, irregular blebs. In one specimen all the lamellae flare at intersections (Fig. 6) suggesting that they are replacement products, or resulted from "exsolution" (due to minor sulfur addition (6)) with consequent coalescing. Chalcopyrite commonly occurs in equidimensional, angular to rounded grains, having a random distribution throughout the sphalerite. In a few samples the chalcopyrite blebs are linearly aligned, having resulted either from exsolution or epitaxial growth. The fact that some chalcopyrite encloses yet smaller blebs of pyrrhotite suggests the latter hypothesis, as it is improbable to get pyrrhotite exsolving from chalcopyrite which was itself the result of exsolution from sphalerite.

In hand specimens the sphalerite is dark brown or black, indicating a high iron content. In thin sections the color ranges from amber to a deep carmine red, corroborating the high iron content and clearly indicating that the Fe concentration in solid solution varies considerably from grain to grain, although no color gradations were seen within individual grains. Predictably, the red samples are those containing exsolved pyrrhotite. Micro-

analyses, using colorimetric methods and Tiron as a reagent, indicate between 9 and 16 mole percent FeS.

Magnetite and Hematite.—Magnetite is less common than sphalerite. Where present it occurs with the iron sulfides in the inner, formerly warmer portions of the contact aureole.

The magnetite surrounds pyrite crystals. In places it occurs between pyrite and pyrrhotite and has serrate borders on both sides, suggesting that it is replacing them. This is substantiated by abundant inclusions of pyrrhotite within the magnetite. The sulfide is in extremely irregular, elliptical, vermicular and highly angular grains, locally resembling shards of broken glass (Fig. 7). Locally chalcopyrite is also in these irregular forms. One of the stranger aspects of the pyrrhotite inclusions is that a group of adjacent grains commonly go to optical extinction together. This suggests that magnetite replaced preëxisting pyrrhotite; this is also observed where it rims and encroaches upon the sulfide (Fig. 8). Locally the magnetite is in thin, arcuate forms along grain boundaries, thereby separating the individual pyrrhotite crystals.

The replacement of pyrrhotite by magnetite is different from the alteration of the pyrrhotite described previously. The end products of that alteration are marcasite or pyrite together with only minor amounts of magnetite in a fine-grained intimate mixture, with fracture control prominent. By contrast, where magnetite replaces pyrrhotite the oxide is in large masses peripheral to the sulfide. It does not contain any pyrite or marcasite. The replacement reaction is presumably a simple oxygen-sulfur exchange.

The magnetite clearly formed later than the pyrrhotite. Such replacement suggests a relative rise in the oxygen fugacity or a decrease in the sulfur fugacity, perhaps produced by a decrease in temperature. In comparison with the deposits at Concepcion del Oro (9), at Tem Piute the magnetite is sparingly altered to hematite. Where present the hematite is in only minor amounts and is generally along the borders of the magnetite.

Molybdenite.—The molybdenite is relatively widespread along the hornfels-skarn contact. The crystals have their folia oriented parallel to the contact and are twinned perpendicular to their length. Molybdenite also occurs along the skarn-quartz monzonite contact and, to a lesser extent, within the skarn. Pieces of skarn on the dump near the northern adit contain over 10 volume percent molybdenite disseminated as crystals a few millimeters in diameter. No such samples were found in place, presumably because they came from an inaccessible lagged area in the northernmost part of the drift. In these, as well as the other samples, no other ore minerals occur with the molybdenite.

Bismuth Minerals and Galena.—Ore minerals other than those previously mentioned are also present, but in minor amounts and with a restricted distribution. The bismuth minerals were observed in specimens located near to the limestone contact and near to sphalerite containing exsolved chalcopyrite but no pyrrhotite. Although the bismuth minerals do occur within and cutting the sphalerite they tend to show a greater preference for replacing pyrite (Fig. 4). They are in irregular aggregates up to one millimeter across, although the individual grains are smaller. Based on optical properties, the

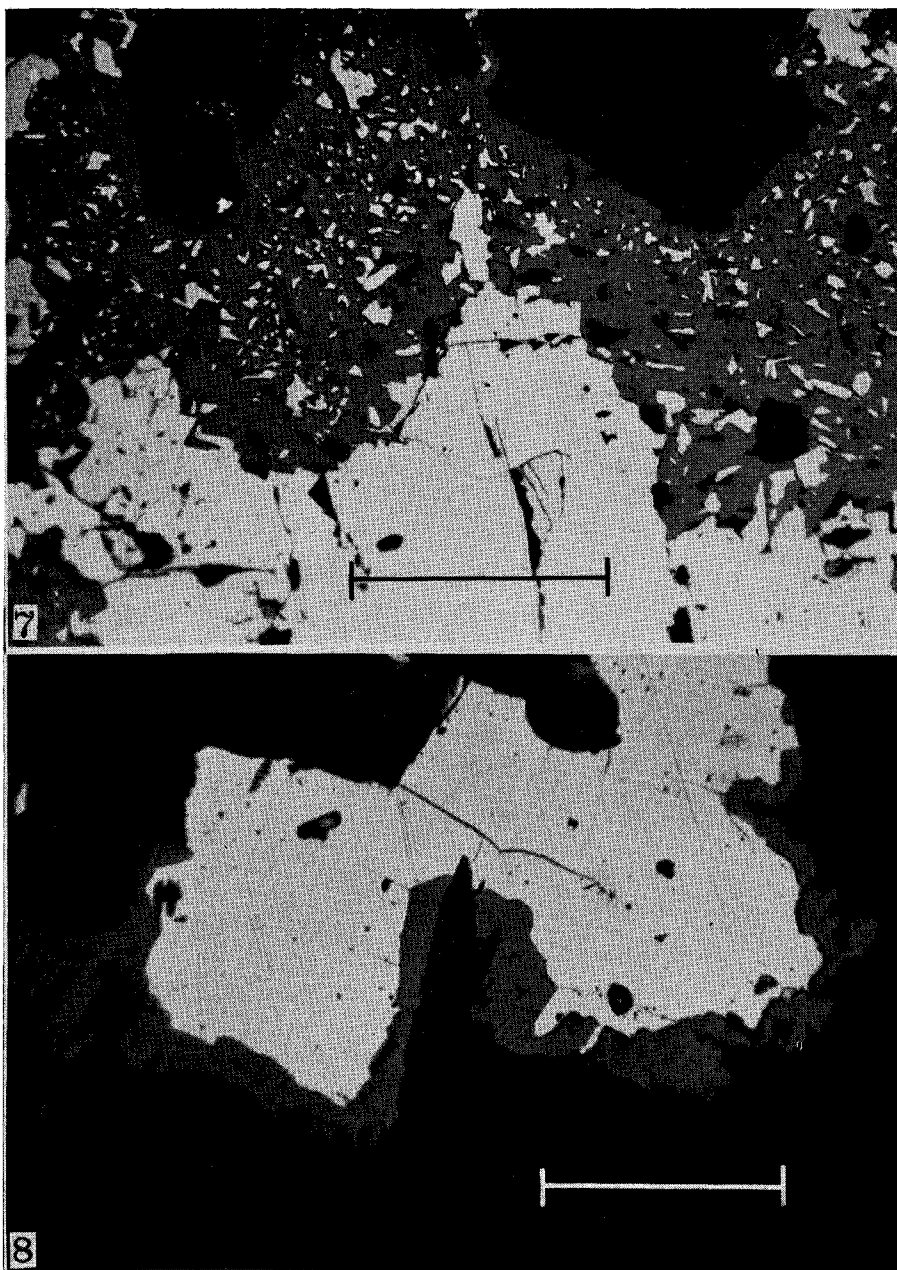


FIG. 7. Magnetite (gray) bordering and replacing pyrrhotite (white); note irregular, sharply angular pyrrhotite remnants within magnetite—these remnants have the same crystallographic orientation as the main pyrrhotite mass. (Oil immersion.) Scale bar = 250 μ .

FIG. 8. Magnetite (gray) surrounding and clearly later than pyrrhotite (white). (Oil immersion.) Scale bar = 50 μ .

main mineral is galenobismutite; it occurs with lesser amount of cosalite. Tiny grains of native bismuth are found within both minerals, and along their borders bismuthinite occurs in short prismatic crystals. Traces of galena also occur with the bismuth minerals.

In the presence of bismuthinite, native bismuth melts at 265°C (26) and thus the observed mineral pair bismuth-bismuthinite must have formed at lower temperatures, although this formation could have been the result of secondary processes. Based on unpublished calculations of Barton and Sepunuk, pyrite plus bismuth react to form bismuthinite plus pyrrhotite at $235 \pm 25^{\circ}\text{C}$ (5). Thus the limiting upper temperature for the observed assemblages of pyrite plus native bismuth is $235 \pm 25^{\circ}\text{C}$, a result consistent with the previous data.

Scheelite.—Scheelite occurs throughout the skarn zone and, with the possible exception of pyrite, is more widespread than the other ore minerals. It generally comprises less than a few percent of the total volume.

The scheelite occurs entirely as discretely disseminated rounded or anhedral grains. In hand specimens the crystals are an undistinctive pale yellowish-white color. Under ultraviolet radiation they fluoresce in colors ranging through blue, bluish-white and, very commonly, yellow. Such yellowish fluorescence indicates the presence of molybdenum and possibly manganese (17). The variations across the contact zone appear to correspond to the presence of molybdenite, for more scheelite fluoresces blue than yellow near the hornfels and the quartz monzonite, where molybdenite is present. This suggests that the molybdenite incorporated much of the available molybdenum near these contacts, thereby leaving the scheelite relatively depleted.

The scheelite appears to be very stable; it is everywhere unaltered and has not reacted with any of the coexisting minerals. It is not particularly associated with the other ore minerals and was observed only locally in contact with most of these minerals. It is common close to pyrite, but this may be because pyrite is the most abundant sulfide. The contemporaneity of scheelite and pyrite is indicated by the fact that scheelite both surrounds and is cut by the early pyrite. This age relationship is supported by the pyrite-scheelite veinlets found within the igneous body.

The scheelite is much more commonly in contact with the silicates than with the other ore minerals; even in this connection it shows no pronounced preference, except for its local favoring of garnet over pyroxene zones in areas where the skarn is banded. It was probably deposited later than these silicates for it surrounds euhedral crystals of both garnet and pyroxene.

Associated Non-metallic Minerals.—Certain non-metallic minerals are characteristically associated with the ore mineralization. The most unusual is ilvaite, an almost opaque silicate generally restricted to contact-metasomatic aureoles. At Tem Piute it was observed only in the formerly hottest portions of the aureole, together with pyrrhotite and molybdenite. It rims them as well as the associated pyrite and chalcopyrite. It is the only silicate that is everywhere later than the sulfides and which replaces the iron sulfides, probably by incorporating some of their iron into its structure.

Just as the ilvaite occurs on the inner portions of the aureole, so fluorite

is concentrated near the limestone, typically together with sphalerite, although also near the other sulfides and scheelite. Whereas the latter associations may be circumstantial, the almost invariable occurrence with sphalerite is taken as strong evidence in favor of a common origin. Fluorite was not observed in the absence of ore minerals.

Although they do not show as consistently unique an association with certain sulfides, a number of gangue minerals are so commonly found with the ore minerals that the associations are probably not fortuitous. These minerals include chlorite, actinolite-tremolite, quartz and phlogopite. Quartz is almost invariably present with the sulfides, primarily as clear, anhedral grains interstitial to the sulfides. Amphibole crystals are abundant near pyrite.

TABLE 2
GENERALIZED PARAGENESIS IN FREE TUNNEL, TEM PIUTE

Garnet	}	_____	
Pyroxene			
Amphibole		_____	
Molybdenite		<u> ?</u>	
Scheelite		_____	
Pyrite		_____
Chalcopyrite		_____
Pyrrhotite		_____	
Magnetite			_____
Marcasite			_____
Ilvaite			_____
Sphalerite		?	-----?
Bismuth minerals	}		
Galena			-----?

Green chlorite with normal interference colors, as well as the rare prochlorite, also occur in mineralized areas but as alteration products of the other silicates.

The age relations of the various minerals is shown diagrammatically in Table 2.

GEOTHERMOMETRY

Arnold (3) determined the phase relations of a portion of the system FeS-FeS₂ and showed that the d₁₀₂ of hexagonal pyrrhotite varies with composition. The composition, in turn, varies with the temperature of crystallization, provided that pyrite was present, so that the pyrrhotite could become sulfur-saturated at the temperature in question. If the pyrrhotite has not re-equilibrated on cooling, then its composition will provide an estimate of the temperature at which it was formed.

X-ray powder diffractograms made with FeK α radiation indicate that monoclinic pyrrhotite, perhaps locally intergrown with hexagonal pyrrhotite, occurs at Tem Piute. Thus, in order to make use of the measurements of

Arnold (3), the pyrrhotite had to be converted to the hexagonal form. This was done in the manner described by Buseck (11). The samples were sealed in evacuated silica glass tubes and heated for 6 minutes at 346° C, and then quenched. The composition of the resulting hexagonal pyrrhotite was measured by powder diffraction techniques using copper radiation to produce high intensity peaks, with silicon as an internal standard. The samples were oscillated using a scanning speed of $\frac{1}{2}^\circ$ per minute and a chart speed of 1" per minute. The results were tabulated by Buseck (11).

The eleven measured pyrrhotite samples are unweathered and occurred in skarn between 0.5 and 16 meters from the igneous contact. Those pyrrhotite samples that were adjacent to pyrite have similar d_{102} values and those that were not in contact with pyrite have consistently larger d_{102} values, as would be expected if they formed in a somewhat sulfur-deficient environment. If the pyrrhotites had originally had the compositions that they displayed after annealing then they would indicate temperatures between 455° and 510° C for the samples with coexisting pyrite and between 390° and 450° C for those samples in which pyrite is absent, the latter then being minimum values for the temperature. These apparent temperatures are very possibly not true estimates of the temperatures of crystallization.

It has been pointed out by Buseck (10, 11), Kullerud *et al.* (20) and, more recently, by Desborough and Carpenter (15) that temperatures indicated by inverted monoclinic pyrrhotite are very possibly spurious. Kullerud *et al.* showed that monoclinic pyrrhotite, at least when coexisting with pyrite, has a limited compositional range. Desborough and Carpenter agree and state it to be stoichiometric Fe_7S_8 . This, however, is not a certainty. The accuracy of the X-ray diffraction method (± 0.25 atomic percent metals for natural pyrrhotites (4)), combined with the observation of Desborough and Carpenter that up to 20 percent admixed hexagonal pyrrhotite is undetectable in an X-ray diffractogram of monoclinic pyrrhotite, precludes the conclusion of stoichiometry for the monoclinic phase from X-ray powder measurements, although the available evidence does suggest a limited compositional range. This means that the original hexagonal pyrrhotite, for all initial compositions other than that of the monoclinic phase, must change composition during the change to the monoclinic form, presumably by forming new "pyrrhotite" phases, or by exsolving pyrite, or perhaps even by reacting with pyrite to become more sulfur-rich.

The possible changes that pyrrhotite may undergo during cooling, unless isochemical, thus severely limit the usefulness of pyrrhotite as a geothermometer. These changes are complicated even more by the laboratory annealing of the low-temperature monoclinic pyrrhotite and associated reaction products. Clearly, in order to have the composition of the resulting hexagonal pyrrhotite be meaningful, material having the *bulk* composition of the initial pyrrhotite must be reheated. In many instances it is possible that the reheating of a sample of pyrrhotite will produce a compositional change and thus indicate an apparent temperature which, depending on the degree of reequilibration and diffusion of material away from the reaction site which occurred during the initial cooling, may be either quite reasonable or totally invalid. Yet in

principle it may still be possible to take bulk samples of low-temperature pyrrhotite assemblages, even if the pyrrhotite is totally or partly monoclinic, and have them yield meaningful temperatures. Recent data of Arnold (2) indicate that coexisting hexagonal and monoclinic pyrrhotites may be associated within very finely intergrown lamellar mixtures. Such intimate intergrowths, when sampled statistically, may well yield the required bulk compositions corresponding to the original high temperature phase. Presumably the most desirable procedure would be to take multiple samples of a single mass of pyrrhotite that is large enough so that the reaction products did not diffuse away. Alternatively, small masses of the low-temperature assemblages could be utilized, provided that these masses were physically isolated from one another, as in the case of disseminations within a skarn host. Such disseminated samples from the Marbridge deposit yielded values with very little scatter between samples (13). In all cases internal consistency between samples would suggest, but not prove, that the results were meaningful. Early pyrite would have to be recognized and distinguished from the reaction products produced by the cooling pyrrhotite. Following the initial (equilibrium) pyrrhotite crystallization, each small pyrrhotite mass would have to remain as an individual closed system. If there were material transfer at high temperatures that would affect the equilibria, or if there had been low-temperature reactions such as the oxidation or sulfurization reactions described by Desborough and Carpenter (15), then the resulting monoclinic pyrrhotite would have very little validity as a geothermometer. Of course, such reactions also invalidate the geothermometric measurements made from the high-temperature hexagonal pyrrhotite.

The limited number of pyrrhotite samples from Tem Piute precludes making a reliable evaluation in regard to the validity of geothermometry using monoclinic pyrrhotites. The presumptive temperatures are, however, reasonable for this type of deposit. Further, the temperatures measured from annealed monoclinic pyrrhotite samples from other deposits are also often consistent with those expected from these deposits. For example, Clark (13) measured many annealed samples and got internally consistent results indicating systematic variations along two parallel drifts, as well as in a cross section parallel to the length and depth of this tabular ore body, with the measured temperatures ranging from 390° to 530° C. Anomalous temperatures have been reported from the northern Pennine orefield by Sawkins *et al.* (23), but Clark (12) points out that in this instance it is hardly surprising that pyrrhotite which crystallized initially in the low-temperature monoclinic form, and thus never existed at the temperature of the hexagonal solvus, gives unreasonable results when its composition is projected up to that solvus.

The apparent reasonableness of temperatures determined from annealed monoclinic pyrrhotites may be fortuitous; it may also suggest that many of the annealed samples have in effect been bulk samples. The evidence however, is contradictory; although this apparent reasonableness points towards the potential validity of the technique when properly applied, the experiments of Buseck (11), Kullerud *et al.* (20), Groves and Ford (18) and Clark (13) indicate that natural pyrrhotite samples commonly change their composition

during prolonged annealing. Such extended heating may result in hexagonal pyrrhotites having an apparent crystallization temperature equivalent to the temperature at which they were annealed. Prolonged heating of natural specimens presumably permits reaction with extraneous mineral grains that did not result from the breakdown of the initial high-temperature phase. The existing experimental work is not extensive enough to provide a conclusive answer and consequently at the present time temperatures derived from completely or partly monoclinic pyrrhotites must be considered suspect. Experimental work on low-temperature reactions and diffusion rates, as well as further work on the low-temperature phase relations in the FeS-FeS₂ system will help clarify some of these points.

SUMMARY AND DISCUSSION

At Tem Piute a barren stock is separated from unmineralized limestone and hornfels by a narrow zone of banded skarn, the banding reflecting minor but original compositional differences within the sediments. Within this skarn zone is a wide variety of ore minerals—pyrite, chalcopyrite, pyrrhotite, magnetite, marcasite, sphalerite, molybdenite, galena, hematite, galenobismutite, cosalite, bismuthinite, and native bismuth, as well as scheelite—an unusually complex suite for a contact metasomatic deposit.

The ore minerals exhibit characteristic associations, as well as a systematic distribution that presumably reflects thermal zoning across and within the aureole (Fig. 9). Such zoning is known from other contact-metasomatic deposits; for example in the Central District of New Mexico sphalerite occurs near the outer edge of the aureole whereas magnetite is concentrated near the igneous contacts (24). Zoning is, however, rarer than in the other kinds of hydrothermal ore deposits.

At Tem Piute there is abundant pyrrhotite, magnetite and, locally, molybdenite in the skarn—close to the quartz monzonite—in the area that was presumably the hottest at the time of mineralization. The concentration of each of these minerals decreases with increasing distance from the igneous contact and, except for molybdenite, they are absent near the limestone and hornfels. Molybdenite is an exception for, although it does not appreciably occur in the intervening skarn, it does occur along the hornfels-skarn contact.

Also in the skarn is another suite of ore minerals that is concentrated in the area near the limestone. Sphalerite is the most abundant of these minerals; it commonly contains exsolved pyrrhotite or chalcopyrite, with the samples containing exsolved pyrrhotite occurring farther from the sedimentary contact than the sphalerite with exsolved chalcopyrite. Galena, bismuthinite, bismuth and the bismuth sulfo-salts occur with sphalerite within the skarn near the outer contact. This association is presumably in response to the lower temperatures occurring near the limestone.

Minerals such as pyrite, chalcopyrite and scheelite are distributed completely across the skarn aureole, apparently not being as sensitive to temperature variations as the afore-mentioned minerals.

The zoning of the ore minerals is also reflected in two gangue minerals: ilvaite occurs only near the igneous contact, primarily together with pyrrhotite and molybdenite. Fluorite also typically occurs in the skarn with sulfides, but it is found near limestone and together with sphalerite and the bismuth sulfo-salts. Because of its association and location it is almost certain that it formed at lower temperatures than the ilvaite. Although there is some evi-

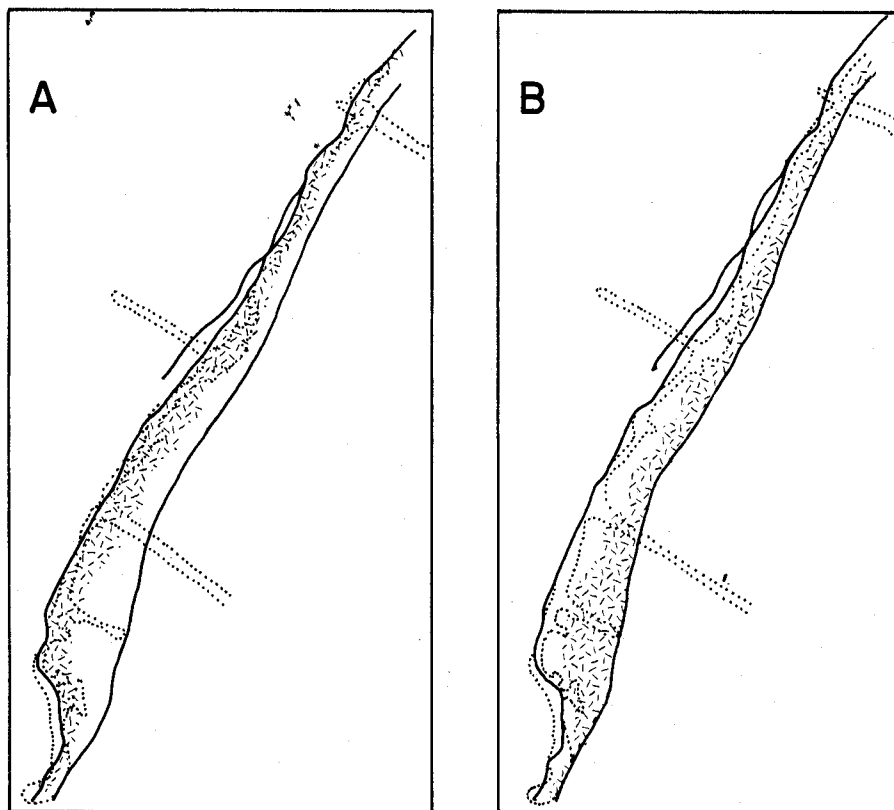


FIG. 9. Schematic geologic map of the Free Tunnel (cf. Fig. 2). The stipled area within the skarn zone in "A" shows the zone of low-temperature mineralization: sphalerite, galena, bismuth minerals, sulfo-salts and fluorite. The stipled area within the skarn zone in "B" shows the high temperature mineralization: pyrrhotite, magnetite and locally molybdenite and ilvaite.

dence for the local controlling of deposition by host composition this is inadequate to fully explain the zoning of the ore and associated gangue minerals, as they do cut across the skarn bands. The suite of minerals associated with sphalerite also maintains a relatively consistent proximity to the limestone-skarn contact, independent of the particular sedimentary horizons that the skarn has replaced.

The measured upper temperature limit for mineralization, applicable for those minerals deposited in the inner portion of the aureole is approximately 500° C. Such a value is surely reasonable, although the reliability of the measurement is questionable in view of the uncertainties of the pyrrhotite geothermometry. The lower temperature limit of mineralization, applicable to those minerals deposited in the outer portion of the aureole and based on calculated sulfo-salt stabilities, is below 235° C, assuming that the relevant minerals are primary. Thus, if these temperatures are valid, it would seem that there was an appreciable temperature range for ore mineral deposition at this deposit.

If the two mineral suites—the one from the inner, and the other from the outer part of the skarn aureole—were deposited at greatly different times, there would be no reason why the suites should be so distinctly localized. On the other hand, their physical distribution and the lack of appreciable physical overlap is readily understandable in terms of a response to a thermal gradient correlated with proximity to the igneous contact. This suggests that deposition of the two suites was essentially simultaneous and that the zoning was indeed the result of temperature differences. Considering the narrow width of the skarn zone, this indicates a remarkably high thermal gradient across the contact aureole, surprising in view of the large heat source and reservoir provided by the adjacent intrusive. It also indicates that ore deposition extended down to rather low temperatures—in the range of mineral deposits normally considered to have been formed by hydrothermal processes.

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