# Mineralization and alteration in calcareous rocks near the Santa Rita stock, New Mexico 

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# MINERALIZATION AND ALTERATION IN CALCAREOUS ROCKS NEAR THE SANTA RITA STOCK, NEW MEXICO 

by<br>RICHARD L. NIELSEN ${ }^{1}$

## INTRODUCTION

This paper briefly describes mineralization and alteration in some sedimentary host rocks surrounding the Chino porphyry copper deposit at Santa Rita. Past production from the Chino mine largely has come from disseminated supergene chalcocite ores in the granodiorite stock, dioritic sills, and shales of the Colorado Formation. Production from primary chalcopyrite-pyrite tactite ores will become increasingly important in the future, and this production will come from altered Oswald() and Syrena Formations, principally in the Lee Hill area. Zoning in highly altered and mineralized limestones and calcareous shales of these formations from the primary zone of the ore deposit outward into unaltered and unmineralized rocks is the principal subject of this investigation. Some implied generalizations concerning origin and zoning of contact metasomatic replacement deposits and their relation to porphyry copper mineralization are also discussed.

The general geology, detailed stratigraphy, and structural features of the district are most recently described by Jones and others (1967) . Geology of the porphyry copper deposit is described by Rose and Baltosser (1966), and the geology, mineralization, and alteration of the nonporphyry ore deposits are reviewed by Hernon and Jones (1968). More detailed investigations of alteration in the porphyry copper deposit are reported by Kerr and others (1950 ), Burnham (1962), and more recently by Nielsen (1968), and Sheppard and others (1969). The reader is referred to these and other papers for a comprehensive review of this complex district.

Most of this study was focused on exposures and drill core samples near the periphery of the Santa Rita stock and surface exposures of the Oswaldo and Syrena Formations extending out to the east (Fig. 1) . This was done to minimize complex mineralogical effects of overlapping metamorphism and alteration produced by multiple intrusions, specifically produced by the nearby Hanover stock on the north and the many granitic dikes together with their associated lead-zinc and zinc mineralization and alteration on the west. Hence, the results hopefully present preliminary information on gross zoning around a fairly typical pyrite-rich porphyry copper deposit such as at Santa Rita.

Chemical analyses, spectrographic analyses, and mineral concentrates were prepared under the supervision of D. Norton, Geochemical Research and Laboratory Division, Kennecott Copper Corporation. Mineralogy of altered limestones and shales was studied using petrographic and X-ray diffraction techniques. Nonsilicated limestone was

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dissolved in dilute hydrochloric acid and the mineralogy of the insoluble residue determined by X-ray diffraction.
W. W. Baltosser, Division Geologist of the Chino mine, and his staff were most helpful in providing samples and detailed information of the mine; their review of this paper is appreciated. It is a pleasure to acknowledge cooperation of Kennecott Copper Corporation which supported the research and permitted publication of the results.

## MINERALIZATION AND ALTERATION IN CALCAREOUS SEDIMENTARY UNITS

## UNALTERED OR BACKGROUND ZONE

The Oswaldo Formation of Pennsylvanian age, the most widely exposed limestone in the district, is the principal sedimentary host rock for disseminated copper mineralization at the margin of the Santa Rita stock. It consists predominantly of gray limestone in massive beds, separated by thin shale partings and a few shale beds. The limestone beds are crinoidal and contain minor argillaceous material. Chert nodules are common. Calcite is the only carbonate found in unaltered Oswaldo limestone. Quartz or chalcedony is the principal impurity. Illite and kaolinite comprise the relatively minor argillaceous components with minor chlorite (Table 1).

The Syrena Formation, also of Pennsylvanian age, overlies the Oswaldo Formation and is exposed in the area north and northeast of Santa Rita and in the Chino mine where it is strongly altered and locally mineralized to ore grade. The lower part of the formation is composed of thick calcareous shales or mudstones alternating with nodular shaly limestones which consist of rounded, flattened, blue-gray limestone nodules in blocky, buff, calcareous shale. The upper part is composed of alternating impure, gray or buff limestone and thin, reddish- to dark-gray calcareous shale. Calcite, quartz, illite, kaolinite, and a little chlorite are the principal mineral constituents of unaltered Syrena Formation (Table 2).

## VISIBLE ALTERATION HALO

Calcareous sedimentary host rocks are completely altered and replaced up to a maximum distance of about 3,000 feet from the Santa Rita stock or its apophyses. Limestone beds of both formations arc locally and erratically mineralized with relatively high-grade primary copper and magnetite up to a maximum distance of about 2,000 feet from the stock contact, with best development of primary grade and tonnage in Oswaldo Formation of the Lee Hill orebody on the northwest margin of the stock. Shaly limestones of the Syrena Formation are mineralized to ore grade only locally


FIGURE 1.

# TABLE 1. MINERAL ZONING AND PARAGENESIS IN LIMESTONE OF THE OSWALDO FORMATION SANTA RITA, NEW MEXICO 

| DISSEMINATED COPPER OREAbout 200 to 2,000 feet from stock contact |  | visible alteration halo approx. 200 to 3,000 feet from stock contact |  | BACKGROUND$>5,000$ feet fromstock contact |
| :---: | :---: | :---: | :---: | :---: |
| $\begin{aligned} & \text { "normal" ore } \\ & \text { py/cp }<10 / 1 \end{aligned}$ | pyrite-rich ore $\mathrm{py} / \mathrm{cp}>10 / 1$ | inner | outer |  |
| ```MAGNETITE ( \(2.40 \mathrm{wt} . \%\) ) PYRITE ( 3 -15 wt. \%) CHALCOPYRITE ( \(1.3 \mathrm{wt} . \%\) ) QUARTZ ANDRADITE Fe-RICH EPIDOTE andradite biotite siderite orthoclase montmorillonite``` | ```MAGNETITE (20.75 wt. %) PYRITE (5-25 wt. %) CHALCOPYRITE (1.3 wt. %) QUARTZ Fe-RICH ACTINOLITE MONTMORILLONITE Fe-RICH EPIDOTE CHLORITE biotite orthoclase siderite zeolite``` | ANDRADITE EPIDOTE DIOPSIDE quartz magnetite actinolite pyrite | CALCITE QUARTZ TREMOLITE kaolinite diopside andradite epidote pyrite sphalerite | CALCITE QUARTZ Qaolinite illite chlorite |

along the stock margin, although all parts of the unit have been completely converted to tactite and calc-silicate hornfels. Chalcopyrite is generally present in this disseminated copper tactite zone (Fig. 1), but unfortunately ore grade is attained only locally.
Visible alteration in limestones, principally in the Oswaldo, extends outward 1,000 to 1,500 feet beyond the orebody assay wall, thus forming a halo of visible tactite alteration or bleached marble with a maximum limit of about 3,000 feet from the stock margin (Fig. 1). Silicification, hornfelsing, and minor pyrite mineralization in calcareous shales of the Syrena Formation are visible up to a maximum of about 5,000 feet from the Santa Rita stock. On the east margin alteration in shaly rocks is readily visible about twice as far as in adjacent limestones of the Oswaldo Formation. X-ray diffraction analyses have detected marked mineralogic alteration in calcareous shales even farther out, perhaps extending the halo of detectable alteration as far as 8,000 feet from the stock contact.
In the outermost part of this extensive visible alteration halo, calcareous shales are converted to greenish-gray, flinty hornfels consisting of quartz, calcite, actinolite, diopside,
and plagioclase, and the appearance of this hornfels marks the outer limit of visible alteration (Fig. 1). Generally, relatively pure limestone interbeds are apparently unaltered, although green actinolite reaction rims are present around limestone nodules enclosed in calcareous shales. Partial silication, which marks the outer limit of visible alteration in relatively pure limestone, generally is confined to thin impure shaly and cherty beds or along structures such as shear zones, faults, or dike margins. Pale yellow-brown or green andradite garnet is present along fractures or breccia zones cutting pure limestone; epidote, tremolite-actinolite, and diopside are common with garnet in shaly horizons. A little sphalerite is commonly disseminated in andradite rock. Adjacent unsilicated limestone is bleached and recrystallized to medium- or coarse-grained, light-gray to white, tremolitic marble.

All calcareous rocks are completely replaced by silicates, principally andradite, epidote, diopside, and actinolite near the inner edge of the alteration halo around ore. Yellowbrown andradite massively replaces relatively pure lime-

TABLE 2. MINERAL ZONING AND PARAGENESIS IN CALCAREOUS SHALES OF THE SYRENA FORMATION SANTA RITA, NEW MEXICO

| DISSEMINATED ORE ZONE <br> up to about 2,000 feet from <br> stock contact |  | visible ALTERATION HALo <br> approx. 200 to 5,000 feet <br> from stock contact |
| :--- | :--- | :--- |
|  |  | inner |

stone. A greenish-gray mottled rock consisting of green, iron-rich epidote, quartz, actinolite, diopside, and albite replaces calcareous shales. Magnetite and sulfides, principally pyrite, become increasingly abundant in tactite near the inner edge of the halo, particularly near the Oswaldo No. 2 shaft. Here, epidote-garnet-magnetite tactite, possibly of the Oswaldo Formation, has weathered, and the ground surface is mantled with, nodules of magnetite. Magnetite and pyrite veinlets laced through brown andraditc-rich tactite suggest late introduction of these ore minerals, but in magnetite-rich tactite the magnetite commonly is present interstitial to or along the margins of garnet crystals, suggesting contemporaneous emplacement. Specular hematite is generally present in small fractures cutting magnetite, possibly a late alteration feature.

Tactite derived from calcareous shale located in the strong pyrite halo on the west margin of the stock contains up to 10 weight percent pyrite, largely in veinlets associated with epidote, montmorillonite, calcite, siderite, and ironrich chlorite, all of which replace early actinolite-garnetdiopside hornfels, forming mottled, massive, gray-green hornfels laced by pyrite veinlets and blebs which are enclosed in greenish-gray alteration envelopes.

## DISSEMINATED COPPER TACTITE ZONE

Within the disseminated copper zone, dark greenish-gray or brownish-green tactite derived from relatively pure limestone, principally from the Oswaldo Formation, consists of magnetite, greenish-brown andradite, epidote, biotite, siderite, chlorite, and montmorillonite. Generally, the garnet, magnetite, and some chalcopyrite appear to be early massive replacement of limestone. Pyrite, chalcopyrite, actinolite, siderite, chlorite, montmorillonite, and much of the epidote appear to be late and are present either as greenish-gray alteration envelopes around quartz-pyrite veins cutting through dark massive magnetite-andradite rock or as light-green-gray patchy replacements. This late hydrous tactite assemblage with pyrite (10-25 weight percent) is common in part of the Lee Hill area, particularly where adjacent igneous rocks are strongly pyritized (4-10 weight percent) . The hydrous tactite assemblage may be equivalent to pyrite-quartz-sericite alteration in adjacent granitic rocks; both are related to quartz-pyrite veinlets.

Calcareous shales, principally of the Syrena Formation, are replaced in the disseminated copper zone by a mottled dark-green tactite consisting of epidote, quartz, pyrite, orthoclase, biotite, montmorillonite, magnetite, and chalcopyrite. Magnetite, pyrite, and andradite are subordinate and epidote more abundant in altered calcareous shales than in nearby tactite derived from massive pure limestone. Biotite and orthoclase veinlets are common, particularly on the east and southeast margins of the stock where adjacent igneous rocks show potassium-silicate alteration assemblages rich in secondary biotite and orthoclase flooding. Montmorillonite, chlorite, siderite, specularite, and epidote are common in alteration envelopes around pyrite veinlets in silicated calcareous shales within the strong pyritic halo on the west margin of the stock.

The width of disseminated copper tactite mineralization is narrower along the east margin of the stock than in the Lee Hill area (Fig. 1) . This possibly reflects a more steeply
dipping contact and less numerous dikes extending from the stock on the east margin than in the Lee Hill area. Indeed, some deep drill holes intersected granodiorite of the Santa Rita stock beneath part of the Lee Hill orebody, suggesting a less steeply dipping west contact.

Total sulfides, pyrite, chalcopyrite, and magnetite are slightly less abundant in tactite along the east margin than on the west. In summary, mineralization appears less intense and alteration zoning is telescoped on this east margin, all of which may reflect stronger fracturing, brecciation, a less steep contact, and a more efficient hydrothermal plumbing system on the west side of the contact compared to the east side. This asymmetry also is manifested in igneous rocks with stronger alteration and sulfide mineralization on the west margin of the stock than on the east margin (Nielsen, 1968).

## RELATION TO ALTERATION AND MINERALIZATION IN GRANITIC ROCKS

Bulk composition of the Santa Rita stock, and widespread "diorite" or quartz diorite sills which form wall rocks around the stock, approximates granodiorite. Both stock and sill rocks have been modified by hypogene alteration associated with primary sulfide mineralization (Nielsen, 1968).

A central zone within the center of the stock is low in sulfides (less than 1 weight percent) and contains abundant quartz veinlets with vein and replacement orthoclase. This quartz-orthoclase rock forms a core largely surrounded by biotite-granodiorite porphyry, much of which shows weak to strong development of potassium-silicate alteration characterized by K-feldspar (Or 90-95) rims and veinlets in plagioclase phenocrysts, biotite veinlets, and biotite aggregates replacing hornblende and biotite phenocrysts. Successive diffuse zones defined by increasing sulfide content and intensity of feldspar-destructive alteration occur outward from the center of the stock and include: (a) montmorillonite biotite after plagioclase (orthoclase unaltered), (b) montmorillonite-kaolinite mixture after plagioclase (orthoclase unaltered), (c) kaolinite after plagioclase (orthoclase unaltered ), and (d) quartz-sericite ( $2 \mathrm{M}_{1}$ muscovite) after plagioclase and orthoclase. Pyrite, by far the most common sulfide in the system, is concentrated in veinlets in the zone of quartz-sericite-pyrite alteration at the margin of the stock and the adjacent altered shale and quartz-diorite sills.

These diffuse alteration zones have not affected all parts of the stock equally. Quartz-sericite alteration is very strong along the west margin of the stock (Fig. 1); clay alteration is moderate through the center and along the northeast margin. Large masses of granodiorite porphyry on the north and southeast ends of the stock are relatively free of claymica alteration. Wherever the clay-mica-sulfide assemblage and the potassium-silicate alteration are found in the same rock, the former is usually superimposed on the latter, and the relative ages of the two alteration types are generally unambiguous.

Calcareous wall rocks contain tactite assemblages similar to alteration assemblages in adjacent altered igneous rocks.

Calcareous shales have been altered to epidote-actinolite-biotite-orthoclase hornfels on the northeast and south where biotite-orthoclase alteration is abundant in adjacent granodiorite. Andradite-magnetite-diopside-epidote tactites are present in replaced limestone and may be equivalent to biotite-orthoclase alteration.
Quartz-orthoclase rock of the stock, the most intense potassium-silicate alteration type, is in contact with limestone in the Lee Hill area, and this area is where the most extensive andradite-magnetite tactite is developed. Granodiorite porphyry at the north end of the stock contains up to 3 or 4 weight percent magnetite disseminated or in replacement veinlets, and replacement of limestone by magnetite (up to 70 weight percent magnetite) is most intense in adjacent tactite on the northwest in the Lee Hill area.
Andradite-magnetite tactite of the Oswaldo limestone in the west part of the Lee Hill area is strongly mineralized with pyrite (up to 25 weight percent ). Actinolite, montmorillonite, chlorite, epidote, and siderite form retrograde alteration envelopes around the abundant quartz-pyrite veinlets. Adjacent igneous rocks are strongly mineralized
with pyrite (up to 10 weight percent) and converted to a quartz-sericite aggregate. Pyritic tactite derived from calcareous shales shows the same retrograde assemblage with epidote, chlorite, montmorillonite, and calcite perhaps more abundant in altered calcareous shales than in altered limestones of this pyritic area.

## CHEMICAL CHANGES IN ALTERATION OF CALCAREOUS ROCKS

Partial chemical analyses of altered and unaltered limestone from the Oswaldo Formation and calcareous shale from the Syrena Formation are given in Table 3. The samples, generally 10 -foot channel samples cut from fresh road cuts along New Mexico Highway 90 or 50 -foot drill core composites, come from the unaltered units, the alteration halo, sulfide-rich ore, and sulfide-lean ore (Fig. 1). Gains and losses of important chemical constituents relative to unaltered limestone and unaltered calcareous shale are shown in Figures 2 and 3. Constant volume replacement is assumed for this comparison. A study of drill logs indicates

TABLE 3. PARTIAL CHEMICAL ANALYSES OF ALTERED AND UNALTERED CALCAREOUS ROCKS SANTA RITA, NEW MEXICO

|  | Limestone from Oswaldo Formation alteration increasing |  |  |  |  |  | Calcareous Shale from Syrena Formation alteration increasing |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $0-1$ | 0.2 | 0.3 | $0 \cdot 4$ | 0.5 | 0-6 | S-1 | S-2 | S-3 | S-4 | S. 5 |
| $\mathrm{SiO}_{2}$ | 1.6 | 36.0 | 31.4 | 19.2 | 28.4 | 52.2 | 44.9 | 35.4 | 48.5 | 38.1 | 35.0 |
| $\mathrm{Al}_{2} \mathrm{O}_{3}$ | 0.21 | 4.27 | 4.35 | 3.34 | 3.35 | 12.40 | 3.76 | 3.59 | 4.99 | 6.76 | 7.12 |
| $\mathrm{Fe}_{2} \mathrm{O}_{3}{ }^{(1)}$ | 0.20 | 26.60 | 51.90 | 61.20 | 57.50 | 9.88 | 1.57 | 1.84 | 17.90 | 35.00 | 32.30 |
| MgO | 0.48 | 0.73 | 3.25 | 1.87 | 1.26 | 3.40 | 1.61 | 1.44 | 3.35 | 1.44 | 1.84 |
| CaO | 53.00 | 28.30 | 2.21 | 3.48 | 4.56 | 10.80 | 24.90 | 30.20 | 20.60 | 5.53 | 11.70 |
| $\mathrm{Na}_{2} \mathrm{O}$ | 0.02 | 0.06 | 0.08 | 0.05 | 0.15 | 1.40 | 0.07 | 0.10 | 0.59 | 0.30 | 0.63 |
| $\mathrm{K}_{2} \mathrm{O}$ | 0.02 | 0.03 | 0.72 | 0.46 | 1.32 | 2.24 | 0.35 | 0.20 | 0.19 | 1.77 | 1.25 |
| $\mathrm{H}_{2} \mathrm{O}^{-}$ | 0.04 | 0.04 | 0.12 | 0.34 | 0.21 | 1.34 | 0.29 | 0.21 | 0.23 | 0.52 | 0.53 |
| $\mathrm{H}_{2} \mathrm{O}^{+}$ | 0.15 | 0.39 | 1.15 | 0.92 | 0.72 | 3.55 | 1.53 | 1.74 | 1.07 | 0.91 | 0.31 |
| $\mathrm{CO}_{2}$ | 40.80 | 1.60 | 0.51 | 1.38 | 2.72 | 2.13 | 19.80 | 23.40 | 6.13 | 0.87 | 1.28 |
| $\mathrm{TiO}_{2}{ }^{(2)}$ | <0.01 | 0.16 | 0.09 | 0.1 | 0.09 | 0.6 | 0.24 | 0.22 | 0.31 | 0.34 | 0.3 |
| $\mathrm{MnO}^{(2)}$ | 0.012 | 0.8 | 0.18 | 0.09 | 0.17 | 0.2 | 0.02 | 0.24 | 0.7 | 0.18 | 0.18 |
| Cu | 0.002 | 0.06 | 0.96 | 0.88 | 0.50 | 0.82 | 0.003 | 0.001 | 0.003 | 0.59 | 0.92 |
| S | 0.009 | 0.67 | 10.1 | 13.5 | 4.0 | 2.6 | 0.02 | 0.01 | 0.003 | 10.6 | 8.4 |
| S.G. | 2.70 | 3.52 | 3.18 | 3.67 | 4.10 | 2.69 | 2.53 | 2.58 | 3.15 | 3.32 | 2.90 |

(Analysts: R. J. Bianchi, A. M. Badawy, R. L. Hendricks, and J. H. Lane)
${ }^{(1)} \mathrm{Fe}_{2} \mathrm{O}_{3}$ is total iron calculated as $\mathrm{Fe}_{2} \mathrm{O}_{3}$
${ }^{(2)} \mathrm{MnO}^{2}$ and $\mathrm{TiO}_{2}$ are spectrographic analyses

Sample Descriptions, Location Shown in Figure 1
0-1 Unaltered massive limestone, Oswaldo Formation; calcite with minor quartz, traces of illite and chlorite.
0.2 Tactite of Oswaldo Formation from silicated halo; epidote, andradite, and quartz with minor actinolite, magnetite, pyrite ( $1 \%$ ), siderite, and K-feldspar.
0.3 Tactite ore of Oswaldo Formation from Lee Hill orebody; magnetite ( $20 \%$ ), pyrite ( $16 \%$ ), chalcopyrite, ( $3 \%$ ), actinolite, epidote, quartz with minor K-feldspar, siderite, biotite, and chlorite.
0-4 Tactite ore of the Oswaldo Formation from Lee Hill orebody; magnetite ( $46 \%$ ), quartz, andradite, pyrite ( $25 \%$ ), chalcopyrite ( $3 \%$ ), with small amounts of siderite, epidote, actinolite, and montmorillonite.
0.5 Tactite ore of Oswaldo Formation from east margin of Santa Rita stock; magnetite ( $48 \%$ ), epidote, quartz, montmorillonite, pyrite ( $6 \%$ ), and chalcopyrite ( $2 \%$ ).
0.6 Tactite "ore" of Oswaldo Formation from south end of Santa

Rita stock; quartz, actinolite, orthoclase, biotite, montmorillonite, epidote, with minor magnetite ( $2 \%$ ), pyrite ( $3 \%$ ), chalcopyrite (2\%), and zeolite.
S-1 Nodular calcareous shale, unaltered Syrena Formation; calcite, quartz, illite, chlorite, and minor kaolinite.
S-2 Nodular shaly limestone, unaltered Syrena Formation; calcite, quartz, illite, with minor kaolinite and chlorite.
S-3 Actinolite marble and hornfels, Syrena Formation, from outer part of alteration halo; calcite, quartz, actinolite, diopside with minor albite, garnet, and epidote.
S-4 Tactite "ore" of the Syrena Formation near east edge of Santa Rita stock; epidote, quartz, actinolite, magnetite, pyrite ( $17 \%$ ), chalcopyrite ( $2 \%$ ), biotite, orthoclase with minor chlorite and siderite.
S. 5 Tactite "ore" of the Syrena Formation near the south end of the Santa Rita stock; epidote, quartz, orthoclase, diopside, montmorillonite, pyrite ( $14 \%$ ), chalcopyrite ( $3 \%$ ), and calcite, with minor biotite, diopside, garnet, and magnetite.

GAIN AND LOSS OF PRINCIPAL ROCK CONSTITUENTS THROUGH ALTERATION AND MINERALIZATION OF LIMESTONE FROM OSWALDO FORMATION
ASSUMING CONSTANT VOLUME REPLACEMENT


GAIN AND LOSS OF PRINCIPAL ROCK CONSTITUENTS THROUGH ALTERATION AND MINERALIZATION OF CALCAREOUS SHALE FROM SYRENA FORMATION ASSUMING CONSTANT VOLUME REPLACEMENT


FIGURE 2.
no appreciable decrease or increase in thickness of stratigraphic units which have been mineralized and replaced by tactite. However, this conclusion is somewhat tenuous because the true thickness of stratigraphic units is difficult to obtain in mineralized areas owing to numerous faults and small dikes encountered in drill core. However, detailed study of altered Oswaldo limestone in underground workings at the Pewabic mine (Schmitt, 1939) shows essentially no change in volume was produced during replacement.

Tactite replacement of relatively pure limestone resulted in a large gain in iron, silicon, and aluminum, and moderate gains in sulfur, magnesium, potassium, sodium, and hydrogen. Sulfide-rich tactite with retrograde alteration near the stock contact shows strong gains in sulfur, potassium, hydrogen, and sodium. Calcium and carbon dioxide were strongly leached from all altered limestone.

Tactite and hornfcls replacement of calcareous shale also resulted in strong gains in iron, silicon, and aluminum, with moderate gains in sodium and magnesium. Strong loss of calcium and carbon dioxide is evident. Potassium and sulfur have been added to sulfide-rich tactite. Hydrogen remains about the same or slightly removed from tactitc near the contact. Apparently dehydration of water-rich illitic calcareous shale was the net effect during alteration and
mineralization.
Chemical analyses of altered granodiorite from the stock (Nielsen, 1968) show that altered rocks of the stock have been leached of aluminum, iron, magnesium, calcium, and sodium. With the exception of calcium, these are the elements which show gains in the adjacent tactite and hornfels. Silicon, potassium, sulfur, and hydrogen apparently have been enriched in altered igneous rocks as well as in adjacent mineralized tactites. Large amounts of calcium and carbon dioxide have been leached from both igneous and sedimentary rocks and apparently have been removed from the system.

## CONCLUSIONS

Formation of mineralized tactites and hornfels in calcareous wall rocks of the Santa Rita stock essentially was contemporaneous with alteration and mineralization of the igneous rocks. In the stock, effects produced by primary igneous processes such as differentiation are overlapped by
postmagmatic hydrothermal alteration, and these are dificult to separate. Similarly, in calcareous wall rocks thermal metamorphic effects overlap and are difficult to distinguish from the metasomatic replacement effects associated with hydrothermal alteration, these chiefly being addition of iron and silica with removal of calcium and carbonate.

An early stage of potassium-silicate alteration resulted in formation of quartz-orthoclase rock near the center of the stock and diffuse zones of biotite-orthoclase alteration replacing igneous minerals. Adjacent relatively pure limestone was converted to tactite, rich in andradite, magnetite, epidote, and quartz. Calcareous shales were converted to tactites and hornfels rich in epidote, quartz, orthoclase, biotite, and magnetite. These alteration assemblages may be superimposed on limestone which had been converted to tremolitic marble, and calcareous shales previously converted to quartz-actinolite-plagioclase-calcite hornfels by thermal metamorphism during emplacement of the stock.

Strong sulfide mineralization, chiefly pyrite with minor chalcopyrite, resulted in clay-mica-pyrite alteration of igneous rocks and a quartz-pyrite-actinolite-montmorillonitesiderite, epidote, retrograde assemblage in the tactite and hornfels.

Evolution of the hydrothermal fluid is highly complex. Evidently the early tactite alteration was produced by a fluid emanating from the stock, which carried large quantities of iron, silica, alumina, sodium, and magnesium. Orthoclase, quartz, and biotite were evidently crystallizing from the fluid within the stock. Late intense hydration of igneous rocks to clay-mica assemblages and associated precipitation of large amounts of pyrite veinlets imply late hydrothermal fluids with high activity of hydrogen ions. In calcareous rocks, the late crosscutting quartz-pyrite veins with associated retrograde montmorillonite, epidote, actinolite, and chlorite which replace garnet also indicate hydration of the early tactite rock, and these late assemblages, characterized
by hydroxyl-bearing silicates, may have been produced by emerging hydrothermal fluids mixing with cooler meteoric waters accompanied by a retreating heat source in the stock interior. This mechanism has been suggested to account for late hypogene clays and micas with quartz-pyrite veinlets in the porphyry (Sheppard and others, 1969 ).
Large amounts of calcium and $\mathrm{CO}_{2}$ were removed from the system by circulating hydrothermal waters, and it is easy to imagine thick accumulations of travertine from hot springs on the ancient land surface overlying the "active" porphyry copper system.

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