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# Wall-Rock Alteration in the Cochin Mining District, New Mexico

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# Abstract

Hydrothermally altered volcanic and intrusive rocks (mainly andesite and monzonite) of Tertiary age are associated with gold- and silverbearing quartz veins. Two stages of epithermal quartz veins occur, but only the first stage is associated with economic mineralization.

Alteration zones, named with respect to clay minerals present in the greatest abundance, are (from the vein outward): (1) dickite, (2) illite-kaolinite, (3) vermiculite-halloysite, and (4) chlorite-montmorillonite.

Interpretation of X-ray spectrometer traces indicates that chlorites become enriched in magnesium in a veinward direction. Montmorillonites become progressively enriched in calcium toward the vein; this generalization is corroborated by chemical analyses. Illite is present in intense zones of alteration as a 1Md (1-layer monoclinic disordered) polymorph.

Base exchange, with resultant mixed-layer clay minerals as intermediate phases, is an important mechanism for transitions between 2:1 clay minerals. Transformation from 2:1 to 1:1 clay minerals has involved, at least partially, selective solution and recrystallization, with amorphous aluminum silicate (allophane) as an intermediate phase. Order of formation of 1:1 clay minerals is apparently allophone $\rightarrow$  halloysite $\rightarrow$  kaolinite $\rightarrow$ dickite.

Chemical analyses of the altered rocks show a marked veinward decrease in basic ions; less significant changes are shown by acidic ions. Analyses of relatively pure illites indicate a general veinward decrease in basic cations.

Alteration associated with the two stages of quartz veins proceeded as acidalkaline fronts, the second stage being more acidic because of previous leaching by first-stage solutions.

Increasing intensity of alteration is regarded as a guide to quartz veins and possible ore deposits.

# Introduction

#### HISTORY OF THE DISTRICT

Gold and silver mining in the Cochiti (Bland) mining district (fig. 1) began in 1889 and reached its peak in 1893. Operations continued until 1902 and have been intermittent to the present time. Production to 1915 was \$1,168,772.

#### NATURE OF THE PRESENT STUDY

Limited geologic information about the district was available; hence, general geologic study was made of the mineralized areas in Bland and Colla Canyons (pl. 1). The project included geologic mapping, a study of the quartz veins and associated ore, and a detailed investigation of wall-rock alteration. Emphasis was placed upon the relation of alteration to lithology and ore deposits. Particular attention was directed to the genesis of clay minerals and their significance in relation to hydrothermal processes.

Numerous mines in the district, most of which had not operated for several years, were examined. Extensive caving in the mines prevented observations below the zone of oxidation; however, the degree of oxidation varies considerably in the accessible mines, permitting a limited comparison between supergene and hydrothermal alteration. Such comparison, however, is limited by the pervasive character of hypogene alteration.

#### PREVIOUS STUDY

Literature on the Cochiti mining district is sparse. The district was included by Lindgren et al. (1910) in a study of the ore deposits of New Mexico. Other geologic studies are presented in brief papers by Barbour (1908), Statz (1912), and Wyncoop (1900), and in unpublished reports by mining engineers. Vieth (1950) described the history of the district.

Recently, C. S. Ross and R. Smith, of the U. S. Geological Survey, completed fieldwork on a regional study of the Jemez Mountains. This study includes the Cochiti mining district.

#### ACKNOWLEDGMENTS

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Chemical analyses were made by Robert F. Conley, Indiana University, and Maynard E. Coller, Indiana Geological Survey. Electron micrographs were taken by Robert Babcock, Indiana University.





INDEX MAP, SHOWING LOCATION OF THE COCHITI MINING DISTRICT

# Geography

## LOCATION AND TOPOGRAPHY

The Cochiti mining district lies in the southeastern part of the Jemez Mountains on the border of the Pajarito Plateau (fig. 1). The district covers approximately 6 square miles and includes the southeastern part of T. 18 N., R. 4 E., the southwestern part of T. 18 N., R. 5 E., the northeastern part of T. 17 N., R. 4 E., and the northwestern part of T. 17 N., R. 5 E., Sandoval County, New Mexico.

The town of Bland (abandoned) was the center of activity during the years of production. This town is located in Bland Canyon, 12 miles east of the Rio Grande, and lies 14 miles southeast of Domingo, a village on the Atchison, Topeka and Santa Fe Railway. A graded road from Domingo joins U. S. Highway 85 approximately 25 miles to the east. From this junction, Santa Fe is about 20 miles north and Albuquerque about 40 miles south, on U. S. Highway 85. A graded and graveled road connects Bland with Los Alamos, 17 miles to the northeast.

The Cochiti district is situated in a deeply dissected plateau of Tertiary volcanic and intrusive rocks. In the southeastern part of the area, the divides show flat upland surfaces cut by narrow V-shaped valleys, but in the northeastern part, the divides commonly are narrow. The steep valley walls are characterized by talus slopes and numerous landslide blocks.

The relief is about 1,900 feet; the high point, 8,544 feet, is on the ridge between Bland and Colla Canyons, and the low point, 6,700 feet, is in Bland Canyon. At the heads of the canyons, the country rises to a series of mountain peaks 10,000 to 11,000 feet high. The stream pattern is radial and drains southeastward to the Rio Grande.

## CLIMATE AND VEGETATION

The climate of the Cochiti district is generally mild. In the summer, the temperature rarely reaches 90°F, and the nights are cool. In the winter months, the climate is variable; snow 3 feet deep has been known to accumulate. The average annual precipitation is about 20 inches. The heaviest rains fall during July, August, and September.

The streams of Colla and Bland Canyons are intermittent except for a few stretches fed by springs. They flow only during periods of melting snow or during summer rains. Immediately after a summer cloudburst, they may become temporary torrents. Media Dia Canyon, immediately north of Bland Canyon, and Peralta Canyon, immediately south of Colla Canyon, contain perennial streams. Water is obtained generally from wells, which must be drilled to depths of 20 to 40 feet. When the mines, however, were in operation, water was pumped from both Peralta and Media Dia Canyons.

The district is covered with cutover forest and brush. The tops of mesas are parklike and largely covered with ponderosa pine. On the slopes are juniper, piñon, spruce, fir, scrub oak, and "prickly pear" cactus.

# Geology

## GENERAL DESCRIPTION

The Jemez Mountains consist of a circular group of volcanic peaks built up almost entirely of Pleistocene rhyolitic and andesitic flows. The Pleistocene rhyolite, which crops out at Bland, had as its source the Valles Caldera, 3 miles north of Bland. Pelado Peak, a conical volcanic pile 11,200 feet high, lies 12 miles north of Bland and, along with other nearby peaks, makes up the core of the Jemez Mountains. These peaks are probably part of a dissected volcanic cone, which had a diameter of about 15 miles and was made up of ash, cinder, and other ejecta (Lindgren et al., 1910). The Pajarito Plateau, a broad outsloping apron averaging about 10 miles in surrounds this dissected cone. This apron represents width. an accumulation of flows from the Valles Caldera, Pelado Peak, and other less significant volcanic centers. The apron of volcanic rocks has been divided into many narrow mesas by deep, narrow canyons cut by radiating streams that head on the lower slopes of the volcanic cones. Commonly, the divides between streams are gently inclined mesas. On the east, Pajarito Plateau has been dropped 300 feet along a large curved fault (Stearns, 1952).

The Cochiti mining district occupies an inlier of Tertiary volcanic, intrusive, and sedimentary rocks, surrounded by Pleistocene volcanic rocks. The oldest rocks exposed are andesite flows that contain interbeds of pyroclastic rocks and sandstone. These rocks have been intruded and slightly matamorphosed by an elliptical monzonite stock. Young andesite porphyry dikes are abundant; they were injected along postmonzonite faults. Still later faults localized the quartz-sulfide ore mineralization. This mineralization was followed by the intrusion of a rhyolite sill and rhyolite dikes. Then another period of faulting occurred, which controlled the deposition of a second group of quartz veins. These veins apparently do not contain ore. Pleistocene rhyolitic tuffs form prominent cliffs around the perimeter of the Cochiti district.

The following rock descriptions are of the least altered rocks that could be found in the area. Because of the pervasive character of the hypogene alteration, fresh samples are not available.

# SEDIMENTARY ROCKS

The only sedimentary rock in the area is a feldspathic sandstone, which is conformably underlain by pyroclastic materials and conformably overlain by andesite flows. This sandstone, dipping about 25° E., crops out along a line of strike approximately north-south from near the Cossak mill, in Bland Canyon, to the mouth of Jenk's Draw, in Calla Canyon. The sandstone, which is extensively jointed and silicified and contains many vein-lets of quartz, is brown to greenish brown, and the bedding is generally obscure.

The microscope reveals that this rock is equigranular and fragmental, and that about 90 percent of it consists of subangular to subrounded fragments of quartz. Microcline, orthoclase, and andesine comprise about 5 percent of the rock and are present as subrounded grains. These feldspar grains have been altered slightly to illite and kaolinite. Minor amounts of ilmenite, magnetite, and epidote are present as small, rounded grains. The cements are, in order of abundance, chalcedony, calcite, illite, chlorite, limonite, and hematite. Near the monzonite intrusive, the quartz grains show some recrystallization.

# **IGNEOUS ROCKS**

#### Andesite Flows

At least two andesite flows of pre-Pleistocene age occur in the Cochiti area. These two flows are separated by the feldspathic sandstone and volcanic breccias and tuffs. The more porphyritic habit of the later andesite is the only significant difference between the two flows. All the andesite has been propylitized and is either dark green or greenish brown. Basal breccias, agglomerates, and flow breccia commonly occur within the andesites. Numerous andesite porphyry dikes have intruded the andesite flows.

The andesites contain plagioclase, biotite, and minor amounts of an unidentified pyroxene set in a microcrystalline and glassy groundmass. Plagioclase (andesine) phenocrysts constitute about 25 percent of the rock; they are commonly zoned, are twinned according to albite and pericline laws, and may be clustered together to form glomeroporphyritic texture. Fractures in the plagioclase are filled with calcite, illite, epidote, and some quartz. Chlorite, pseudomorphic after biotite, comprises about 2 percent of the rock. Stubby pyroxene prisms, completely replaced by chlorite, epidote, and magnetite, constitute about 2 percent of the rock. Wedge-shaped euhedral titanite crystals, partly altered to leucoxene, are rare. Numerous equidimensional and irregular grains of magnetite and ilmenite are disseminated throughout the groundmass. Both minerals have been partly altered to limonite and hematite, and ilmenite shows moderate alteration to leucoxene. Small amygdules of finely crystalline calcite and spherulitic chlorite are contained in well-rounded vesicles, which average 0.1 mm in diameter. Apart from the above, the rock consists of about 50 percent glass and 20 percent minerals, including feldspar microliter and minor fine-grained quartz.

#### Contact Metamorphosed Andesite Flows

The andesite flows have been mildly metamorphosed at the contacts with the monzonite stock and andesite dikes. An auriole near the monzonite is as much as 50 feet in width, whereas around the dikes it reaches a maximum of 2 feet. Metamorphosed andesites occur as nonporphyritic hornfelses, which grade into porphyritic andesites. Megascopically, the hornfelses are a dense dark-green rock in which the phenocrysts have been almost completely destroyed. On the south side of Bland Canyon, these hornfelses form a steep hogback ridge parallel to the limits of the monzonite.

Incipient contact metamorphism has produced small ovoid accumulations of chlorite (Turner, 1948). Feldspar phenocrysts have been replaced by microcrystalline aggregates of new feldspars, quartz, and magnetite. Minor amounts of comparatively clear feldspar appear to indicate some recrystallization. Later hydrothermal alteration has partly obscured the effects of contact metamorphism.

#### Volcanic Breccias and Tuffs

Volcanic breccias and tuffs occur as an interbedded unit within the andesite flows. Dark-green breccias, containing large fragments, grade into grayish-green tuffs which, in turn, grade into the feldspathic sandstone. Thin lenses of breccia are abundant, giving these units a well-bedded appearance. They are conformable with the andesite flows and dip about 25° SE., away from the monzonite stock.

The volcanic breccia consists of subrounded andesite fragments as much as 7 cm in diameter. Most of the fragments are welded together, but some are cemented by chlorite, quartz, and chalcedony. Equidimensional clastic fragments of subangular to subrounded quartz occur in minor amounts as interstitial grains. Feldspars show minor epidote alteration.

The volcanic tuff consists of glass shards that show extensive devitrification and contain feldspar microliter. Ragged fragments of chlorite, pseudomorphic after biotite, are present in minor amounts. Subangular to sub-rounded clastic quartz fragments are abundant and are deposited in well-stratified layers. Clastic quartz grains increase in abundance as the sandstone contact is approached.

#### Monzonite Stock

An elliptically shaped stock of monzonite intrudes all the rocks described above. A fine-grained marginal phase of the monzonite shows a gradual transition to an inner, coarser grained phase. Propylitization and argillization are intense throughout the monzonite, and unaltered rock was not found. Propylitized rock is grayish green, and argillized rock is white. Roof pendants and xenoliths of sandstone and volcanic rock are abundant. Andesite dikes are common; cutting the monzonite, they form vertical walls and pinnacles.

In thinsection, the coarse-grained phase of the monzonite has a holocrystalline, hypidiomorphic, and seriate texture. Plagioclase (andesine), orthoclase, quartz, and chlorite are the main minerals. Plagioclase grains comprise about 65 percent of the rock. They have a maximum length of 3.5 mm and are twinned according to carlsbad, albite, and pericline laws. Alteration of plagioclase consists largely of calcite, with minor amounts of illite, epidote, and quartz. Microfaults in the feldspar grains have been filled with silica.

Orthoclase grains as much as 2 mm long make up about 20 percent of the rock. Some of the grains show carlsbad twinning. Replacement by il-

lite, kaolinite, and quartz is slight. Many of the grains contain abundant inclusions of euhedral apatite. Quartz comprises about 8 percent of the minerals present and occurs interstitially with a maximum diameter of 0.2 mm. Chlorite, pseudomorphic after biotite, constitutes about 7 percent of the rock; it has been partly altered to magnetite. Ilmenite, partly altered to leucoxene, and magnetite, partly altered to limonite and hematite, occur as widely disseminated grains. Pyrite partly replaces some of the magnetite and ilmenite.

The fine-grained border phase of the monzonite is porphyritic and has a trachytic groundmass. Phenocrysts include feldspar and quartz; also chlorite, epidote, and magnetite, which are pseudomorphic after hornblende and biotite. Laths of plagioclase (andesine) and orthoclase form the groundmass. Percentages of the minerals present are plagioclase, 62 percent; orthoclase, 20 percent; mafic minerals, 15 percent; and quartz, 3 percent. Magnetite is present in minor amounts.

These percentages show that the fine-grained border phase contains about 8 percent more mafic minerals and about 5 percent less quartz than the coarse-grained phase. This variation in mineral content of the two phases of the monzonite suggests that the fine-grained border phase is a basic border facies.

Chemical and modal analyses of the coarse-grained phase of the monzonite are shown in Table 1. These analyses are in accord with average chemical analyses for monzonite as listed by Nockolds (1954).

#### Andesite Dikes

Andesite dikes of postmonzonite age are extremely abundant throughout the Cochiti area. The dikes show both porphyritic and glomeroporphyritic textures. Glomeroporphyritic dikes, which are confined to the monzonite intrusive, near the margins of the monzonite commonly grade into andesite porphyry dikes. The glomeroporphyry dikes are light grayish green, and the porphyritic dikes are dark greenish gray.

The dikes, where they penetrate the monzonite intrusive and andesite flows, stand out as vertical ridges and pinnacles. Columnar jointing and amygdaloidal texture are present in some of these dikes. Porphyritic and glomeroporphyritic andesites also occur as sills and godlike bodies.

These andesites are holocrystalline and contain phenocrysts of andesine and an unidentified pyroxene set in a trachytic groundmass that consists largely of plagioclase laths. Many of the plagioclase phenocrysts have been partly resorbed by the groundmass. These phenocrysts attain a maximum length of 3 mm and are twinned according to albite and albitecarlsbad laws. Illite and minor calcite, epidote, and quartz have developed as alteration products after plagioclase. Chlorite, epidote, and limonite have been introduced along fractures in the feldspar grains.

Short, stubby, octagonal pyroxene grains have been completely altered to epidote, biotite, chlorite, magnetite, and quartz. Apatite grains are poikilitically included in the pyroxene grains.

	Chemical an	alysis* Modal analy	vsis
SiO <sub>2</sub>	57.37	61	
TIO2	1.29	1	
Al2Ô3	15.38	19	
Fe2O3	3.35	3	
FeO	2.16	2	
MnO	0.11		
MgO	2.38	1	
CaO	5.37	7	
Na2O	3.77	4	
K2Õ	4.02	3	
P2O5	0.58	Line and the second	
H <sub>2</sub> O+	2.06	I LONGE STOLEN	
H2O-	0.23	nag shengder af r <del>e</del> ma	
CO2	1.88	element of the second second	
s -	0.00	d the strength of	
Total	99.95	101	

TABLE 1. CHEMICAL AND MODAL ANALYSES OF MONZONITE

\* Analyst: H. B. Wiik, Helsinki, Finland.

The trachytic or diabasic groundmass consists largely of plagioclase, with minor amounts of chlorite, apatite, and ilmenite. Ilmenite has been largely altered to leucoxene. Some introduced quartz is also present in the ground-mass. The rock is about 85 percent plagioclase. Rounded vesicles up to 2 mm in diameter are common and generally have been filled with calcite, quartz, chlorite, and epidote.

It is suggested that the glomeroporphyry dikes are hybrid rocks, resulting from the assimilation of the monzonite by the later andesite magma. The mineral composition of the andesite magma was changed; about 2 percent quartz and about 2 percent orthoclase was added. These constituents were not observed in the porphyry dikes.

## Quartz Veins

Quartz veins and lodes of variable size which penetrate all the pre-Pleistocene rocks are widely distributed throughout the area. Two sets of quartz veins are recognized. The first set, which is postandesite dike and prerhyolite intrusive, contains ore. The second set is postrhyolite intrusive and represents the final exudations of pre-Pleistocene igneous activity. Ore concentrations have not been found in these veins. A detailed description of quartz veins is included under the section on mineral deposits.

#### **Rhyolite Intrusives**

Rhyolite intrusives, including dikes and a sill, are limited to the Colla Canyon area. The rhyolite is apparently the youngest of the Tertiary rocks in the Cochiti district. It is flow banded and characterized by platy cleavage, and may be either white, red, or reddish green, depending upon the state of alteration. The intense hydrothermal alteration in the host rocks adjacent to late quartz veins near rhyolite intrusive rocks is noteworthy.

The !hyalite is holocrystalline and porphyritic. Orthoclase, quartz, and minor biotite phenocrysts are set in a trachytic groundmass which is largely altered to chlorite. Many orthoclase and biotite crystals have been resorbed by the groundmass to form relict crystals.

## **Bandelier Formation**

The Bandelier formation (Pleistocene) in the Cochiti area is composed of rhyolite flows and rhyolitic tuffs. The base of the section consists of a soft, white pumaceous material, which commonly erodes into pinnacles and hoodoos. Overlying the tuff is a gray rhyolite flow, overlain in turn by a tan welded rhyolitic tuff. This welded tuff shows columnar jointing and caps the mesas in the area. Fragments of older rocks up to 2 feet in diameter are commonly present in the tuff. C. S. Ross (personal communication, 1951) attributes the origin of this tuff to a gas-ash emulsion which flowed out over the surface. The Bandelier formation has not been affected by hydrothermal alteration.

#### STRUCTURE

Joint systems in the Cochiti area show, in general, only vague patterns. The most distinctive patterns are exhibited by two conjugate joint systems striking generally north-south and east-west. The east-west set of joints has an average dip between 75° S. and 80° N., and the north-south set has an average dip between 60° E. and 65° W. Joints do not appear to be affected by individual rock types and transgress contacts without significant changes in trend. In general, the joints are discontinuous and have not greatly influenced the localization of ore.

Abundant faults of minor displacement are evident in the mines. These faults generally strike from northwest to northeast and dip 50° W. to vertical. Commonly, the faults die out in short distances. Gouge, invariably associated with the faults, ranges in width from less than an inch to 30 feet. Quartz fragments as large as 4 inches in diameter which have been rolled along the fault planes are common in postvein faults. The maximum displacement on these faults is about 50 feet; the average is probably not more than 3 or 4 feet.

At least five major periods of faulting have taken place in the Cochiti district. The first was subsequent to the intrusion of the monzonite stock, and many andesite dikes cross or occupy these faults. This was followed by a second period of faulting, and along these faults quartz veins were in-

jected. The third period is represented by faulting penecontemporaneous with development of the quartz veins. Brecciation of the quartz veins resulting from these displacements provided channelways along which sulfide ore and vein quartz were deposited. The fourth period, after the rhyolite intrusion, caused fracturing of the quartz ore veins, and quartz veins (second stage) were deposited along these fractures. The fifth period of faulting displaced the Pleistocene volcanic rocks.

#### SUMMARY OF GEOLOGIC HISTORY

Tertiary andesite flows are the oldest rocks exposed in the Cochiti area. The extrusion of this andesite was followed by explosive volcanic activity,

during which, first, volcanic breccia, and then ash, were ejected. During the deposition of the ash, thin beds of volcanic breccias were also deposited. Where the volcanic ejecta were laid down in water, they were mixed with detrital material from various sources. After the interval of explosive volcanism, feldspathic sandstone was deposited. Subsequently, this sandstone was partly covered by flows of andesitic lava.

This period of volcanic activity was followed by the intrusion of a monzonite stock, andesite dikes, and quartz veins. First, the monzonite intruded and domed the older rocks. In Bland Canyon, the earlier andesite flows near the monzonite have been tilted to a near-vertical attitude, and in Colla Canyon, the andesites, sandstone, and rhyolite dip away from the monzonite at an angle of about 25 degrees. The intruded rocks were subjected to only mild contact metamorphism.

Faulting occurred after intrusion of the monzonite, and andesitic magma at places was intruded along these faults. Faulting recurred after the intru-

sion of the andesite, and these faults acted as channelways for the movement of hydrothermal solutions. The circulating hydrothermal solutions altered the country rock and deposited the quartz and sulfide minerals of the veins.

Faulting penecontemporaneous with the deposition of quartz kept the channel open and thus made it possible for the later sulfide minerals to be deposited. Intrusive activity continued during Tertiary time with the injection of rhyolite

dikes and a sill. A recurrence of faulting subsequent to the rhyolite intrusions provided channels for the deposition of a second set of quartz veins. Apparently, no ore was deposited in these veins.

Erosion ensued until the Pleistocene, when the Valles volcano collapsed with concomitant extrusion of rhyolite flows and tuffs. Faulting apparently followed this extrusive activity. Radial streams then became incised in the rhyolite tuffs. Colla and Bland Canyons were cut through the rhyolite into the underlying Tertiary rocks. A rapid retreat of the cliffs followed, caused by the undercutting of poorly consolidated volcanic tuffs. The surface on which the rhyolite flowed was uneven; observed relief on this surface is of the order of several hundred feet.

# Mineral Deposits

#### HISTORY AND PRODUCTION

Major Edward Beaumont visited the Cochiti area in 1880. Subsequently, it was claimed that the Cochiti mining district was part of a private land grant. This claim, however, was not upheld in court, and prospecting in the area began. In 1889, many mineral deposits were located, and by the fall of 1893, the entire district had been claimed by prospectors.

In 1896, the R. W. Woodbury mill was constructed, about 7 miles below the present site of Bland. The Cochifi Gold Mining Co. in 1899 constructed a mill of 300-ton capacity at the Albemarle mine. Electrical power for the mill and other uses was transmitted 35 miles from the coal mines at Madrid (Jones, 1904). In 1915, the Cossak Mining Co. constructed a mill in Bland Canyon; it operated for only a short time. In 1943, another mill was built, below the iron King Mine, but its short period of production was successful.

Up to 1904, the district produced \$695,000 in gold and \$345,000 in silver. In 1915, the Cossak Mining Co. produced \$83,107 in gold and \$45,671 in silver. The total production reported from the district is \$1,168,778 (Finlay, 1922).

## CHARACTER AND CLASSIFICATION OF THE DEPOSITS

Quartz veins and lodes, widely distributed throughout the area, contain shoots, pockets, and irregular bodies of sulfides. The veins, with a maximum length of about 1,500 feet, commonly show extreme variations in width over short distances. Where the veins pinch out completely, alteration often continues for some distance, and the veins may or may nor reappear along the projection of the zones of alteration. Adjacent to the larger veins, the country rock may contain many small offshoots. Where the veins pir.ch out, their place is commonly taken by many small shoots or veinlets. Generally, these veinlets do not have a uniform strike; characteristically, they anastomose. Brecciation and shattering of the vein minerals is common, and fault-breccia fragments from the adjacent country rock are also present in the veins. Some of the veins contain cavities, as much as 2 feet in diameter, which have been produced by the weathering out of breccia fragments. The observed quartz veins range in width from a fraction of an inch to 50 feet, whereas at depth they have been reported to be as wide as 150 feet. Major veins are along faults; the location of some of the smaller veins has been controlled by joints.

The quartz veins are believed to be largely of the replacement type, but open spaces have been filled with banded chalcedony and sulfides. Druses and comb structure are abundant. Precious metals are unevenly distributed through the lodes and are separated by extensive areas of barren quartz. Sufficient evidence was not available to the author to determine the persistence of ore at depth. The deepest mine in the district, 725 feet, is inaccessible. Although sulfides have been reported to be plentiful at this level, the amount of precious metal had decreased considerably (Lindgren et al., 1910).

Because all the deeper workings are inaccessible, the depth to which oxidation has taken place could not be determined. Limonite, hematite, melanterite, and gypsum are abundant in the oxidized zone, and the sulfides (pyrite, chalcopyrite, sphalerite, and argentite) have been largely carried away in solution. Lindgren et al. (1910) reported abundant sulfides on the 425-foot level in the Albemarle mine. Practically no water was encountered in this mine. Most of the ore above the 425-foot level is believed to have been oxidized. In the Iron King mine, water was encountered 136 feet below the surface, and sulfides were plentiful. According to Lindgren, the gold apparently has been enriched in the oxidized zone,but marked variations in the silver content of the oxidized ore were not encountered.

The extensive brecciation, abundance of druses, and comb structure, along with the banded chalcedony and sulfides, indicate that these are epithermal veins deposited near the surface. The quartz, calcite, pyrite, chalcopyrite, sphalerite, and argentite contained in the veins, and the nature of the rock alteration, are in close accord with characteristics of deposits formed near the surface (Lindgren, 1933). Presence of dickite (described below), however, is indicative of higher temperatures than those proposed for epithermal deposits. According to Niggli (1929), many shallow deposits have originated at high temperatures. Fenner (1936) presents data which show that pressures higher than hydrostatic can be stable near the surface.

Because of these discrepancies with regard to Lindgren's classification, Schmidt (1950) has proposed a less rigid taxonomy. Following Schmidt's classification, the ore deposits in the Cochiti mining district are grouped as Tertiary siliceous (which includes deposits formerly classified as Tertiary), epithermal, shallow, or volcanic.

#### MINERALOGY

The mineralogy of the ore deposits is comparatively simple. The veins and lodes, without exception, are composed principally of quartz accompanied by small amounts of sulfides and, rarely, carbonate. Sulfides, in order of abundance, are pyrite, argentite, sphalerite, chalcopyrite, and galena. How the gold occurs is not known, but apparently it is associated with the pyrite. In general, the pyrite content of the ore increases as the gold content increases; however, an abundance of pyrite does not necessarily imply a high gold content. Many of the mines in lower Bland Canyon contain gold with the associated pyrite, but the other sulfides are practically absent. Some of the veins contain significant amounts of calcite and iron oxides. Iron oxides are generally favorable to the occurrence of gold, but a calcite gangue is not.

The following mineral descriptions are based upon field observations and polished-section studies. Each of the minerals was identified by the standard

microchemical techniques (Short, 1940).

Calcite occurs as a coarsely crystalline mineral, generally in the form of thin, tabular rhombohedrons. Few sulfides are present in the calcite gangue. Quartz shows wide textural and grain-size variations and ranges from chalcedonic quartz to crystals 1 in. long. Commonly, quartz occurs as lamellar plates pseudomorphic after calcite. Large crystals present in comb structures are commonly amethystine and are reported to be an indication of high gold content. Where abundant finely disseminated sulfides are present, the quartz is dark gray. Alternating bands of radiating quartz, chalcedony, and sulfides commonly occur as open-space fillings. Both fluid and solid inclusions are abundant near the periphery in many of the quartz grains.

Pyrite is the most abundant sulfide. It varies in amount from vein to vein, as well as in different parts of the same vein. Much of the pyrite is brecciated. The grains are generally rounded, but some show crystalline outlines. Ordinarily, pyrite is not more than 1 mm in diameter, but grains as much as 2 mm in diameter occur. Cubic solution cavities, as much as 8 mm in diameter and formerly occupied by pyrite, are common in the quartz. In zones of brecciated vein material not filled with later minerals, pyrite commonly occurs as loose crystalline crusts on the brecciated fragments. Lindgren et al. (1910) suggest that such incrustations of pyrite are a recent phenomenon caused by descending waters.

Chalcopyrite is widely disseminated as minute anhedral to subhedral grains and is less uniformly distributed than the pyrite. Sphalerite, which is rare, generally occurs as aggregates of minute, black crystals. These aggregates are as much as 5 mm in diameter. Galena is the least abundant of the sulfides and, like sphalerite, is disseminated erratically as minute grains and larger granules. The grains are as much as 4 mm in diameter.

Argentite occurs as minutely crystalline aggregates and veinlets. A chemical analysis of this mineral (Lindgren et al., 1910) indicates the presence of silver and absence of antimony, which eliminates the possibility of polybasite.

Limonite and hematite, the most conspicuous secondary minerals, occur as stains and incrustations on the quartz veins. Limonite is commonly pseudomorphic after pyrite cubes. Scant amounts of manganese oxides occur as thin films and dendrites along with the iron oxides.

## PARAGENESIS OF VEIN MINERALS

During the first phase of mineralization, calcite was deposited along the numerous faults. This was followed by a fine-grained quartz which replaced calcite and country rock. Many veins contain quartz pseudomorphous after lamellar calcite. Lamellar calcite which has not been replaced by quartz is uncommon.

A reopening of the replacement veins was followed by a second phase of mineralization which cemented and replaced the quartz breccia. Minerals introduced at this time, in order of deposition, were pyrite, chalcopyrite, sphalerite, galena, quartz, pyrite, and argentite. The first phase of

pyrite deposition is represented largely by pyrite cubes which replace quartz. Chalcopyrite was the next mineral to be deposited, replacing pyrite and quartz along automorphic outlines. Subsequent sphalerite deposition fills fractures which penetrate the quartz, pyrite, and chalcopyrite. Sulfide deposition continued, with introduction of galena, which penetrates and partly replaces sphalerite and quartz.

Mineralization continued with further quartz deposition, and fracture fillings of quartz penetrate all the previously deposited minerals. A second phase of pyrite mineralization followed,occurring as veinlets, irregular grains, cubes, and pyritohedrons, within both phases of quartz. Although conclusive evidence was not found, it is believed that gold is associated with this phase of pyrite. Argentite was the last sulfide to be deposited, penetrating and replacing the older sulfides. Many fragments of country rock included within the vein have been partly replaced by argentite.

A second stage of mineralization, which occurred after the intrusion of the rhyolite, included the formation of extensive quartz veins and abundant pyritization. Sulfides other than pyrite were not observed in this stage of mineralization, and precious metals have not been reported.

In general, this mineral paragenesis is similar to the usual sequence in other mining districts containing epithermal or Tertiary siliceous mineral deposits. Although calcite is generally later than quartz, an earlier calcite gangue is not uncommon (Lindgren, 1933).

# Wall-Rock Alteration

## INTRODUCTION

The study of wall-rock alteration in the Cochiti mining district was undertaken as a mineralogical study, relating mineralogy to ore deposition, structure, and hydrothermal transformation processes. From this study, it has been concluded that alteration is related to at least two stages of sulfide deposition. Mineralogical zones in the altered rocks are considered as reaction aureoles which represent the subsiding activity of altering solutions. Sales and Meyer (1948), in their study of wall-rock alteration at Butte, have presented convincing evidence of this interpretation. In a later stage of alteration, hydrothermal activity continued and resulted in the expansion of previously formed alteration zones, along with the formation of more intense zones adjacent to some veins.

The collection of samples for a detailed mineralogical study of the alteration zones involved the sampling of seven mines: the Lone Star, Daisy, Blue Bell, and Sambo, in Bland Canyon; the Sun and Albemarle, in Colla Canyon; and the Washington, located on the mesa separating these two canyons (pl. 3). The mines from which sample suites were collected were selected to include the entire range of alteration intensity and rock type. Because the deeper mine workings were inaccessible, samples were collected from upper levels and have undergone at least some oxidation. In order to establish a possible relation between supergene and hydrothermal effects, samples showing different degrees of oxidation were collected. Attention was directed to areas of widely spaced veins, to avoid effects of superimposed alteration. This was necessary in order to establish mineralogical and chemical trends. Intervals between samples were determined by observed changes in the color and texture of the altered host rock. Gouge, breccia, and compact rock were considered separately with respect to the relative effects caused by the altering solutions.

As soon as possible after the samples were collected, they were wetted and packed in sealed containers. This precaution was taken to prevent dehydration of minerals which lose water at low temperature, such as halloysite.

To establish a relation between wall-rock alteration and sulfide deposition, samples of vein materials were collected. The nature and mineralogy of the quartz veins are described in a previous section.

#### ANALYTICAL PROCEDURE

Samples were prepared in the laboratory for thin- and polished-section study, clay mineral determinations, and chemical analyses.

Thinsections were prepared from each sample for correlative study with X-ray diffraction and chemical analyses. Examination of thinsections was carried out to determine genetic and paragenetic relations between clay and nonclay minerals. Polished sections were utilized only for the study of opaque minerals.

A representative portion of each sample, 400 to 600 grams, was crushed with a tool-steel mortar and pestle. The crushed material was pulverized in an agate mortar and passed through an 80-mesh screen. The sample was split into two portions, one for clay-mineral study and the other for chemical analyses.

The sample split for clay-mineral study was dispersed in distilled water. To prevent flocculation, soluble salts were removed by successive decantations with distilled water. In those samples which contained excessive soluble salts, in addition to washing, ammonium hydroxide was added as a dispersing agent.

Parallel orientation of clay aggregates was obtained by allowing clay suspensions to settle on glass slides. This procedure has been described by Grim (1934). After removal of the slides, they were dried at room temperature. The clay suspensions containing less than 2-micron particles were siphoned and dried at less than 45°C. This material was used for X-ray powder-diffraction and differential thermal analyses. Samples of this type which were composed almost entirely of illite, as indicated by X-ray spectrometer traces, were submitted for chemical analyses. Extremely dilute clay suspensions were separated and mounted on films for electron micrographs.

Diffraction traces of oriented clay aggregates were recorded with a General Electric XRD-3D spectrogoniometer. Samples for powder photographs were mounted in collodion spindles and recorded with a General Electric XRD powder camera. Both types of diffraction patterns were obtained, using nickel-filtered copper radiation. Grim (1951) has described a differential thermal unit similar to the apparatus used in the present investigation.

Chemical analyses were performed on the samples, in general, by methods described by Shapiro and Brannock (1956). These methods employ the rapid analytical techniques of flame photometry, colorimetry, and titrimetry.

# CLAY-MINERAL IDENTIFICATION

Clay minerals found in the alteration zones include chlorite, montmorillonite, vermiculite, illite, halloysite, kaolinite, and dickite. Mixed-layer associations of three-layer clays were found in the following combinations: chlorite-montmorillonite, chlorite-illite, illite-montmorillonite-chlorite, vermiculite-chlorite, and illite-montmorillonite.

Diffraction data of the clay minerals were obtained from both film-recorded patterns and X-ray spectrometer traces. Differential thermal analyses and electron microscopy were utilized where diffraction data were considered inadequate for the resolution of diagnostic criteria.

In order to amplify intensities of the characteristic 001 reflections on diffraction patterns, oriented clay aggregates were used. Additional patterns were made from oriented aggregates treated with ethylene glycol and heated to 200°, 450°, and 600°C for 1 hour, 45 minutes, and 30 minutes, respectively.

Two general types of chlorite can be recognized from X-ray diffraction data: iron-rich chlorites characterized by weak (001) and (003) intensities relative to (002) and (004), and magnesium-rich chlorites characterized by relatively intense odd-order reflections. According to Brindley and Robinson (1951), substitution of  $Mg^2$ + by Fe2+ in octahedral positions causes considerable reduction in intensity of odd-order reflections.

Chlorites as a group were identified on the basis of an integral sequence of orders related to a 14A periodicity, which are unaltered following glycolotion and heat treatment to 450°C. In the event of weak (001) reflections for iron-rich chlorites, the sample was heated to 600°C. Brindley and Robinson have demonstrated that such treatment causes a partial dehydration of chlorite structure which enhances the 14A reflection. Except when iron-rich, well-resolved diagnostic reflections for chlorite occur at both 14A and 4.7A. Additional diagnostic features can be obtained by heat treatment in the range 400° to 575°C (Bradley, 1954); this method is particularly advantageous with admixtures of chlorite and kaolinite. Following this treatment, the 7A feature of chlorite is displaced to a smaller angle, and the 3.5 feature to a larger angle, both relative to kaolinite.

Kaolin materials, including halloysite, kaolinite, and dickite, are abundant constituents in the altered rocks. Each of these clay minerals gives an integral series of reflections related to a 7A periodicity. Difficulty was experienced in differentiating mixtures of kaolinite and chlorite. This is particularly true where odd-order reflections for chlorite are weak. In addition to the criteria listed above for chlorite characterization, the following features were used for distinguishing kaolin material.

Although most of the 00l reflections for kaolinite are synonomous with 00l reflections for chlorite, a distinguishing feature is found in the kaolinite (003) reflection. This reflection corresponds to the (006) chlorite, and at this position chloritic materials have little or no intensity. Bradley (1954) states that this generalization is not unequivocal but has considerable supplementary value. Murray (1954) points out that when both chlorite and kaolinite are present in a sample, the reflection at 3.5A may show two distinct peaks or a deflection on the high-angle side caused by the (004) chlorite reflection.

According to Johns et al. (1954), heat treatment of kaolinite and poorly crystalline chlorite mixtures to 450°C for 45 minutes provides a method for differentiating the two components. The 450°C temperature was selected because they had not found a kaolinite which would break down under these heating conditions, whereas reflections of poorly crystalline chlorite are destroyed. Although this generalization may apply in special cases, loss of diffraction effects at 3.5A and 7A was not considered as necessarily indicative of chlorite, because Vaughn (1955) has demonstrated that the above conditions of heat treatment can be sufficient to break down some kaolinites. Angular displacement of diffraction effects can be relied upon as more accurate criteria (Bradley, personal communication).

Characterization of kaolin species did not present excessive difficulties; however, an efficient method for differentiation of kaolinite and halloy-

site (partially hydrated) was not resolved. Optical examination of the powdered samples indicates that both species are present. Differential thermal analysis of glycolated samples (Sand and Bates, 1953) was utilized to determine the presence or absence of fully hydrated halloysite. Electron micrographs were taken of all samples in which the presence of halloysite was indicated by X-ray spectrometer traces. Diffraction patterns of fully hydrated, partially hydrated, and dehydrated halloysite mixtures are characterized by a broad weak band from about 7A to 10A (Bradley, 1945). Expansion following glycolation and increase of intensity of the 7A spacing after heat treatment also aid in the identification of halloysite.

Dickite was identified from film-recorded diffraction patterns and differential thermal analysis. Electron micrographs also aided in its identification.

Vermiculite, a moderately abundant constituent of the alteration clays, was identified with respect to characteristics of the 14A reflection. The 14A line is strong, whereas the remaining 001 reflections are relativelyweak (Grim, 1953). Diagnostic features of the 14A peak include sharpness, intensity, expansion with glycolation, and displacement following heat treatment. Bradley (personal communication) believes that many vermiculites, like montmorillonite, will expand to 17A. For this reason, vermiculite was distinguished from montmorillonite largely by sharpness of the 14A peak.

Vermiculite-chlorite mixed layering is also of common occurrence. The presence of interlayer chlorite apparently inhibits adsorption of glycol. This mixed-layer association was identified by decrease in intensity of the 14A reflection following heat treatment to 450°C. Treatment to this temperature would not be expected to affect the 14A peak if it were represented by pure chlorite.

Montmorillonite was distinguished from chlorite and vermiculite by diffuseness of 00/ reflections, expansion with glycol, and displacement to higher angles of 20 following heat treatment. Two general types of montmorillonite were approximated by the variation in position of their respective (001) spacings. Diffraction patterns of oriented aggregates obtained at low relative humidities indicate a range in spacing from about 12A to 15A. Barshad (1950) has shown that with monovalent cations the basal spacing is that resulting from a single water layer, and with bivalent cations, from a double water layer. Ideally, under controlled humidity conditions, sodium montmorillonite would have an (001) spacing of 12.1A, and calcium montmorillonite would have a spacing corresponding to 15.4A. McAtee (1956) has demonstrated a method of determining the degree and type of Na-Ca mont-

morillonite interstratification directly from measured X-ray data. Effect of humidity upon basal spacings has been studied by Milne and Warshaw (1956). They have shown that the basal spacings of a calcium montmorillonite may vary from 11.7A, at 1 percent relative humidity, to 15.6A at 85 percent relative humidity. The present investigation was carried out at low relative humidities which did not vary more than about 10 percent.

Characteristic basal reflections of the illite group correspond to an integral sequence of reflections related to a 10A periodicity. The spacings are not affected by glycolation. X-ray powder photographs were taken in an attempt to identify the polymorphic phases of illite in the alteration zones.

Mixed-layer associations of montmorillonite-chlorite, montmorilloniteillite, and illite-chlorite were identified with regard to the positions of maxima relative to their respective (001) positions. The OOl spacings are average values resulting from the simultaneous scattering by the layer types involved. Heat treatment and glycolation afford identification of the mixed-layer components (Weaver, 1956). Discussions of the theory of identification of mixed-layer clays can be found in papers by Bradley (1945, 1950, 1953), Brown and MacEwan (1950), Hendricks and Teller (1942), and MacEwan (1949).

Analyses of such complex mixtures present difficult problems when quantitative evaluation of discrete clay types is desired. In order to establish trends of clay-mineral species in the alteration zones, it was necessary to use available quantitative methods. Johns et al. (1954) have developed a usable method for quantitative evaluation of discrete clay types. Weaver (1956) describes a procedure for estimating the ratio of mixed-layer components. These methods apply to idealized diffraction patterns; for practical use, they must be considered, at most, as semiquantitative estimates. Clay minerals developed in hydrothermal alteration zones commonlyare represented in all stages of transformation. Under such conditions of chemical alteration, presentation of a precise quantitative picture, with present methods, is not possible. The quantitative techniques, however, were useful for establishing broad generalizations as to spatial relations of the predominant clay-mineral types.

## ZONAL DISTRIBUTION AND MINERALOGY OF CLAY COMPONENTS

Areas of unaltered Tertiary rocks are not exposed in the Cochiti district. Clay-mineral alteration, therefore, is ubiquitous and becomes increasingly abundant toward the quartz veins. Intensity functions of alteration, listed in their approximate order of importance, are: (1) spatial relation with respect to stages of alteration, (2) spatial relation to quartz veins, (3) permeability and porosity of gouge and breccia, (4) width of quartz veins, and (5) grain size and mineralogy of wall rock.

As discussed in an earlier section, at least two stages of alteration have been superimposed upon the Tertiary rocks in the district. A general spatial zonation of alteration can be discerned between the mineralized areas of Colla Canyon and Bland Canyon. The more intense alteration in the Colla Canyon area is indicated by the abundance of illite and kaolinite, and by the presence of dickite. Within the Bland Canyon area, illite and kaolinite are much less abundant, and dickite is absent.

Alteration zones generally show an orderly sequence of minerals relative to quartz veins. Less commonly, permeable zones not penetrated by veins represent centers of intense alteration.

Structures existing within the rocks have cawed significant variations in

the degree of alteration. Of particular importance are the numerous gouge and breccia zones existing throughout the area. These zones of weakness have provided materials of relatively high permeability and porosity. Gouges are commonly penetrated by abundant quartz veinlets, which are indicative of high permeability. Without exception, gouges were found to be altered more intensely than the adjacent compact rocks. Anomalies in clay-mineral sequences are related largely to the presence of gouge and breccia. This phenomenon is well exemplified in the halloysite alteration zone, where the amount of halloysite present is directly related to the degree of rock pulverization. Leaching was achieved readily in these zones; thus, the environment was unstable for clay minerals, which normally require alkali metals or alkaline earths in their structure. It is also noteworthy that dickite, which occurs in the most intense zones of alteration, was found only in gouge zones.

The width of alteration zones generally is related to vein width. To a limited extent, alteration intensity is controlled by vein width. Commonly, narrow zones of intense alteration occur adjacent to narrow veins.

Lithology has exerted an observable, but much less significant, control on alteration. Although wide variations in lithologic types exert a marked influence upon intensity of alteration, the similar mineralogical composition of rocks in the Cochiti area has minimized the importance of this control on relative intensity. Most recent alteration studies indicate that in igneous rocks the finegrained groundmass has altered at a slower rate than the phenocrysts; however, some alteration studies of present hot-spring environments indicate the opposite relationship. In the Cochiti district, solutions which permeated channels along grain boundaries have produced more alteration in the finegrained than in the coarse-grained rocks. For example, the relatively coarsegrained monzonite generally displays less alteration than the fine-grained andesites. Feldspar phenocrysts in the andesite porphyry dikes generally are less altered than the fine-grained groundmass. In contrast, augite, hornblende, and biotite phenocrysts have undergone more intense alteration than the groundmass. Thus, mineralogy has effected an additional alteration control. Exceptions to these generalizations are not uncommon.

Zonal classification was complicated somewhat by these alteration-intensity controls. Megascopically, the alteration zones are divisible into three general categories: (1) the propylitic zone, as defined by Lindgren (1933), (2) the argillic zone, as defined by Lovering (1941), and (3) the silicified zone.

The propylitized rocks are characteristically green, and the degree of alteration varies but little throughout large portions of the area. Predominant clay minerals are chlorite and montmorillonite. Minor amounts of vermiculite, kaolinite, halloysite, and illite occur sporadically throughout this zone. Nonclay alteration minerals include quartz, epidote, clinozoisite, ilmenite, magnetite, leucoxene, pyrite, jarosite, and calcite.

Argillic alteration, although not as extensive as propylitization, may exceed widths of 1,000 feet in areas adjacent to wide fissure veins. Near the surface, this zone has been leached and is white, whereas at depth it

is greenish gray to bluish gray. Clay minerals include those found in the propylitized zone, but the dominant clay is illite. Dickite commonly becomes dominant in narrow zones adjacent to veins. Common nonclay alteration minerals are ilmenite, magnetite, hematite, leucoxene, alunite, jarosite, secondary biotite, and pyrite.

Silicification is a widespread phenomenon, commonly occurring in areas far removed from known quartz veins. A zone of silicified wall-rock adjacent to veins is not always present; however, its presence can be expected along the extension of any given quartz vein. This zone, as much as 30 feet wide, commonly grades imperceptibly into the fissure vein. Clay minerals contained in the silicified areas adjacent to veins are dominantly illite, kaolinite, and dickite. Pyritization generally is abundant.

X-ray diffraction studies of the clay-mineral components provide a relatively precise means of zonal classification. Such zonal classification is not applicable from a megascopic study; however, a detailed X-ray diffraction investigation is necessary to aid in the interpretation of problems in ore genesis and alteration mechanisms. It should be emphasized at this point that the stability conditions of clay minerals comprise wide ranges of temperatures and pressures. Roy (1954) emphasized the metastable persistence of claymineral phases. In the present study, it was found that montmorillonite and chlorite commonly are persistent phases throughout the alteration zones but attain their greatest abundance in the fringe areas of alteration.

Relative to clay minerals present in the greatest abundance, the following clay zones have been established from the vein outward: (1) dickite, (2) illite-kaolinite, (3) vermiculite-halloysite, and (4) montmorillonite-chlorite.

In general, this sequence of alteration is in agreement with other recent studies of wall-rock alteration (Sales and Meyer, 1948; Peterson et al., 1946; Lovering, 1941, 1949; Kerr et al., 1950, 1951; Schwartz, 1953; Tooker, 1956). Kaolin clays and illites are reported in the most intense alteration zones, whereas montmorillonite and chlorite are characteristic of the fringe zones. It can be expected that many of the minor variations which have been reported are related to differences in clay-mineral nomenclature and methods of identification. Although vermiculite has not been reported in previous hydrothermal studies, it is doubtful that its occurrence is peculiar to the altered rocks in the Cochiti district.

The distribution of clay minerals is not confined to discrete clay types. Mixed-layer associations of 2:1 clay minerals (sheet structures composed of two layers of silica tetrahedrons and a central dioctahedral or trioctahedral layer) are abundant and apparently represent a transition state between discrete clay types. Base exchange, with resultant mixed-layer clay minerals as intermediate phases, has been an important mechanism for transition among 2:1 clay minerals. This phenomenon commonly arises from substitutions within the clay-mineral lattice. Aluminum may substitute for silicon in tetrahedral positions, whereas magnesium and iron may replace aluminum in octahedral positions. Resultant charge deficiencies are commonly balanced by K+, Na+, or Ca<sup>++</sup> ions.

All possible combinations of mixed layering exist in the altered rocks

between ill ite, montmorillonite, chlorite, and vermiculite. The type of cation which occurs between these layers determines the type of clay mineral. Replacement of interlayer cations can lead to mixed layering and, with complete replacement, to the formation of a distinct and different clay species. For example, replacement of interlayer cations in montmorillonite by potassium ions is a well-known phenomenon (CaWere et al., 1948). That this illitization process has taken place in the Cochiti area is indicated by the occurrence of gradational sequences from montmorillonite through montmorillonite-illite mixed layers to illite. The general sequence of mixed layering toward the vein is chlorite-montmorillonite, vermiculite-chlorite, and illitemontmorillonite. A typical sequence of clay minerals is illustrated by spectrometer traces in Figures 2 to 8.

In addition to random mixed-layer clay minerals, regular mixed-layer types occur rarely in the chlorite-montmorillonite zone. This is indicated on spectrometer traces by a basal reflection at about 24A (fig. 9). Mixed layers of this type have been named stevensite and are described by Faust and Murata (1953) and Brindley (1955). According to Brindley, a partially regular alternation of layers 10A and 14A thick would account for a weak reflection at 24A.

The presence of a regularly interstratified montmorillonite-chlorite is indicated by a 29A reflection in Figure 10 (Earley et al., 1956). This spacing would be expected from the regular alternation of two 14A clay minerals. The relatively weak reflection is indicative of partially regular alternation. Lippman (1954) has proposed the name "corrensite" for a swelling type of chlorite mineral.

Although the formation of regular mixed-layer clay minerals may have some relation to physicochemical environment, the entropy factor (tendency for disordering) would appear to be a more fundamental control mechanism. Many arrangements of atoms can constitute a disordered system, but fewer can constitute an ordered system. Therefore, the system of greatest randomness is the system of highest probable occurrence. Moore (1950) defined the probability of a distribution as equal to the number of ways of realizing the distribution.

This concept may also be applied, to some extent, to the relation between mixed-layer and discrete clay minerals. Composition of pore solutions, obviously, would limit the degree and type of mixed layering. Pure clay-mineral species, with respect to probability, would be the exception rather than the rule. Adequate methods of resolving all degrees and types of mixed layering have not been developed.

The spatial distribution of apparent discrete clay-mineral species cannot be generalized as readily as the proposed zonal distribution described above. Chlorite and montmorillonite, montmorillonite and vermiculite, and vermiculite and halloysite commonly are inverted in their relative positions of maximum abundance. Such anomalies can be accounted for by lithologic and structural variations. From a consideration of the gross aspects, however, a generalized quantitative sequence toward the quartz veins can be listed: (1) chlorite, (2) montmorillonite, (3) vermiculite, (4) halloysite, (5) illite,







Figure 5

X-RAY SPECTROMETER TRACES OF SAMPLE TRANSITIONAL BETWEEN VERMICULITE-HALLOYSITE AND ILLITE-KAOLINITE ZONES



X-RAY SPECTROMETER TRACE OF SAMPLE FROM ILLITE-KAOLINITE ZONE (B)

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X-RAY SPECTROMETER TRACES, SHOWING REGULAR MIXED-LAYER CHLORITE-MONTMORILLONITE (6) kaolinite, and (7) dickite. It should be understood clearly that this sequence does not represent the order of abundance of clay minerals but indicates the relative spatial position at which a particular clay type assumes its maximum abundance.

Chlorite, apparently, is representative of the mildest form of alteration. No attempt was made to differentiate chlorite species. Spectrometer traces of oriented clay aggregates, however, indicate that the chlorite is predominantly a magnesium-rich variety. This observation is inferred from relatively intense 14A reflections. Iron-rich chlorites occur in minor quantities and are apparently limited to fringe areas of alteration and to zones which have been subjected to intense supergene processes.

Montmorillonites were differentiated with respect to the position of the (001) reflections (McAtee, 1956). In general, montmorillonites containing one layer of water occur farthest from the vein, whereas those containing two layers of water occur closest to the vein. This observation indicates that montmorillonites become progressively richer in a bivalent cation, possibly calcium, toward intense zones of alteration. Data collected by Hofmann and Klemen (1950) indicate that the exchange capacity of calcium montmorillonite shows an abrupt decrease after heating from 300° to 390°C, whereas sodium montmorillonite shows only a moderate drop following heat treatment. Thus, the high temperatures which possibly were attained in the alteration zones provided a mechanism for the stabilization of calcium montmorillonite.

This trend in montmorillonite composition is corroborated by chemical analyses (see below).

The relative abundance of vermiculite is variable but generally parallels the amount of chlorite present in the fringe zone of alteration. Decrease of montmorillonite relative to vermiculite, which can be considered a coarsegrained montmorillonite (Weaver, 1956), indicates the veinward increase of magnesium stability in the montmorillonite structure. Hofmann and Endell (1930) believe that heat treatment causes exchangeable cations to migrate inside the montmorillonite lattice. Because of the small ionic radius of Mg++, magnesium can fit into the structure. Such a structural change decreases base-exchange capacity and, therefore, increases the stability of the clay structure.

An additional factor which may play a significant role in stability is the coarser grain size of vermiculite compared to montmorillonite. As solubility generally decreases with increasing grain size, it may be suggested that vermiculite is a more stable form.

The term illite is used in this paper as a group name to specify micalike clay minerals (Grim et al., 1937). Observed variations, limited to microscopic examination, indicate that illites become more coarse grained toward highintensity alteration zones. Illite generally is distributed throughout the altered rocks and is the most abundant clay mineral in zones of intense alteration. Film-recorded data of relatively pure samples indicate that the 1Md (1-layer monoclinic disordered) polymorph occurs in the intensely altered zones (fig. 11). Measured interplanar spacings are in agreement with those listed by Levinson (1955). Particularly characteristic of the 1Md structure





is the faint haze between 4.48A and 2.57A, with the exception of a strong basal reflection at 3.33A. Reflections at 3.07A and 3.62A are extremely weak or absent. Levinson points out that the cause of polymorphic variations is unknown. Previous workers have reported 1Md polymorphs only in sedimentary environments.

An electron micrograph of a relatively pure illite from the Washington mine is shown in Figure 12. Many of the crystals are unusually well developed and have a morphology similar to an illite reported by Weaver (1953) as occurring in certain portions of the Oswego formation (Ordovician). Analyses of the Ordovician illite indicate an unusually low iron and magnesium content. Weaver suggests that the presence of relatively large quantities of these constituents inhibits the growth of well-developed crystals.

Clay minerals of the type 1:1 (sheet structures composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons) increase in abundance toward intense centers of alteration. The order of stability from the vein outward is dickite, kaolinite, and halloysite.



Figure 12

ELECTRON MICROGRAPH OF WELL-DEVELOPED ILLITE CRYSTALS (WASHINGTON MINE) Magnification X 26,500.
An X-ray powder photograph of dickite from the Sun mine is shown in Figure 13. The interplanar spacings are in close agreement with dickite spacings listed by Brindley and Robinson (1946). A differential thermal curve (fig. 14) further illustrates the high degree of crystallinity of this sample.



Figure 13 X-RAY POWDER PHOTOGRAPH OF DICKITE



D. T. A. CURVE OF DICKITE TAKEN ADJACENT TO VEIN

According to Grim (1953), an intense endothermic reaction occurs at about 600°C for well-crystallized kaolinite. The intensity, size, and temperature of the peak are affected by particle size and crystallinity. For dickite, the endothermic peak temperature is about 100°C higher than for kaolinite. Dickite is a most highly organized member of the kaolin group and thus has a slightly different differential curve. The loop is characteristically skewed toward the low-temperature side of the endothermic peak, and the high-temperature side has a noticeably steeper slope (Rowland, 1955). The small endothermic peak which occurs just before the exothermic reaction between

900°C and 1,000°C is characteristic of well-crystallized kaolinites (Grim and Bradley, 1948). The exothermic reaction is less intense but takes place over a relatively narrow temperature range for well-crystallized varieties. An electron micrograph of this dickite sample is shown in Figure 15.



Figure 15 ELECTRON MICROGRAPH OF DICKITE (SUN MINE) Magnification X 24,100.

The presence of halloysite and kaolinite mixtures was determined from electron micrographs. Figures 16 and 17 illustrate the occurrence of both clay minerals. The tubular morphology of halloysite as originally described by Bates et al. (1950) is well illustrated in Figure 17. The presence of partially hydrated halloysite rather than fully hydrated halloysite was determined from differential thermal analysis of glycolated samples. Sand and Bates (1953) have demonstrated a quantitative method for the determination of fully hydrated halloysite and kaolinite (and/or halloysite). They have shown that the endothermic peak temperature for glycolated partially hydrated halloysite is about 550°C, and that of the fully hydrated variety about 500°C. Figure 18 shows a differential thermal curve of glycolated halloysite, and Figure 17 is an electron micrograph of this sample.

A differential thermal curve of kaolinite with minor illite (fig. 19) corresponds reasonably well with that of a well-crystallized kaolinite. Comparison may be made with **the** dickite curve in Figure 14. As discussed above,



Figure 16 ELECTRON MICROGRAPH OF HALLOYSITE AND KAOLINITE Magnification X 30,300.



Figure 17 ELECTRON MICROGRAPH OF HALLOYSITE The tubular morphology is particularly well illustrated in the upper right portion of the photograph. Magnification X 23,400.





the peak temperature for the endothermic reaction occurs at about 600°C, which corresponds to that of a well-crystallized kaolinite. A small endothermic peak also occurs just before the exothermic reaction, which is further evidence for a well-crystallized kaolinite. An electron micrograph (fig. 20) indicates that well-developed kaolinite crystals are present.



Figure 20 ELECTRON MICROGRAPH OF KAOLINITE Note well-rounded forms in lower portion of photograph. Magnification X 54,600.

# PARAGENESIS OF ROCK ALTERATION

The rock types which have been most affected by the hydrothermal solutions include andesite, andesite porphyry, and monzonite. Because of their similar mineralogical and chemical composition, divergence in alteration mineralogy is minor. Rhyolite intrusives comprise a relatively minor quantity of the host rock. Their mineralogy is noticeably different from the mineralogy of the more basic rocks in the less intense alteration zones, whereas their mineralogy is similar to that of the other rock types in the most intense zones of alteration. Mild alteration of rhyolite has involved illitization of orthoclase and silicification. Intense alteration has led to the formation of kaolinite, dickite, and illite mixtures. Convergence in alteration has been emphasized by Schwartz (1950).

Although vein materials in the region are composed predominantly of quartz, calcite veins are present in the Sambo mine. Alteration products in the carbonate environment are comparable to those in the high-silica environment.

The petrology of the primary rocks has been described in a previous section. The approximate increasing order of stability of the primary minerals in relation to the hydrothermal solutions is as follows: (1) pyroxene, (2) hornblende, (3) biotite, (4) plagioclase, (5) apatite, (6) orthoclase, and (7) quartz. This sequence is in general accord with the order of stability of igneous rock minerals toward weathering (Goldich, 1938). As this order is the reverse of Bowen's reaction series, the last-formed minerals of igneous rocks, with the exception of apatite, are the most stable under the conditions of alteration to which the host rocks have been subjected.

#### Chlorite-Montmorillonite Zone

As the alteration front migrated outward from the fissure wall, the first minerals to be affected were hornblende and an unidentified pyroxene. Because all the rocks in the area have undergone some alteration, incipient changes in these ferromagnesian minerals could not be observed. Chlorite, epidote, magnetite, calcite, biotite, quartz, and montmorillonite are pseudomorphic after hornblende and. pyroxene.

Biotite displays varying degrees of alteration, but in its initial stages it is bleached along cleavage planes. Progressing within this zone, biotite gradually is converted to chlorite until complete transformation results. This first-formed chlorite is an iron-rich variety, penine. A considerable amount of titanium was separated from biotite, as indicated by the presence of ilmenite and leucoxene. Occurrence of abundant ilmenite and leuxocene parallels complete transformation to chlorite.

Sometime during the chloritization of biotite, plagioclase was altered to montmorillonite along cleavage zones and twin planes. Potassium ions, derived from the breakdown of biotite, initiated minor illitization of mont-morillonite. The effects of illitization become increasingly intense toward the vein. Figure 21 shows an illite veinlet which penetrates chlorite pseudomorphic after biotite, leucoxene, and a plagioclase groundmass.

Epidotization of plagioclase follows closely the beginning of montmorillonite alteration. Commonly, epidote is pseudomorphic after plagioclase(fig. 22).

Clinozoisite generally is associated with epidote but is less abundant. Epidote veinlets are abundant and penetrate the first-formed chlorite.

Chloritization of plagioclase is not uncommon, and chlorite pseudo-morphs are numerous (fig. 23). Abundance of chlorite-montmorillonite mixed layering, as shown by X-ray spectrometer traces, indicates that montmoril-



Figure 21 PENETRATION OF CHLORITE, LEUCOXENE, AND FELDSPAR GROUNDMASS BY ILLITE VEINLET Crossed nicols. Magnification X 100.



Figure 22 REPLACEMENT OF PLAGIOCLASE PHENOCRYST BY EPIDOTE Phenocryst outlined in ink. Crossed nicols. Magnification X 100.



Figure 23 CHLORITE PSEUDOMORPH AFTER PLAGIOCLASE PHENOCRYST Crossed nicols, Magnification X 150.



Figure 24 INCIPIENT ALTERATION OF ORTHOCLASE ALONG CLEAVAGE AND FRACTURE ZONES Crossed nicols. Magnification X 200.

lonite may be an intermediate step in this process. Chloritization, in part, apparently has taken place by the action of magnesium and iron-bearing solutions on montmorillonite. Such solutions undoubtedly were derived from the breakdown of ferromagnesian minerals. Synthesis of poorly crystalline chlorite has been accomplished by Calliere et al. (1948).

Within the inner edges of this zone, chlorite becomes less abundant with respect to montmorillonite. The presence of mixed layering between these two minerals may also indicate transition of chlorite to montmorillonite by the leaching of magnesium and iron from the chlorite lattice. This leaching process is indicated also by the appearance of vermiculite and mixed-layer vermiculite-chlorite.

An isotropic mineral having an index of refraction close to allophone occurs sporadically. It is associated generally with argillized plagioclase. Pyritization of ilmenite and magnetite is common, increasing in degree toward the vein. Kaolinite and halloysite are minor constituents and apparently are associated with plagioclase alteration. Silicification is minor, occurring as veinlets and replacements of both primary and secondary minerals. Chemical loss of silica by recrystallization of the feldspars provides a reasonable mechanism for silicification. Euhedral apatite laths show moderate replacement by chlorite.

## Vermiculite-Halloysite Zone

With further advance of the alteration front, halloysite and vermiculite become characteristic and dominant clay-mineral associations. Although kaolinite, chlorite, and montmorillonite occur in this zone, their presence is sporadic.

Remnants of ferromagnesian minerals have completely disappeared. Chlorite and montmorillonite are replaced extensively by vermiculite and illite. The common occurrence of vermiculite and vermiculite-chlorite mixed layering, and the noticeable decrease of montmorillonite, are significant. This would appear to indicate leaching of some magnesium from the chlorite lattice and subsequent adsorption of magnesium by montmorillonite. The chlorite which remains is no longer the iron-rich variety, penine, and this loss of iron is reflected in the greater abundance of pyrite and iron oxides. Ilmenite is completely replaced by leucoxene.

Clay minerals pseudomorphically replace the remnants of plagioclase crystals. Rarely, plagioclase shows relatively minor alteration. In such instances, protective envelopes of silica have inhibited the contact of plagioclase with the altering solutions. Epidote alteration is minor to absent, but minor amounts of clinozoisite persist.

Orthoclase displays initial stages of alteration to illite and kaolin minerals. The alteration is noted first along cleavage zones and fractures (fig. 24).

Alunite is associated abundantly with halloysite. Its formation time covers a wide span, beginning before halloysite crystallization and continuing throughout dickite crystallization. Figure 25 illustrates the penetration of



Figure 25 ALUNITE PENETRATED BY HALLOYSITE VEINLETS Crossed nicols. Magnification X 100.



Figure 26 BIOTITE SECONDARY AFTER CHLORITE AND ILLITE Dark areas indicate biotite. Crossed nicols. Magnification X 100.

alunite by a halloysite veinlet. Jarosite is also widespread and is present in all the alteration zones in about equal abundance. It occurs as yellow earthy incrustations on fracture surfaces.

Allophane occurs sporadically, as it does in the chlorite-montmorillonite zone. Apatite shows considerably more alteration and has been replaced largely by illite, montmorillonite, and chlorite. Silicification and pyritization have increased in intensity.

Secondary biotite is common but is limited to the inner fringes of this zone and to the outer fringes of the illite-kaolinite zone. Apparently, it has recrystallized from illite and chlorite. Figure 26 shows veinlets and irregular masses of secondary biotite.

# III ite-Kaol inite Zone

Within this intense alteration zone, kaolinite and, particularly, illite are the most characteristic mineral assemblages. Noteworthy is the abundance of fine-grained quartz interspersed with these clay minerals. Increase in free silica is reflected by the almost complete breakdown of the remaining primary minerals and by the increase in clay minerals (1:1) having a relatively high aluminum-to-silicon ratio. In many well-crystallized micas, up to onefourth of the silicon in the lattice is replaced by aluminum. Orthoclase has been converted largely to illite, kaolinite, and fine-grained quartz (fig. 27). Much of the illite has been recrystallized into coarse-grained particles having optical properties which correspond to those of muscovite.

Although a considerable amount of the 1:1 clay minerals may have formed directly from the decomposition of potash feldspar, transition from 2:1 clays apparently has been an active phenomenon. This is indicated by the gradual increase in 1:1 and gradual decrease of 2:1 clay types. The mechanism of transition from 2:1 to 1:1 clay minerals is not clear. Sales and Meyer(1948), in their study of wall-rock alteration at Butte, suggest that mixed layering occurs between montmorillonite and kaolinite, as interpreted from differential thermal curves. Grim and Johns (1954), in their study of sediments in the northern Gulf of Mexico, implied that a solid-state transition from kaolinite to chlorite may have taken place. They point out that this transition would involve a shift in silicon positions of every other silicon sheet, and replacement of some aluminum by magnesium within the structure. Although this process, in reverse, may have been active during the alteration of the Cochiti rocks, it is not obvious how its occurrence can be demonstrated. Brindley and Gillery (1954) reported an occurrence of kaolinite-chlorite mixed layering in an X-ray study of "daphnite" from Cornwall, England. Because of the availability of relatively large crystals, this determination was based upon single-crystal analysis.

Sand (1956), in his study of weathered feldspathic rocks in the southern Appalachians, concluded that secondary mica is an essential intermediate product in the formation of kaolinite from feldspar. He points out that a completely leached and hydrated muscovite has the same ratio of aluminum, silica, and water as kaolinite, but that the mechanism of transfer of silicon and aluminum from a 2:1 to a 1:1 type is unknown.



Figure 27 ILLITE AND KAOLINITE, PSEUDOMORPHIC AFTER ORTHOCLASE PHENOCRYST, PENETRATED BY QUARTZ VEINLETS

Euhedral pyrite has replaced phenocryst and quartz veinlets. Crossed nicols. Magnification X 100.



Figure 28 ILLITE AND SECONDARY BIOTITE PENETRATED BY ALUNITE VEINLETS Crossed nicols. Magnification X 100.

Roy (1954) stated that in nature, endellite and kaolinite form under apparently similar conditions of temperature and water-vapor pressure. It is not clear which is the more stable under these formation conditions. Both Roy and Sand emphasize the compositional and structural control exerted by the original mineral.

Ross and Kerr (1934) suggested that halloysite crystallizes from allophane, and that kaolinite, in turn, crystallizes from halloysite.

All these transition processes may have been operative, but it is believed that crystallization from allophane has been a significant mechanism. Aggregates of minute and isotropic particles having a refractive inde<sup>x</sup> near that of allophane occur in minor quantities within this zone. An electron micrograph (fig. 20) shows a mixture of kaolinite and almost perfectly rounded particles believed to be allophane. Hauser (1954) indicated that rounded forms are characteristic of amorphous aluminum silicates. This association of well-rounded forms and well-developed kaolinite strongly suggests that a crystallization process, with allophane as the intermediate phase, has been active. The occurrence of halloysite veinlets (fig. 25) is indicative of formation via a solution phase.

Alunite, although not as abundant as in the vermiculite-halloysite zone, has persisted as a common alteration product. Figure 28 illustrates its occurrence as a replacement mineral of secondary biotite and illite.

Leucoxene and jarosite are common alteration minerals. Apatite has been replaced completely by clay minerals.

#### Dickite Zone

Dickite is limited to narrow bands adjacent to veins, and to inclusions within the veins. This most intense alteration has resulted in the removal of almost all alkali. Quartz and pyrite are the only other major constituents.

The veinward increase in crystallinity of 1:1 clay minerals (halloysite $\rightarrow$  kaolinite $\rightarrow$ dickite) is indicative of a progressive increase of formation temperature. This order of stability has been substantiated by synthesis experiments (Roy and Osborn, 1954; NoII, 1944; Ewell and Insley, 1935).

An additional factor which may be significant in determining the degree of crystallinity is the catalytic influence of ions which do not enter into the composition of the final product. Henin (1956) has shown from a synthesis study that NaCI improves the crystallinity and rate of formation of clay minerals. In contrast, she found that the presence of potassium ions appears to impede the formation of well-crystallized products. It is of interest to note that decrease in potassium, indicated by decrease in illite, parallels increase in crystallinity of 1:1 clay minerals.

#### SUPERGENE ALTERATION

It has been stated (Kerr, 1955) that with sufficient time even weak concentrations of acidic or basic solutions, along with small amounts of alkaline elements, alumina, and silica, may produce sizable clay deposits. Increased temperatures and solution concentrations, for the most part, affect only the kinetics of clay-mineral formation. Because of the wide range in stability conditions of clay minerals, differentiation of clays formed by supergene processes versus hydrothermal processes presents a difficult problem.

The more obvious products of supergene processes are limonite, gypsum, and melanterite. Oxidation of iron-bearing minerals, particularly pyrite, has given rise to the widespread occurrence of limonite (mixture of goethite and lepidocrocite). Melanterite (FeSO4.7H20) is also a product of pyrite oxidation. The following are some theoretical equations for the oxidation of pyrite (Gottschalk and Buehler, 1912):

- (1)  $FeS_2 + 70 + H_2O \rightarrow FeSO_4 + H_2SO_4$ ;
- (2)  $FeS_2 + 30 + H_2O \rightarrow FeSO_4 + H_2S_;$
- (3)  $2FeSO_4 + 0 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O_3$ ;
- (4)  $Fe_2(SO_4)_3 + 3H_2O \rightarrow Fe_2O_3 + 3H_2SO_4$ .

If equation (2) has been operative in the Cochiti area, the action of H2S on Fe++ and Fe+++ solutions may have precipitated supergene pyrite (Bastin, 1926). Hydrogen sulfide is produced by similar reactions with other sulfides. Although the presence of supergene pyrite was not demonstrated conclusively, this process would account for the occurrence of loose crystalline crusts of pyrite, believed by Lindgren et al. (1910) to be a phenomenon caused by descending waters. Reaction of sulfuric acid with calciumbearing solutions has caused the precipitation of gypsum, which occurs abundantly as an efflorescene on mine walls.

Replacement of pyrite by halloysite-kaolinite mixtures (fig. 29) is noteworthy and common. Reaction of sulfuric acid with the adjacent illite may conceivably be the formation mechanism for this particular occurrence of 1:1 clay minerals. Ross and Kerr (1934) and Callaghan (1948) have suggested a similar mechanism for the formation of halloysite.

Clearly, illitization is a common process during hydrothermal alteration, and it is probable that illite is being formed under the present supergene processes. The pervasive occurrence of highly soluble minerals, such as alunite [K2AI6 ( $^{OH}$ )12 ( $^{SO}$ 4)4] and jarosite [K2Fe6(OH)12 (SO4)41, indicates that K+ ions are abundant constituents of present ground-water solutions. The fixation of potassium in the interlayer positions of montmorillonite has been discussed in a previous section. In this connection, it is also significant that illite veinlets commonly penetrate and surround alunite masses.

Precipitation of alunite generally has been ascribed to the reaction of sulfuric acid with minerals containing potassium and aluminum in hydrothermal environments (Lovering, 1949). Leonard (1927) synthesized alunite from solutions containing H2SO4, K2SO4, Na2SO4, and Al2(SO4)3 at 200°, 100°, and 22°C. Although the abundant occurrence of alunite in hydrothermally altered rocks indicates formation at relatively high temperatures, it also seems probable that some alunite has formed under supergene conditions.

It is inevitable that clay minerals will form through the agencies of supergene alteration, and this is attested by the numerous deposits formed in nonhydrotheimal environments. Nevertheless, the zonal distribution of clay minerals, and the undeniable spatial relation to quartz veins in those



Figure 29 REPLACEMENT OF PYRITE BY HALLOYSITE AND KAOLINITE

(H-K) Halloysite and kaolinite, (1) illite, (P) pyrite. Crossed nicols. Magnification X 150.

deposits, preclude the possibility that extensive supergene clay formation has taken place. Murray and Leininger (1956), in their study of soil and till profiles in southern Indiana, found that montmorillonite is the most abundant clay mineral in the most highly weathered zones. Weathering processes apparently are not so advanced in the Cochiti area. Schwartz (1956) does not believe that weathering develops much additional clay in the relatively arid Southwest.

Because the stability of the primary minerals in relation to hydrothermal alteration corresponds to the same stability sequence with respect to weathering, it follows that hydrothermal processes may be considered as an intensified form of weathering. The products of alteration appear to be largely dependent upon the chemistry of the altering solutions, whereas the intensity of alteration is largely a function of temperature and time.

#### CHEMICAL ANALYSES

Total-rock samples and illite clay fractions were analyzed chemically. Analyses of the total-rock samples are shown in Tables 2 and 3. These analyses are plotted in Figures 30 and 31 and indicate relationships of chemical trends to alteration zones and quartz veins. The analyses are expressed as cation content, similar to the method of Barth (1955). As pointed out by Tooker (1956), this method seems warranted because the system involves transfer of ions in an oxygen structural network rather than as oxides.

Silicon does not show a noticeable veinward decrease, except in intensely argillized zones where 1:1 clay minerals are abundant. Increase in 1:1 clay minerals is coincident with increase in aluminum. According to Krauskopf (1956), contrary to commonly accepted geologic assumption, the solubility of silica is little affected by changes in pH in the range 0 to 9. A significant increase in solubility of silica increases considerably. Aluminum is practically insoluble over the pH range 5 to 9 but is readily soluble in strongly acid or alkaline solutions (Correns, 1949). Consideration of these solubility data and of the silicon-aluminum trends indicates that the pH of the altering solutions probably did not extend beyond the range of 4 to 10 at any given time. If the pH of the altering solutions had exceeded 9 to

Zones							
Constituent	Chlorite-montmorillonite Vermiculite-halloysite					Illite-kaolinite	
	(1)*	(2)*	(3)*	(4)*	(5)*	(6)*	
Al	9.63	8.48	9.47	8.67	8.52	9.15	
Ca	1.87	1.94	1.72	1.23	.86	1.7	
Fe	4.09	3.12	2.87	2.87	2.18	15.7	
к	7.0	3.75	4.05	5.10	8.0	.37	
Li	.003	.003	.003	.003	.003	.003	
Mg	2.61	2.08	2.29	2.41	3.35	4.1	
Mn	.098	.06	.06	.08	.04	.02	
Na	2.03	.86	1.07	1.42	.42	.08	
Р	.19	.11	.12	.13	.019	.28	
S	.53	.60	.43	.26	.50	1.40	
Si	27.0	30.0	28.7	29.0	29.7	17.5	
Ti	.52	.41	.12	.49	.42	.11	
CO2	.09	.24	.09	.06	.18	.12	
H <sub>2</sub> Ō	1.90	2.59	3.14	2.68	2.18	7.64	

TABLE 2. CHEMICAL ANALYSES<sup>1</sup> (LONE STAR MINE)

Analysts: R. F. Conley and M. E. Coller, Bloomington, Indiana.

Sample numbers.

		Zon	es			-
Constituent	Chlorite- montmorillonite	Vermiculite-halloysite		Illite-kaolinite Dickite		
	(1)*	(2)*	(3)*	(4)*	(5)*	(6)*
Al	8.25	8.41	7.78	7.41	9.52	14.9
Ca	1.52	1.57	1.33	.69	.71	.79
Fe	2.87	2.47	3.52	.56	2.69	10.1
ĸ	2.80	2.20	2.85	1.60	1.65	.03
Li	.003	.003	.003	.003	.003	.003
Mg	3.50	3.13	3.48	.49	.95	.37
Mn	.04	.05	.05	.008	.006	.004
Na	.75	1.69	1.54	.04	.17	.07
Р	.12	.10	.10	.30	.041	.09
S	.89	1.83	2.12	.39	.65	2.85
Si	28.9	29.7	28.9	35.1	30.0	20.2
Ti	.37	.37	.35	.20	.42	.03
CO <sub>2</sub>	.03	.04	.05	.09	.10	.09
H <sub>2</sub> Õ	3.18	2.87	2.83	3.04	4.15	11.5

TABLE 3. CHEMICAL ANALYSES (SUN MINE)

Analysts: R. F. Conley and M. E. Coller, Bloomington, Indiana.

\* Sample numbers.

10, aluminum, along with silicon, would have been depleted near the vein. Because of its somewhat soluble character at increased temperatures and over the pH range 0 to 9, veinward depletion of silica would be expected regardless of the pH of the altering solutions.

Inasmuch as apatite is destroyed in the illite-kaolinite zone, the overall veinward decrease in phosphorus up to this zone is to be expected. The excessive increase in phosphorus within the illite-kaolinite zone is difficult to explain. Although the extent of fixation of phosphorus by clay minerals is not great, Stout (1939) has noted that halloysite and kaolinite have the highest phosphate-fixation power. In addition to its fixation in clay minerals, phosphorus may substitute for silicon in the oxygen-silicon framework of silicates (Rankama and Sahama, 1950). This diadochy arises from the similar ionic radii of silicon (0.42) and phosphorus (0.35). Butler (1953), in a study of rock weathering, suggested that phosphorus released from apatite is fixed as PO4<sup>---</sup> ions by iron oxide derived from biotite. He further suggested that some phosphorus has replaced atoms in silicate lattices. Hemwal I (1957) has shown experimentally that phosphorus is fixed by clay minerals by reaction with soluble aluminum, originating from exchange sites or from lattice dissociation, to form a highly insoluble aluminum phosphate. Noddack and Noddack (1931) found that magmatic sulfides may contain a relatively



Figure 30 CHEMICAL TRENDS (LONE STAR MINE)





high percentage of phosphorus; however, its occurrence within the sulfide structure is not understood. In the present study, it appears significant that increase in phosphorus roughly parallels increase in kaolin minerals and pyrite.

In general, titanium decreases in a veinward direction. Titanium is concentrated in dark silicate minerals such as biotite, hornblende, and pyroxene (Rankama and Sahama, 1950), and decrease in titanium is coincident with the destruction of these dark minerals. Because soluble salts of titanium are hydrolyzed readily, migration of titanium is limited. McLaughlin (1955), in a study of rock weathering, attributed a high concentration of titanium in clays to the almost immediate precipitation of the oxide on clay particles. The anhydrous oxide of titanium is sparingly soluble in either acids or bases, but the hydrated forms are somewhat soluble in both (Latimer, 1952). Because of the relatively high electronegativity of titanium, it follows that titanium is somewhat more soluble in basic solution. These observations indicate that, near the vein, titanium has been leached by either relatively strong acids or bases.

Increase in water parallels increase in clay-mineral content. This gain is particularly pronounced in zones containing 1:1 clay minerals; therefore, water increase parallels increase in aluminum.

The hydrothermal emanations apparently contained some carbon dioxide. This is indicated by the presence of carbonate in the fringe areas of alteration. The somewhat erratic distribution of CO2 may indicate minor fixation of calcium, magnesium, and iron.

Veinward increase in sulfur is coincident with increase in pyrite. The somewhat erratic distribution of sulfur corresponds to the distribution of alunite and jarosite.

Because a rapid and reproducible method for the quantitative determination of Fe++ and  $Fe++^+$  has not been developed (Hillebrand et al., 1953), iron analyses are reported only as Fe. Iron shows a general veinward decrease but near the vein shows a marked increase. Abundance of pyrite near the vein accounts for the high iron content. High concentrations of pyrite near the vein may result from the transition of alkaline to acidic solutions. As sulfides are most soluble in alkaline solution, the decrease of pH provides a precipitation mechanism.

Manganese shows a progressive decrease in concentration toward the vein. Because of its low oxidation potential, bivalent manganese is the only stable oxidation 'state during crystallization of natural silicate melts (Rankama and Sahama, 1950). In general, manganese, like titanium, is concentrated in dark silicate minerals. Destruction of these minerals parallels the veinward decrease in manganese. As bivalent manganese is the most mobile and is most soluble in acid solutions, the manganese trend reflects a progressive increase in basicity of the altering solutions away from the vein.

Both sodium and potassium decrease in a veinward direction. A maximum for sodium occurs at the transition area between the chlorite-montmorillonite zone and the vermiculite-halloysite zone. This maximum corresponds roughly to the position at which montmorillonite is most abundant. A maximum for potassium occurs at the outer edge of the illite-kaolinite zone and generally corresponds to the position at which illite is the most abundant.

Calculation of K:Na ratios (table 4) indicates a marked increase in potassium over sodium in the illite-kaolinite zone. At the inner edge of this zone and in the dickite zone, potassium apparently has been leached more readily than sodium. It is not clear why this relationship exists. According to Rankama and Sahama (1950), potassium goes into solution first during weathering but does not remain dissolved, because of adsorption by clays. This adsorption is limited, for the most part, to clay minerals of the 2:1 type. Grim (1953) stated that kaolinite has substantially no power to fix K+ ions. It is significant that the marked decrease in K:Na ratio occurs where kaolinite becomes abundant.

Lone Star mine		Sun mine		
Sample	K:Na	Sample	K:Na	
1	3.44	1	3.73	
2	4.35	2	1.30	
3	3.80	3	1.85	
4	3.58	4	57.14	
5	19.00	5	15.00	
6	4.60	6	0.43	

TABLE 4. POTASSIUM : SODIUM RATIOS

Calcium and magnesium, in general, decrease toward the vein. This decrease coincides with destruction of montmorillonite and vermiculite. Because the relative veinward decrease in potassium and sodium is much greater than for calcium and magnesium, it follows that the more strongly polarizing alkaline earths Ca++ and Mg++ ions, by virtue of their higher covalent character, have formed more stable structures under the conditions of alteration.

Chemical analyses of relatively pure illites also indicate observable trends (tables 5, 6 and figs. 32, 33). Minor amounts of kaolinite and montmorillonite contained in some of the samples were determined quantitatively from X-ray diffraction data and were considered in calculation of the chemical analyses.

In general, the chemical analyses indicate a veinward decrease in basicmetal ions. The illites analyzed grade veinward from those containing a slight amount of interlayered expandable material to those containing minor amounts of kaolinite. The element trends indicate chemical changes which take place in transitions through montmorillonite, illite, and kaolinite.

As in the total-rock analyses, the K:Na ratio decreases in a veinward direction. This trend seems to indicate initial stages in the transition from illite to kaolinite.

Co	onstituent		Intensity of		
		(1)*	(2)*	(3)*	(4)*
	Ca	1.0	0.8	1.3	1.1
	Fe	0.66	0.81	2.58	0.71
	К	6.5	10.0	9.0	8.0
	Li	.003	.003	.003	.003
	Mg	1.3	1.4	1.0	1.1
	Na	.05	.06	.13	.06

TABLE 5. CHEMICAL ANALYSES OF ILLITES (ALBEMARLE MINE)

Analysts: R. F. Conley and M. E. Coller, Bloomington, Indiana.

\* Sample numbers.

Constituent				Intensity of		
			(1)*	(2)*	(3)*	(4)*
	Ca		0.6	0.7	0.6	0.5
	Fe		1.71	.50	.75	2.04
	К		3.55	2.60	4.00	1.80
	Li		.003	.003	.003	.003
	Mg		1.2	0.9	1.0	0.9
	Na		.08	.05	.07	0.12

TABLE 6. CHEMICAL ANALYSES OF ILLITES (SUN MINE)

Analysts: R. F. Conley and M. E. Coller, Bloomington, Indiana.

\* Sample numbers.

The striking parallel trend of sodium and iron is strongly suggestive of contemporaneous substitution in illite. To establish electrical neutrality, replacement of Al+++ by Fe++ requires equivalent substitution by a monovalent cation. This requirement is satisfied readily by sodium.

A slight veinward decrease in calcium and magnesium corresponds roughly to decrease in mixed layering. As K:Mg and K:Ca ratios also decrease in a veinward direction, it is suggested that there has been some substitution for potassium by magnesium and calcium in illite.

It is of interest to note that ionic potential ( $\Phi$ =cation charge/cation radius)bears a direct relation to mobility of the elements. A plot of ionic potentials, modified after Goldschmidt (1937), is shown in Figure 34. According to Mason (1952), ionic potential is significant in all mineral-forming processes in an aqueous medium. Increase in ionic potential is associated with strong polarizing effects and thus with increased covalence (Moeller, 1953). It follows, therefore, that minerals formed from elements with high ionic po-





CHEMICAL TRENDS IN ILLITE COMPOSITION (ALBEMARLE MINE)



Figure 33

CHEMICAL TRENDS IN ILLITE COMPOSITION (SUN MINE)



tentials are less soluble and as a result are more stable in electrolytic solutions. With the exception of carbon and sulfur, which can be precipitated as soluble complex anions, those elements with the highest ionic potentials have been affected the least by the altering solutions. Alkali metals and alkaline earths, in contrast, show notable veinward depletions. It should be mentioned also that alkali metals and alkaline earths with lower ionic potentials are adsorbed readily and thus do not move far from their source; those with somewhat higher potentials remain longer in solution and are carried farther from their source.

The geochemical behavior of less common elements not ordinarily included in analyses may, in general, be predicted by use of ionic-potential plots.

#### ALTERATION MECHANISM

Localization of andesite dikes and quartz veins along faults trending north-south indicates a close relationship between faulting, intrusion, and mineralization. The sequence of the Tertiary igneous rocks andesite, monzonite, andesite, and rhyolite, all closely associated in time and space, is indicative of a common parent magma. Faulting apparently had reached a magma reservoir and provided avenues of escape for portions of a differentiating magma and for later hydrothermal emanations.

The original composition of hydrothermal solutions can be deduced generally from the known composition of volcanic emanations. A typical analysis of gases evolved from the lava lake at Kilauea is shown in Table 7 (Groton, 1945).

Constituent	Average analysis		
H <sub>2</sub> O	45.12		
CO2	20.71		
co	0.69		
H2	0.06		
N2	7.93		
A	0.30		
SO <sub>2</sub>	16.67		
S2 -	2.47		
SO3	5.51		
Cl2	0.54		

TABLE 7. ANALYSIS OF KILAUEA GASES

This analysis shows that the major constituents are H20, CO2, and SO2. CO2 forms a weak acid in solution; SO2 a relatively strong acid. Sulfurous acid is oxidized to sulfuric acid (a strong acid) in the presence of oxygen and halogens (Moeller, 1953).

Schmitt (1950) stated that volcanic emanations generally contain superheated steam, CO2, H2S, and smaller amounts of NH3, CH4, HCI, NaCI, and NH4CI. Ore metals commonly accompany these gases. From such analyses, an original acid solution is logically postulated.

Hydrothermal solutions generally are believed to be originally acid, but information concerning their composition is scant (Grim, 1953). With continued reaction with silicate rocks, the solutions become alkaline and remain alkaline until the alkalies and alkaline earths are no longer available for solution.

Analyses collected by many investigators indicate that volcanic gases show significant local and regional changes, and for a single eruption vary from time to time and from place to place (Clarke, 1924). Because the

ascending gases react with the host rocks, some of their constituents are precipitated, and some new volatile compounds may be acquired. Temperature of the emanations affects their chemical composition, which depends, in turn, on the distance traveled from the source. Analyses generally indicate that carbon dioxide is characteristic of waning volcanic activity or of areas farthest removed from the center of activity. As "beidellite" (a mixture of clay minerals; Grim and Rowland, 1942) is characteristic of least intense alteration zones, it is significant that Norton (1939) synthesized this material by the action of CO2-charged water on albite at 275° to 325°C. Gases of sulfur and, finally, chlorine become predominant with increasing volcanic intensity.

Effects of hydrothermal solution types are clearly observable in altered rocks resulting from present fumarolic activity. Burbank (1950) pointed out that clay-mineral suites associated with many hydrothermal deposits closely resemble alteration effects in fumarolic and hot-spring areas having solfataric environments. An example of this type is afforded by the Red Mountain district in Colorado. In this district, dickite represents the most intense product of solfataric alteration, and away from the channels, "beidellite," montmorillonite, and chlorite become dominant.

In the Yellowstone Park area, Fenner (1936) noted that near the surface, kaolinite is formed by the attack of acid sulfate on feldspars, whereas at depth "beidellite" is formed. This relation implies that the altering solutions increase in pH with increasing depth. In this connection, Schmitt (1950) pointed out that in hot-spring areas, where H2S is in excess near the surface, oxidation may produce sufficient sulfuric acid to neutralize originally alkaline solutions or make them acid. Solutions of this type bring about alteration characterized by kaolin types of clay minerals, sulfates, and commonly silicification. According to Schmitt, some epithermal deposits (e.g., Goldfield, Nevada) show a marked similarity to this system. This similarity is also striking in the Cochiti area.

Synthesis experiments with clay minerals provide an additional insight into the mechanism of alteration. Because of the wide range in stability of clay minerals, the specific geochemical environment under which they were formed can only be generalized. In addition, a definitive work has not been carried out for a comprehensive understanding of clay-mineral equilibrium; however, abundant synthesis data are available.

Ewell and Insley (1935) and Noll (1944) synthesized kaolinite in the range 250° to 400°C. Greater pressures are required for its formation at the lower temperatures. Dickite has been produced by Ewell and Insley in the range 345° to 365°C. Noll has emphasized the effect of temperature on rate of reaction and points out that kaolinite was produced at 300°C in 1 hour but required 111 hours to form at 200°C. Noll (1934) indicated that kaolinite will form below 400°C in neutral solutions free of alkali metals or in acidic solutions containing alkali metals. Above this temperature, muscovite is formed. Gruner (1944) pointed out that kaolinite will form below about 350°C at all concentrations of potassium if the ratio of Al:Si is about 1:1.

Up to the present time, halloysite has not been synthesized. Geological evidence seems to indicate that halloysite is formed by the action of sulfate-bearing solutions upon other clay minerals (Ross and Kerr, 1934; Swineford et al., 1953). Synthesis experiments and geologic evidence indicate that the order of stability of kaolin minerals with respect to temperature, from most stable to least stable, is dickite, kaolinite, and halloysite. An upper stability limit of about 405°C has been established for these minerals (Roy and Osborn, 1954).

Noll (1936) has shown that at 300°C kaolinite and montmorillonite can be formed simultaneously in a dilute solution containing either alkalies or alkaline earths. Montmorillonite becomes the predominant product as the sodium or potassium concentration is increased. Although magnesium is the more effective agent, high concentrations of calcium or magnesium result in the formation of pure montmorillonite. At relatively high concentrations of potassium, mica is produced.

In summary, acid conditions, low temperatures, and low pressures favor the formation of clay minerals of the kaolinite group. Kaolinite forms below 350°C with optimum silica and alumina concentrations regardless of the concentrations of potassium. Alkaline conditions favor the formation of montmorillonite; however, if the potassium concentration is optimum, mica will form.

Along with the assumption that the original hydrothermal emanations were acidic, it is also assumed that a progressive change in pH ensued throughout each alteration stage in the Cochiti district. With respect to the general clay-mineral time sequence (chlorite, montmorillonite, vermiculite, halloysite, illite, kaolinite, and dickite), the original solutions, after traversing and leaching host rocks at depth, must have been alkaline. This clay mineral sequence is suggestive of a proximate time trend in pH:

Chlorite→montmorillonite→ vermiculite→ halloysite→Illite→ kaolinite→dickite.

Reversion to alkaline conditions during intensive illite formation is ascribable, to the decomposition of potash feldspar and subsequent solution of potassium (Sales and Meyer, 1948). The abundance of alunite in the vermiculitehalloysite zone and the illite-kaolinite zone corresponds to transitional phases in pH between alkaline and acidic solutions. Lovering (1949) pointed out that  $AI(OH)_3$  is stable in sulfuric acid only down to pH 4.3. He suggests that the hydroxyl radical incorporated in alunite can appear only in solutions that are very nearly neutral. It is postulated further that alunite is precipitated from cooling nearly spent acid solutions with a pH slightly less than 7.

The author does not believe that successive hydrothermal-alteration stages of initially different composition are necessary for the formation of successive alteration zones. Instead, assuming constant temperature and pressure, the intensity of alteration is a function of time and pH. Variation of temperature

and pressure would largely affect the reaction rate and to a much lesser extent the type of clay mineral formed. Alteration stages in the Cochiti district are considered as the result of a continuing process, in that the second stage of alteration continued as an acid-alkaline front after the first stage terminated. During the second alteration stage, solutions were conceivably more acidic than those emanating at the close of the first stage. These later solutions retained a relatively low pH because large quantities of alkalies and alkaline earths had already been leached from the channel walls during the previous alteration stage. The clay-mineral end product of action by acid hydrothermal solutions is apparently dickite. Clay minerals, characteristic of low-intensity alteration zones but occurring in minor quantities in intense-alteration or may be effects incurred during the waning stages of hydrothermal activity.

# Suggestions for Prospecting

Ore produced in the Cochiti district has generally been of low grade, averaging during production about \$6 per ton. Rich pockets of ore, however, were found. Most of the known veins crop out at the surface, but many, as yet unknown, may be concealed at depth. Prospecting carried out along veins known to have contained minable shoots of sulfide ore and along veins of demonstrated continuity could expose additional ore. Vein intersections, as well as wide portions of veins, are not necessarily highly mineralized but are nevertheless considered favorable areas for prospecting.

Increasing intensity of wall-rock alteration may be regarded as a guide to ore channels and favorable structural zones. Argillic alteration zones, although not associated with exposed veins, may warrant drilling. Intense zones of alteration containing dickite or an abundance of kaolinite and illite are not associated in time with economic mineralization. This most intense alteration, however, has been superimposed upon zones of less intense alteration and, therefore, commonly is associated spatially with economic mineralization.

Controlling structural features presumably extend far below any ore that will ever be reached by mining. The vertical range of the ore undoubtedly is determined by physicochemical conditions. Epithermal gold and silver deposits, however, characteristically do not form at great depths below the surface. Inasmuch as there is no evidence of mesothermal mineralization in the district, it would seem that most attention should be directed to a search for ore bodies along extensions of known veins and lodes.

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## NEW MEXICO BUREAU OF MINES AND MINERAL RESOURCES

BULLETIN 59 PLATE I



# GEOLOGIC MAP OF THE COCHITI MINING DISTRICT, NEW MEXICO





NEW MEXICO BUREAU OF MINES AND MINERAL RESOURCES

MAP OF QUARTZ VEINS AND MINE WORKINGS OF THE COCHITI DISTRICT, NEW MEXICO