ARGILLIZATION IN THE COCHITI MINING DISTRICT, NEW MEXICO

by

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ABSTRACT

Volcanic and intrusive rocks (mainly andesite and monzonite) of Tertiary age are associated with gold- and silver-bearing quartz veins. Hydrothermal alteration took place in two stages. The first and less intense alteration stage is associated with economic mineralization; metallization during the second and more intense stage is limited to pyrite.

Alteration zones from the vein outward include: (1) dickite, (2) illite–kaolinite, (3) vermiculite–halloysite, and (4) chlorite–montmorillonite. Mixed-layer associations of 2 : 1 clay minerals are abundant and represent transitions between discrete clay minerals. Apparent occurrence of allophane in the illite–kaolinite zone indicates that amorphous aluminum silicates are intermediate phases in transitions from 2 : 1 to 1 : 1 clay minerals.

Alteration of ferromagnesian minerals and plagioclase resulted largely in the formation of 2 : 1 clay mineral types. Orthoclase is altered chiefly to illite and kaolinite. Dickite and quartz are end products of the most intense alteration in the area.

Chemical analyses of the altered rocks in general show a decrease in basic ions toward the vein. Less significant changes are shown by acidic ions. Analyses of illites indicate that substitution of K by Na, Fe, Ca and Mg has taken place near the vein as shown by an overall decrease in $\frac{K}{Na}$, $\frac{K}{Fe}$, $\frac{K}{Ca}$ and $\frac{K}{Mg}$ ratios. Both sodium and potassium seem to be instrumental in the formation of well-developed illite crystals.

Alteration stages operative in the Cochiti district were developed by the action of solutions probably ranging in pH from 4 to 10. Alteration zones were formed penecontemporaneously with gradual outward migration of the least intense zones.

INTRODUCTION

A study of wall rock alteration in the Cochiti mining district (Fig. 1), was undertaken to relate mineralogy with ore deposition, structure, and hydrothermal transformation processes. It is 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, 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.

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Samples were collected from seven mines: the Lone Star, Daisy, Blue Bell and Sambo in Bland Canyon, and the Sun and Albemarle in Colla Canyon. Samples were also collected from the Washington mine, located on the mesa separating these two canyons. 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 obtained 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 rocks. Gouge, breccia and compact rock were considered separately with respect to the relative effects caused by the altering solutions. As soon as possible after collection, the samples were wetted and packed in sealed containers.

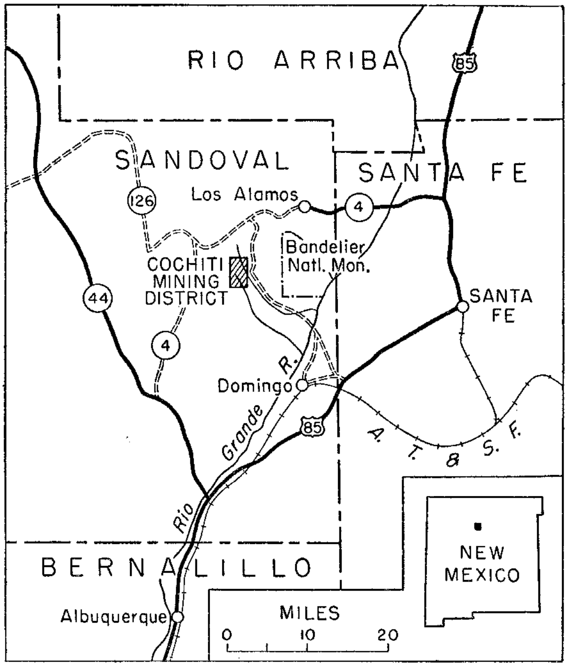

FIGURE 1.—Index map of New Mexico showing location of Cochiti mining district.

Samples were prepared in the laboratory for thin and polished section study, clay mineral determinations, and chemical analyses. Thin sections were prepared from each sample for correlative study with x-ray diffraction and chemical analyses. The thin sections were examined to determine genetic and paragenetic relations between clay and non-clay minerals. Polished sections were utilized only for the study of opaque minerals.

A representative portion of each sample, 400–600 g, 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 analysis.

Diffraction traces of oriented clay aggregates (Grim, 1934) were recorded with a General Electric XRD-3D spectrogoniometer, using nickel-filtered copper radiation. Grim (1951) has described a differential thermal analysis 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.

ACKNOWLEDGMENTS

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GEOLOGY

The Jemez Mountains consist of a circular group of volcanic rocks constructed 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 ft 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 another dissected volcanic cone, which had a diameter of about 15 miles and was made up of ash, cinder, and other ejecta (Lindgren, Graton and Gordon, 1910). The Pajarito Plateau, a broad outsloping apron averaging about 10 miles in width surrounds this core. This apron represents an accumulation of flows from the Valles Caldera, Pelado Peak, and other less significant volcanic centers. The apron of volcanics has been divided into many narrow mesas by deep, narrow canyons cut by radiating streams that head against the core. Bland and Colla are two of these radiating streams. The upper portions of the canyons cut by these two streams occur within the Cochiti mining district.

The Cochiti mining district is an inlier in Pleistocene volcanic rocks, where erosion has exposed Tertiary volcanic, intrusive and sedimentary rocks. The oldest rocks exposed are andesite flows that contain an interbedded unit of pyroclastic rocks and sandstone. These rocks have been intruded by a monzonite stock, which has mildly metamorphosed the host rocks. Younger andesite porphyry dikes are abundant and were injected along post-monzonite faults. A later stage of faulting has controlled subsequent quartz–sulfide veins. Final stages of Tertiary igneous activity are presented by the intrusion of a rhyolite sill and rhyolite dikes. Later faulting which has controlled a second stage of quartz veins, apparently not associated with economic mineralization, followed this intrusive activity.

Primary minerals contained in the igneous rocks are tabulated in the order of their abundance:

ANDESITE FLOWS
plagioclase (andesine)
biotite
pyroxene (unidentified)
ilmenite
magnetite
apatite

ANDESITE PORPHYRY DIKES
plagioclase (andesine)
pyroxene (unidentified)
biotite
ilmenite
magnetite
apatite

MONZONITE STOCK
plagioclase (andesine)
orthoclase
quartz
biotite
hornblende
ilmenite
magnetite
apatite

RHYOLITE INTRUSIVES
orthoclase
quartz
biotite

Epithermal quartz veins and lodes, widely distributed throughout the Tertiary rocks, contain shoots, pockets, and irregular bodies of sulfides. The sulfides in order of abundance are pyrite, argentite, sphalerite, chalcopyrite and galena. The occurrence of gold is not clearly understood but gold apparently is associated with pyrite. Metallization during the second stage of quartz veins is seemingly limited to pyrite.

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 are listed in their approximate decreasing order of importance.

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.
5. Grain size and mineralogy of wall rock.

As discussed above, 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 toward the quartz veins. Less commonly, permeable zones not penetrated by veins represent centers of intense alteration.

Structures existing within the rocks have caused significant variations in degree of alteration. Of particular importance are the numerous gouge and breccia zones throughout the area, and these zones of weakness have provided materials of relatively high permeability and porosity. Without exception, gouges were found to be more intensely altered than the adjacent compact rocks. Anomalies in clay mineral sequences are largely related to the presence of gouge and breccia. This phenomenon is best exemplified in the halloysite alteration zone, where the amount of halloysite present is directly related to the degree of rock pulverization. Leaching was readily achieved in these zones, and 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.

Width of alteration zones is generally related to vein width. To a limited extent, alteration intensity is controlled by vein width. Commonly, however, 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. Some recent alteration studies indicate that in igneous rocks the fine-grained 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 that permeated channels along grain boundaries produced more alteration in fine-grained than in coarse-grained rocks. For example, the relatively coarse-grained monzonite generally displays less alteration than fine-grained andesites. Feldspar phenocrysts in the andesite porphyry dikes are generally less altered than the fine-grained groundmass. In contrast, pyroxene, hornblende and biotite phenocrysts have undergone more intense alteration than the groundmass. Exceptions to these generalizations are common.

x-Ray diffraction studies of clay mineral components in the altered rocks provide a relatively precise means of zonal classification. It should be pointed out that the stability conditions of clay minerals comprise wide ranges of temperatures and pressures. Roy (1954) emphasized the metastable persistence of clay mineral phases. In the present study it was found that montmorillonite and chlorite, for example, 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) chlorite–montmorillonite.

In general, this sequence of alteration is in agreement with other recent studies of wall rock alteration (Sales and Meyer, 1948; Peterson, Gilbert and Quick, 1946; Lovering, 1941, 1949; Kerr and others, 1950; Kerr, 1951; Schwartz, 1953; Tooker, 1956).

The distribution of clay minerals is not confined to discrete types. Mixed-layer associations of 2 : 1 clay minerals are abundant and apparently represent a transition state between discrete clay mineral 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 deficiences are commonly balanced by K^+, Na^+ or Ca^{2+} ions (Johns and Jonas, 1954).

All possible combinations of mixed-layering between illite, montmorillonite, chlorite and vermiculite exist in the altered rocks. 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 (Callière, Hénin and Mériaux, 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.

In addition to random mixed-layer clay minerals, regular mixed-layer types occur rarely in the chlorite–montmorillonite zone. The presence of a regularly interstratified montmorillonite-chlorite is indicated by a 29 Å reflection in Fig. 2A (Earley and others, 1956). This spacing would be expected from the regular alternation of two 14 Å clay minerals. The relatively weak reflection is indicative of a partially regular alternation. Regular mixed-layers that have a basal reflection at about 24 Å (Fig. 2B) have been named stevensite and are described by Faust and Murata (1953) and Brindley (1955). According to Brindley, a partially regular alternation of layers 10–14 Å thick would account for a weak reflection at 24 Å.

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 numerically fewer arrangements can constitute an ordered system. Therefore, the system of greatest randomness is the system of highest probable occurrence (Moore, 1950).

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, should be the exception rather than the rule.

The spatial distribution of clay mineral species can not be generalized as readily as the proposed zonal distribution described above. Chlorite and montmorillonite, montmorillonite and vermiculite, and vermiculite and halloysite are commonly 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, (6) kaolinite and (7) dickite.

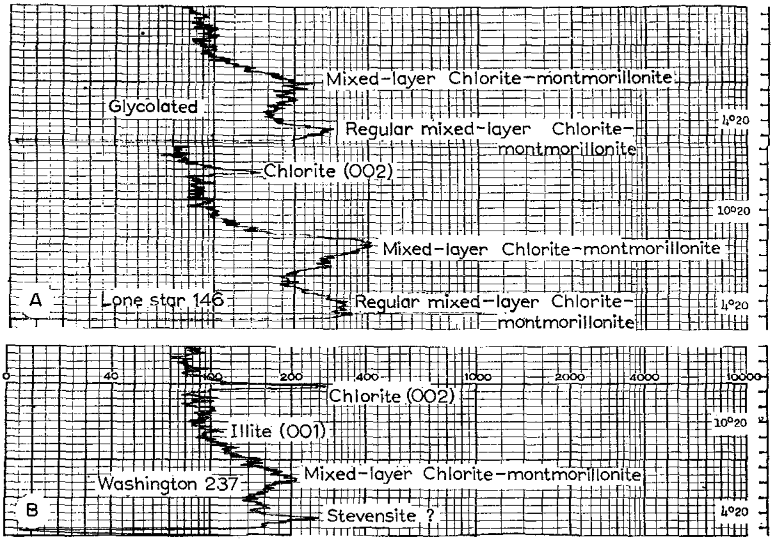

FIGURE 2.—x-Ray spectrometer traces. A, Regular mixed-layer chlorite–montmorillonite. B, Stevensite.

It should be clearly understood 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 alteration. Relatively intense 14Å reflections in spectrometer traces of oriented clay aggregates indicate that the chlorite is predominantly a magnesium-rich variety (Bradley, 1954). Iron-rich chlorites occur in minor quantities and are limited to fringe zones of alteration.

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

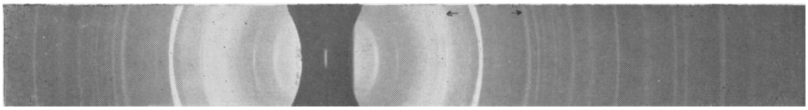

Figure 3.—x-Ray powder photograph of 1Md mica polymorph. Minor quartz and kaolinite contamination. Arrows point to 4.48 and 2.57 reflections.

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layers of water occur closest to the vein. This observation indicates that montmorillonites become progressively richer in a bivalent cation, probably calcium, toward intense zones of alteration. Exchange capacity data collected by Hofmann and Klemen (1950) indicate that calcium tends to become fixed on montmorillonite following heat treatment. Thus, the high temperatures that possibly were attained in the alteration zones provided a mechanism for the stabilization of calcium montmorillonite.

Vermiculite, a moderately abundant constituent of the altered clays, was identified with respect to characteristics of the 14 Å reflection. Diagnostic features of the 14 Å peak include include sharpness, intensity, expansion with glycolation, and displacement following heat treatment. Bradley (personal communication, 1957) believes that many vermiculites, like montmorillonite, will expand to 17 Å. For this reason, vermiculite was distinguished from montmorillonite largely by sharpness and relative intensity of the 14 Å peak.

Decrease of montmorillonite relative to vermiculite, which can be considered a coarse-grained montmorillonite (Weaver, 1956), indicates the veinward increase of magnesium stability in the montmorillonite structure. Hofmann and Endell (1939) believe that heat treatment causes exchangeable cations to migrate inside the montmorillonite lattice. Because of the relatively small ionic radius of Mg^{2+}, it can easily fit into the structure. Such a structural change decreases base exchange capacity and, therefore, increases the stability of the clay mineral structure.

The term illite is used in this paper as a group name to specify mica-like clay minerals (Grim, Bray and Bradley, 1937). Following the suggestion of Yoder and Eugster (1955), illite is identified as to its polymorphic form and type of clay mineral with which it is interlayered. Film-recorded x-ray data of relatively pure samples indicate that the 1Md polymorph occurs in the intensely altered zones (Fig. 3). Measured interplanar spacings are in agreement with those listed by Levinson (1955). Particularly characteristic of the 1Md structure is the faint haze between 4.48 and 2.57 Å with the exception of a strong basal reflection at 3.33 Å. Reflections at 3.07 and 3.62 are extremely weak or absent. The illites occur in all degrees of mixed-layering with montmorillonite and to some extent with chlorite.

Illite is generally distributed throughout the altered rocks and is the most abundant clay mineral in zones of intense alteration. Microscopic examination indicates that the illites become coarser grained toward high-intensity alteration zones.

Clay minerals of the type 1 : 1 increase in abundance toward centers of intense alteration. The order of stability from the vein outward is dickite, kaolinite and halloysite.

Dickite was identified from x-ray powder photographs and DTA curves. A differential thermal curve of dickite is shown in Fig. 4. 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. The presence of halloysite and kaolinite mixtures was determined from electron micrographs. Presence of partially hydrated halloysite rather than fully hydrated halloysite was determined from differential thermal analysis of glycolated samples by the method of Sand and Bates (1953).

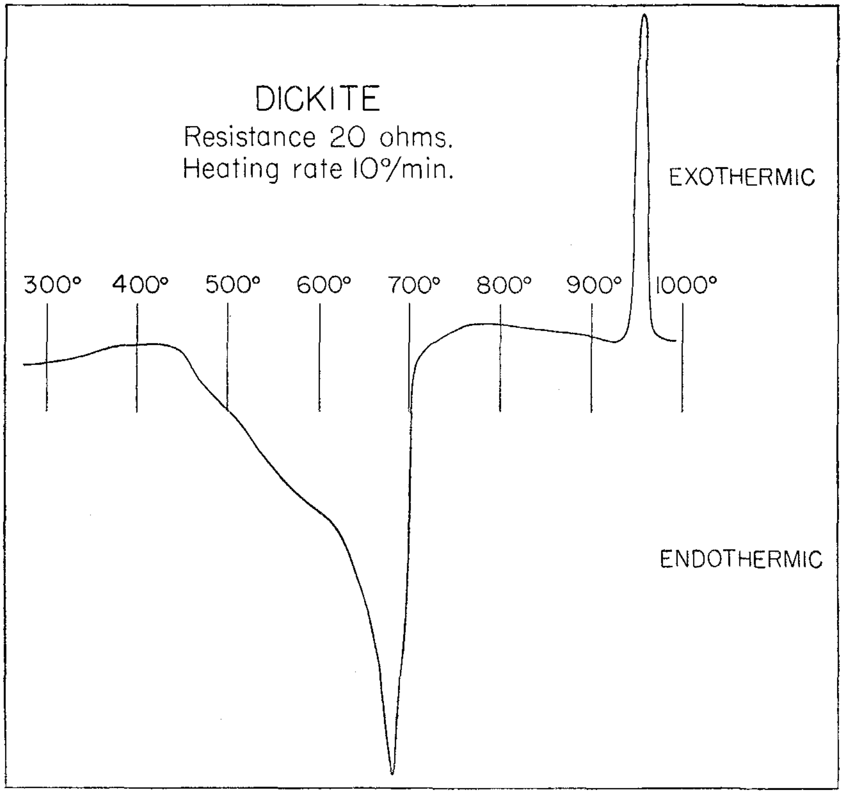

Figure 4.—Differential thermal curve of dickite.

PARAGENESIS OF ROCK ALTERATION

The rock types that have been most affected by 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. They show noticeable variations in the less intense alteration zones, whereas their mineralogy converges with the other rock types in the most intense zones. 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 approximate increasing order of stability of the primary minerals in 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 (except apatite) are 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 a minimum of 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.

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

Sometime during the chloritization of biotite, alteration of plagioclase to montmorillonite began along cleavage zones and twin planes. Potassium ions, derived from the breakdown of biotite, initiated minor illitization of montmorillonite. Effects of illitization become increasingly intense toward the vein.

Epidotization of plagioclase follows closely the formation of montmorillonite. Commonly, epidote is pseudomorphic after plagioclase. Clinozoisite is generally associated with epidote but is less abundant. Epidote veinlets are abundant and penetrate the first-formed chlorite.

Chloritization of plagioclase is common, and chlorite pseudomorphs are numerous. Abundance of chlorite–montmorillonite mixed-layering, as shown by x-ray spectrometer traces, indicates that montmorillonite may be an intermediate step in this process. Chloritization seemingly has taken place by the action of magnesium and iron-bearing solutions on montmorillonite. Such solutions undoubtedly are derived from the breakdown of ferromagnesian minerals.

Within the inner edges of the chlorite–montmorillonite zone, chlorite becomes less abundant relative 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 also indicated by the appearance of vermiculite and mixed-layer vermiculite–chlorite.

An isotropic mineral having an index of refraction similar to allophane occurs sporadically. It is generally associated with argillized plagioclase. Pyritization of ilmenite and magnetite is common and increases in degree toward the vein. Kaolinite and halloysite are minor constituents and are apparently associated with plagioclase alteration. Silicification is minor and is indicated by quartz 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 crystals show moderate replacement by chlorite.

Vermiculite–Halloysite Zone

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

Remnants of ferromagnesian minerals have completely disappeared. Chlorite and montmorillonite are extensively replaced 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 that remains is no longer the iron-rich variety, penninite, and 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. Plagioclase rarely shows relatively minor alteration. In such instances protective envelopes of silica have inhibited contact of plagioclase with the altering solutions. Epidote alteration is minor to absent and, although scarce, clinozoisite persists.

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

Abundant alunite is associated with halloysite. Its formation time covers a wide span, beginning before halloysite crystallization and continuing throughout dickite crystallization. Jarosite is also widespread and is present in all 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 extensively by illite, montmorillonite and chlorite. Silicification and pyritization have increased in intensity.

Secondary biotite is common but is limited to the inner fringes of the vermiculite–halloysite zone and to the outer fringes of the illite–kaolinite zone. Seemingly it has recrystallized from illite and chlorite.

Illite–Kaolinite Zone

Within this intense alteration zone, kaolinite and particularly illite are the most characteristic minerals present. Noteworthy is the abundance of fine-grained quartz interspersed with these clay minerals. Increase in free silica is reflected by almost complete destruction of the remaining primary minerals, and the increase in clay minerals (1 : 1) having a relatively high aluminum to silicon ratio. In many well-crystallized micas up to one-fourth of the silicons are replaced by aluminum (Grim, 1953). Orthoclase has been converted mainly to illite, kaolinite and fine-grained quartz. A small portion of the illite has been recrystallized into coarse-grained particles having optical properties that 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 seemingly has been an active phenomenon. This transition is indicated by the gradual increase in 1 : 1 and gradual decrease in 2 : 1 clay mineral 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 the differential thermal curves. Grim and Johns (1954), in their study of sediments in the northern Gulf of Mexico, imply 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, its occurrence can not easily be demonstrated. Brindley and Gillery (1954) reported an occurrence of kaolinite–chlorite mixed-layering from 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, concludes 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 structure is unknown.

Roy (1954) states that, in nature, endellite and kaolinite form under apparently similar temperature and water vapor conditions. Both Roy and Sand emphasize the compositional and structural control exerted by the original mineral.

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

All these transition processes may have been operative; however, it is believed that crystallization from allophane has been a significant mechanism. Aggregates of minute and isotropic particles having a refractive index near that of allophane occur in minor quantities within this zone. An electron micrograph shows a mixture of kaolinite and almost perfectly rounded particles believed to be allophane. Hauser (1955) indicated that rounded forms are characteristic of amorphous aluminum silicates. This association of well-rounded forms and well-developed kaolinite is strongly suggestive that a crystallization process, with allophane as the intermediate phase, has been active.

Alunite, although not as abundant as in the vermiculite–halloysite zone, has persisted as a common alteration product. Jarosite and leucoxene are also common alteration minerals. Apatite has been replaced completely by clay minerals.

Dickite Zone

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

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

An additional factor which may be significant in determining degree of crystallinity is the catalytic influence of ions that do not enter into the composition of the final product. Hénin (1956) has shown from a synthesis study that NaCl improves crystallinity and rate of formation of clay minerals. In contrast, Hénin found that potassium ions seem to impede 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

Kerr (1955) has stated 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.

In the Cochiti area obvious products of supergene processes are gypsum, limonite and melanterite. Oxidation of iron-bearing minerals, particularly pyrite has given rise to the widespread occurrence of limonite (mixture of goethite and lepidocrocite). Melanterite ($FeSO_4 \cdot 7H_2O$) is also a product of pyrite oxidation. The following are some theoretical equations for the oxidation of pyrite (Gottschalk and Buehler, 1912):

$$FeS_2+7O+H_2O \rightarrow FeSO_4+H_2SO_4 \quad (1)$$
$$FeS_2+3O+H_2O \rightarrow FeSO_4+H_2S \quad (2)$$
$$2FeSO_4+O+H_2SO \rightarrow Fe_2\,(SO_4)_3+H_2O \quad (3)$$
$$Fe_2\,(SO_4)_3+3H_2O \rightarrow Fe_2O_3+3H_2SO_4 \quad (4)$$

If equation (2) has been applicable in the Cochiti area, the action of H_2S on Fe^{II} and Fe^{III} 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 conclusively demonstrated, 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 calcium-bearing solutions has caused the precipitation of gypsum which occurs abundantly as an efflorescence on mine walls.

Replacement of pyrite by halloysite–kaolinite mixtures 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 illite probably is being formed under the present supergene processes. The pervasive occurrence of highly soluble minerals as alunite $[K_2Al_6(OH)_{12}(SO_4)_4]$ and jarosite $[K_2Fe_6(OH)_{12}(SO_4)_4]$ indicate that K^+ ions are abundant constituents of present ground-water solutions. The fixation of potassium in the interlayer positions of montmorillonite has been discussed above. In this connection it is also significant that illite veinlets commonly penetrate and surround alunite masses.

It is inevitable that clay minerals will form through the agencies of supergene alteration, and this is attested by the numerous deposits formed in nonhydrothermal environments. Nevertheless, the zonal distribution of clay minerals and undeniable spatial relation to quartz veins 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 seemingly are not this advanced in the Cochiti area. Schwartz (1956) does not believe that weathering develops much additional clay in the relatively arid southwest.

CHEMICAL ANALYSES

Total rock samples and illite clay fractions were analyzed chemically. Analyses of total rock samples are shown in Tables 1 and 2. These analyses are plotted in Figs. 5 and 6, and indicate relationships of chemical trends to alteration zones and quartz veins. Analyses are expressed as cation content according 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.

TABLE 1.—CHEMICAL ANALYSES[1] (LONE STAR MINE)

	Zones					
	Chlorite–Montmorillonite		Vermiculite–Halloysite			Illite–Kaolinite
Constituent	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	0.86	1.7
Fe	4.09	3.12	2.87	2.87	2.18	15.7
K	7.0	3.75	4.05	5.10	8.0	0.37
Li	0.003	0.003	0.003	0.003	0.003	0.003
Mg	2.61	2.08	2.29	2.41	3.35	4.1
Mn	0.098	0.060	0.06	0.08	0.04	0.02
Na	2.03	0.86	1.07	1.42	0.42	0.08
P	0.19	0.11	0.12	0.13	0.019	0.28
S	0.53	0.60	0.43	0.26	0.50	1.40
Si	27.0	30.0	28.7	29.0	29.7	17.5
Ti	0.52	0.41	0.12	0.49	0.42	0.11
CO_2	0.09	0.24	0.09	0.06	0.18	0.12
H_2O	1.90	2.59	3.14	2.68	2.18	7.64

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

TABLE 2.—CHEMICAL ANALYSES[1] (SUN MINE)

	Zones					
	Chlorite–Montmorillonite	Vermiculite–Halloysite		Illite–Kaolinite		Dickite
Constituent	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	0.69	0.71	0.79
Fe	2.87	2.47	2.52	0.56	2.69	10.1
K	2.80	2.20	2.85	1.60	1.65	0.03
Li	0.003	0.003	0.003	0.003	0.003	0.003
Mg	3.50	3.13	3.48	0.49	0.95	0.37
Mn	0.04	0.05	0.05	0.008	0.006	0.004
Na	0.75	1.69	1.54	0.04	0.17	0.07
P	0.12	0.10	0.10	0.30	0.041	0.09
S	0.89	1.83	2.12	0.39	0.65	2.85
Si	28.9	29.7	28.9	35.1	30.0	20.2
Ti	0.37	0.37	0.35	0.20	0.42	0.03
CO_2	0.03	0.04	0.05	0.09	0.10	0.09
H_2O	3.18	2.87	2.83	3.04	4.15	11.5

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

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 0–9. A significant increase in solubility occurs, however, with increasing temperature. Above a

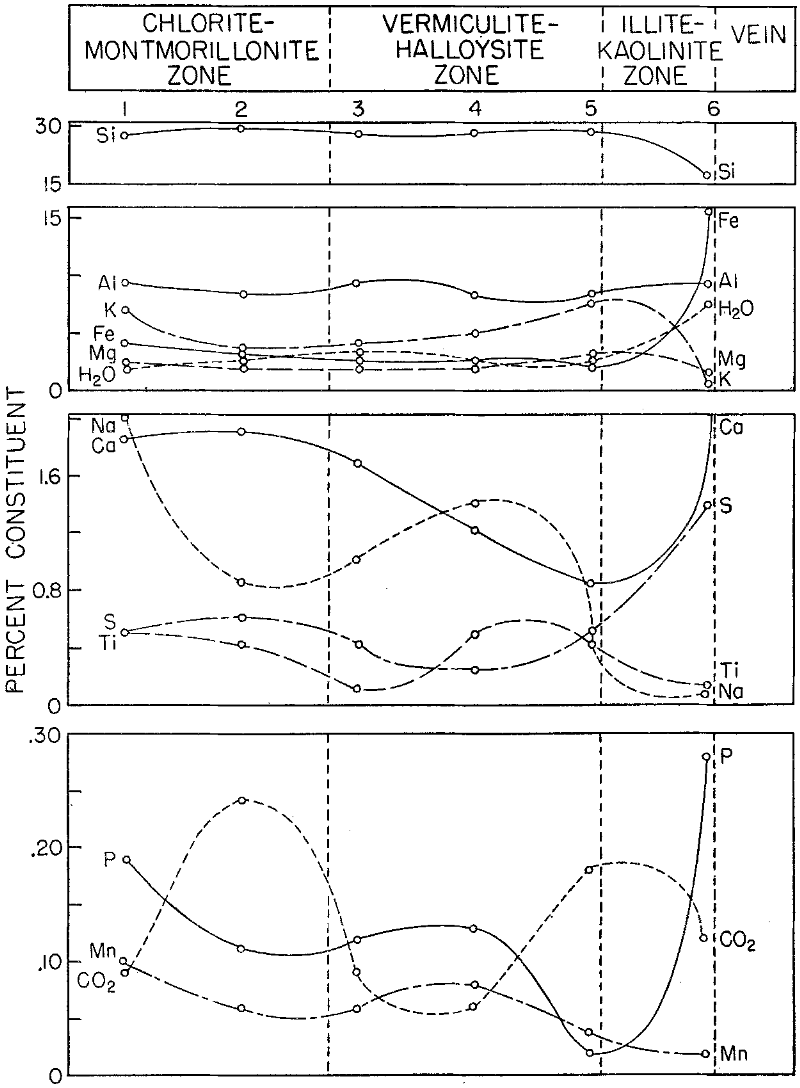

Figure 5.—Chemical trends in Lone Star Mine.

pH of 9 the solubility of silica increases considerably. Aluminum is practically insoluble over the pH range 5–9 but is readily soluble in strongly acid or alkaline solutions (Correns, 1949). Consideration of these solubility data and of the silicon and aluminum trends indicates that the pH of the altering solutions probably did not extend beyond the range of 4–10 at any given time. If the pH of the altering solutions had exceeded 9–10, then aluminum

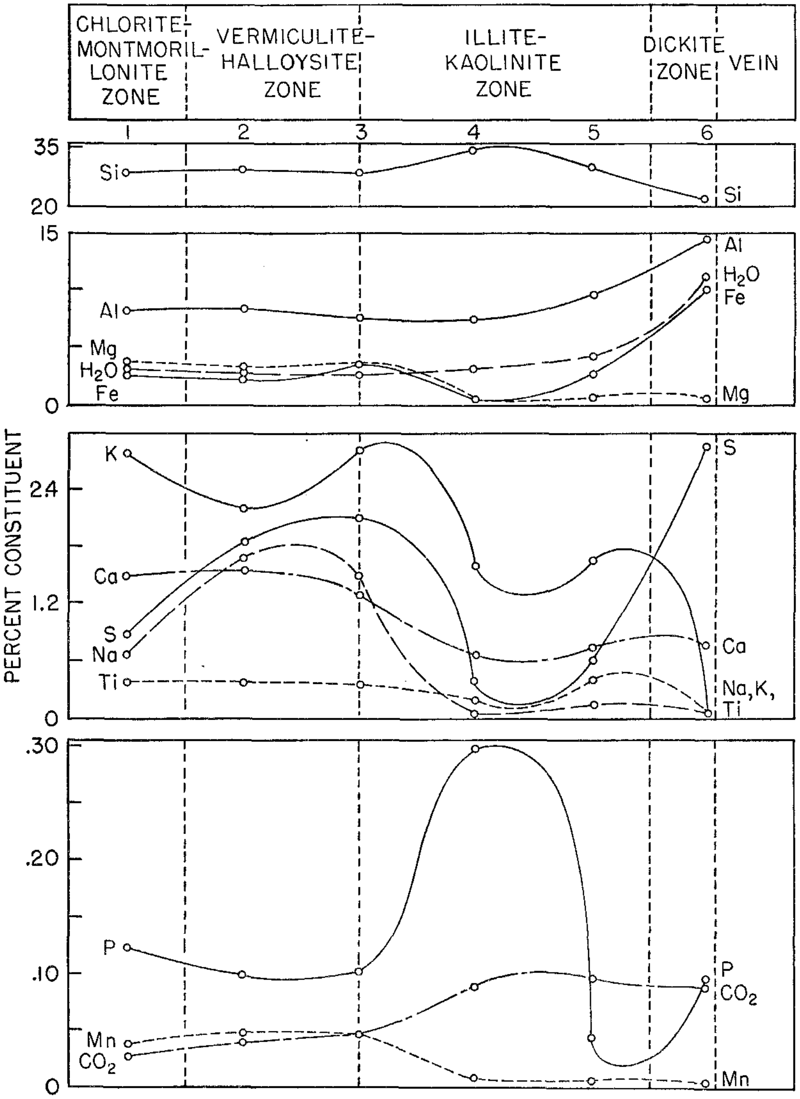

Figure 6.—Chemical trends in Sun Mine.

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

Because apatite is progressively destroyed in a veinward direction, an overall veinward decrease in phosphorus is to be expected. The excessive increase in phosphorus within the illite–kaolinite zone, however, 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 (1954), in a study of rock weathering, suggested that phosphorus released from apatite is fixed as PO_4^{3-} ions by iron oxide derived from biotite. He further suggested that some phosphorus has replaced Si^{IV} atoms in silicate lattices. Hemwall (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 high percentage of phosphorus; its occurrence within the sulfide structure, however, 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 destruction of these minerals. Because soluble salts of titanium are readily hydrolyzed, 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 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, and, therefore, water increase parallels increase in aluminum.

The hydrothermal emanations seemingly contained some carbon dioxide, as indicated by the presence of carbonate in the fringe areas of alteration and by the presence of minor carbonate veins. The somewhat erratic distribution of CO_2 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^{II} and Fe^{III} has not been developed (Hillebrand and others, 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 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 and vermiculite–halloysite zones. 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 3) 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 has been leached more readily than sodium. The explanation for this relation is not clear. According to Rankama and Sahama (1950) potassium goes into solution first during weathering but, because of adsorption by clays, does not remain dissolved. 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.

TABLE 3.—POTASSIUM/SODIUM RATIOS

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

Calcium and magnesium in general progressively 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^{2+} and Mg^{2+} 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 4, 5 : Figs. 7, 8). In general the analyses indicate a veinward decrease in basic ions.

TABLE 4.—CHEMICAL ANALYSES[1] OF ILLITES (ALBEMARLE MINE)

	Intensity of Alteration			
	Sample Number			
Constituent	1	2	3	4
Ca	1.0	0.8	1.3	1.1
Fe	0.66	0.81	2.58	0.71
K	6.5	10.0	9.0	8.0
Li	0.003	0.003	0.003	0.003
Mg	1.3	1.4	1.0	1.1
Na	0.05	0.06	0.13	0.06

TABLE 5.—CHEMICAL ANALYSES[1] OF ILLITES (SUN MINE)

	Intensity of Alteration			
	Sample Number			
Constituent	1	2	3	4
Ca	0.6	0.7	0.6	0.5
Fe	1.71	0.50	0.75	2.04
K	3.55	2.60	4.00	1.80
Li	0.003	0.003	0.003	0.003
Mg	1.2	0.9	1.0	0.9
Na	0.08	0.05	0.07	0.12

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

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

The striking parallel trend of sodium and iron is strongly suggestive of contemporaneous substitution in illite. To establish electrical neutrality, replacement of Al^{III} by Fe^{II} requires equivalent substitution by a mono-

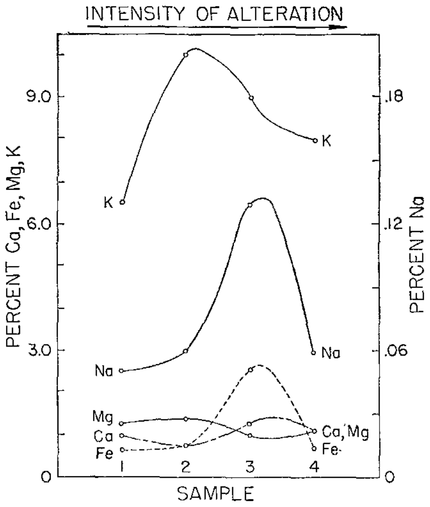

Figure 7.—Chemical trends in illite composition (Albemarle Mine).

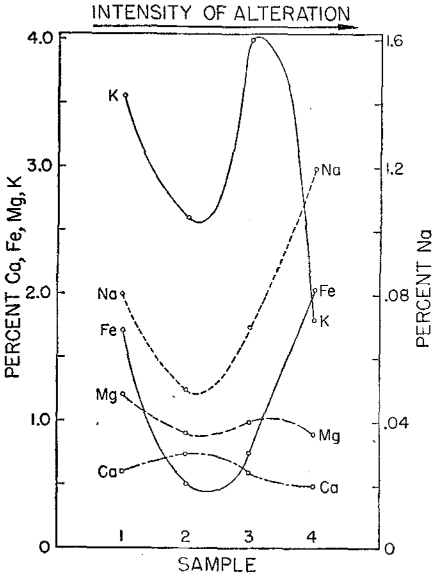

Figure 8.—Chemical trends in illite composition (Sun Mine).

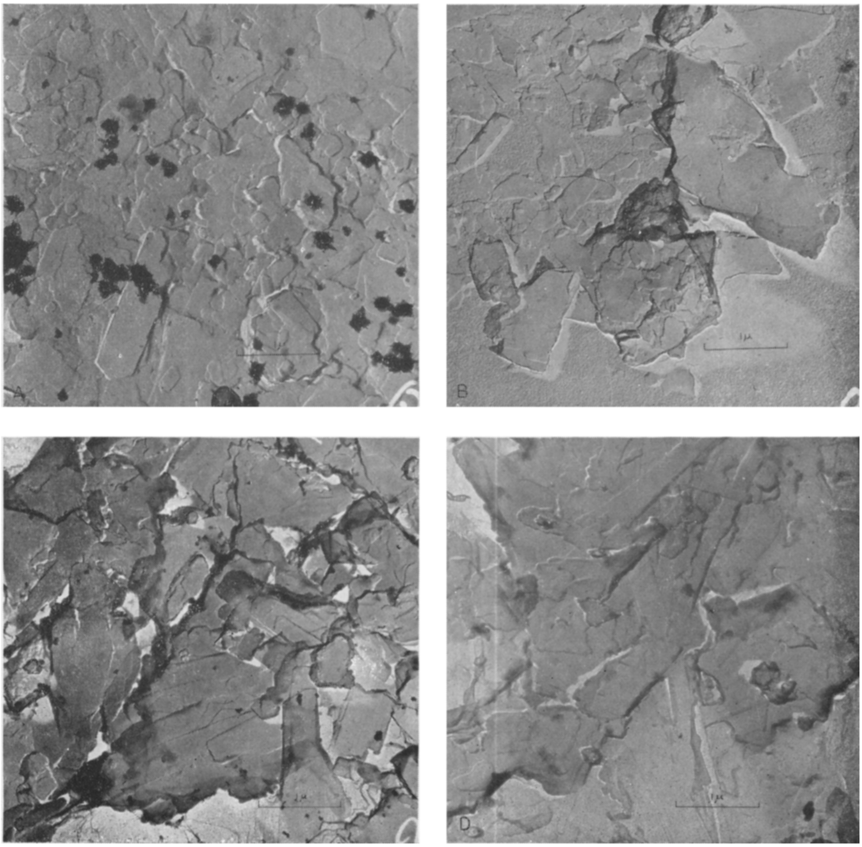

Figure 9.—Electron micrographs. A, Illite containing high K and high Na. B, Illite containing low K and low Na. C, Illite containing low K and high Na. D, Illite containing high K and low Na.

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valent cation. This requirement is readily satisfied by sodium. As K/Mg and K/Ca ratios also decrease in a veinward direction, it is suggested that there has been some substitution of magnesium and calcium for potassium in illite.

Many of the illites show unusually well-developed crystals, seemingly indicating a high concentration of K or Na, or both. This crystallinity is illustrated by electron micrographs, which were made by John Brown at the Engineering Experiment Station, Georgia Institute of Technology, using a carbon replica technique. x-Ray diffraction data support the observed differences in crystallinity. Figure 9A shows an illite that is high in both K and Na. Figure 9B illustrates an illite with low K and low Na which seemingly gives rise to relatively poorly developed illite crystals. Figure 9C shows an illite containing low K and high Na, whereas Fig. 9D shows an illite with low Na and high K, both of which exhibit a relatively high degree of crystal development.

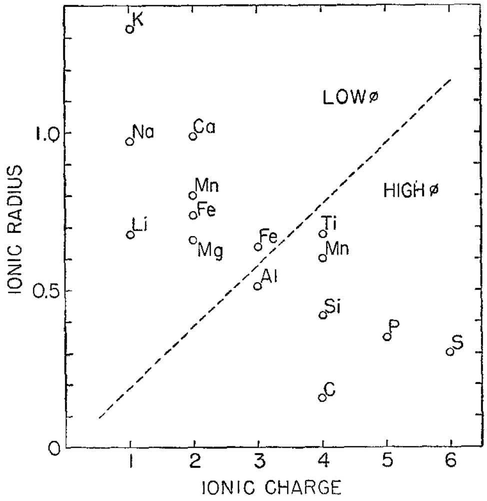

FIGURE 10.—Ionic potential (φ) plot of cations.

It is of interest to note that ionic potential

$$\left(\phi = \frac{\text{cation charge}}{\text{cation radius}}\right)$$

bears a direct relation to mobility of the elements. A plot of ionic potentials, modified after Goldschmidt (1937), is shown in Fig. 10. 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, 1952). It follows, therefore, that minerals formed from elements with high ionic potentials are less soluble and as a result are more stable in electrolytic solutions. With the exception of carbon and sulfur, which may be precipitated as soluble complex anions, these elements with the highest ionic potentials have been dissolved the least by the altering solutions. Alkali metals and alkaline earths, in contrast, show notable veinward depletions. It should be mentioned that alkali metals and alkaline earths with lower ionic potentials are readily adsorbed, and thus do not move far from their source, and those with higher potentials remain in solution and are carried farther from their source.

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

DISCUSSION OF ALTERATION MECHANISM

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

Original hydrothermal emanations are generally believed to be acid. With continued reaction with the wall rock these solutions become more and more basic. Analyses of volcanic emanations indicate that the constituents are generally gases of sulfur, carbon dioxide and superheated steam (Schmitt, 1950). An originally acid solution for hydrothermal emanations can thus be postulated. Observations of effects of solutions on rocks in present day solfataric and hot spring environments indicate that acid solutions bring about the formation of 1 : 1 clay minerals and alkaline solutions favor the formation of 2 : 1 clay minerals (Burbank, 1950; Fenner, 1936; Schmitt, 1950). Synthesis studies on clay minerals are in agreement with this generalization (Ewell and Insley, 1935; Gruner, 1944; Noll, 1934, 1936, 1944; Roy and Osborn, 1954).

Along with the assumption that the original hydrothermal emanations were acidic, it is also assumed that a progressive increase in pH ensued throughout both alteration stages 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 permeating and leaching host rocks at depth, must have been alkaline. This clay mineral sequence is suggestive of a proximate time trend in pH:

alkaline → alkaline → alkaline → acid → alkaline → acid → acid

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 vermiculite–halloysite zone and the illite–kaolinite zone corresponds to transitional phases in pH between alkaline and acidic solutions. Lovering (1949) points out that $Al(OH)_3$ is stable in sulfuric acid down only to pH 4.3. He suggests that the hydroxyl radical incorporated in alunite can appear only in solutions that are nearly neutral. It is further postulated that alunite is precipitated from cooling, nearly spent, acid solutions having a pH slightly less than 7.

With advance of the hydrothermal solutions the alteration zones were formed penecontemporaneously and produced initially the least intense zones adjacent to the vein. Alteration continued to progress with outward migration of low-intensity alteration zones, and with the final formation of intense zones adjacent to the vein. Because of previous leaching by first-stage solutions the second-stage solutions were more acidic, and they produced in relative abundance clay minerals indicative of intense alteration: illite, kaolinite and dickite.

SUMMARY

Hydrothermally altered Tertiary rocks of intermediate composition (mainly andesite and monzonite) are associated with epithermal gold and silver-bearing quartz veins. Although two stages of quartz veins are present, economic mineralization is limited to the first stage.

Hydrothermal alteration zones, present in the host rock, have been named relative to the clay minerals present in the greatest abundance. These zones from the vein outward are: (1) dickite, (2) illite–kaolinite, (3) vermiculite–halloysite and (4) montmorillonite–chlorite.

A generalized paragenetic sequence of the clay minerals is as follows:

(1) chlorite, (2) montmorillonite, (3) vermiculite, (4) halloysite, (5) illite, (6) kaolinite and (7) dickite.

Magnesium-rich chlorite occurs in greatest abundance. Iron-rich chlorites are limited to the fringe areas of alteration. Montmorillonites become progressively richer in calcium in a veinward direction, as shown by x-ray and chemical analyses. Illite is present as a 1Md (1-layer monoclinic disordered) polymorph. The order of stability of 1 : 1 clay minerals from the vein outward is dickite, kaolinite, halloysite.

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. This transformation process is indicated by the gradual increase in 1 : 1 clay minerals at the expense of 2 : 1 clay minerals.

An approximate order of stability of the primary minerals has been determined as follows: (1) pyroxene, (2) hornblende, (3) biotite, (4) plagioclase, (5) apatite, (6) orthoclase and (7) quartz.

Ferromagnesian constituents have altered chiefly to chlorite, montmorillonite, epidote and ilmenite. Plagioclase alters mainly to montmorillonite, illite and epidote, whereas orthoclase changes to illite and kaolinite. The end products of intense alteration are dickite and quartz.

Chemical analyses of the altered rocks indicate a general veinward decrease in basic ions. Acidic ions show less significant decreases, and some, as aluminum and phosphorus, show a marked increase. Analyses of relatively pure illites show a general decrease in basic ions toward the vein. Veinward decrease in K/Na, K/Mg, K/Ca ratios indicate that sodium, magnesium and calcium have substituted for potassium. Parallel trends of iron and sodium are indicative of contemporaneous substitution in illite. Both sodium and potassium seem to be instrumental in the formation of well-developed illite crystals.

Field observations and synthesis experiments indicate that the clay mineral sequence corresponds to an approximate time trend in pH:

alkaline → alkaline → alkaline → acid → alkaline → acid → acid

chlorite → montmorillonite → vermiculite → halloysite → illite → kaolinite → dickite

Alteration stages that were operative in the Cochiti district developed by the action of solutions probably ranging in pH from 4 to 10. Alteration zones were formed penecontemporaneously with the gradual outward migration of the least intense zones.

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